PROCESSING AND KINETIC STUDIES OF THE REACTIVE BLENDS OF POLY(VINYL CHLORIDE) AND THERMOPLASTIC POLYURETHANES

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PROCESSING AND KINETIC STUDIES OF THE REACTIVE BLENDS OF POLY(VINYL CHLORIDE) AND THERMOPLASTIC POLYURETHANES

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Dissertation

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ABSTRACT

A novel reactive blending process was investigated to produce poly(vinyl chloride)/thermoplastic polyurethane (PVC/TPU) blends of significant commercial interest. The reactive blending process took place in two stages. The thermally stabilized PVC was plasticized with the polyol monomers of TPU, and then the polyols reacted with diphenylmethane diisocyanate (MDI) to polymerize TPU in-situ with the PVC. In the first stage of the reactive blending, either a polyester or a polyether polyol and 1,4-butanediol (BDO), which forms the TPU’s hard segment, were blended with PVC. The polyester polyols included poly(butylene adipate) (PBA), poly(hexamethylene adipate) (PHA) and poly(propylene adipate) (PPA), while the polyether polyol was poly(propylene glycol) (PPG). In the second stage of the reactive blending, several commercial MDIs, including 4,4’-diphenylmethane diisocyanate (SMDI), a mixture of 4,4'-diphenylmethane diisocyanate and 2,4'- diphenylmethane diisocyanate (LMDI), and carbodiimide Modified 4,4 Diphenylmetane Diisocyanate (CDMDI) were used.

Initially, blends of PVC with the various polyols were prepared in a batch internal mixer. The PBA and PHA were partially miscible with the PVC in a wide range of compositions. The PPA turned out to be partially miscible with PVC only at high concentrations of PVC, and the polyether (PPG) was immiscible with PVC. The miscibility and resultant morphology of the blends were determined by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), respectively.
The reactive blending studies were performed in both a batch internal mixer and a continuous counter-rotating intermeshing twin-screw extruder. The miscibility, morphology, and mechanical properties of the blends were determined by differential scanning calorimetry (DSC), Fourier transformed infrared (FTIR), scanning and transmission electron microscopy (SEM and TEM), and Instron tensile testing respectively. The study in the batch internal mixer revealed that PVC was miscible with the TPU s produced when the TPU was formed from the polyester polyols, i.e. PBA, PHA and PPA. TEM revealed that the PVC/TPU blends had a multiphase morphology at room temperature, with varying morphologies that depended on the monomers used. The mechanical properties of the reactive blends depended on the MDI used and they showed superior tensile properties than the analogous melt blends.

The reactive extrusion (REX) in a continuous counter-rotating intermeshing twin-screw extruder was shown to improve the PVC/TPU (LMDI) properties compared to those obtained by a batch internal mixer. In REX a liquid MDI was required to assure accurate MDI feeding, given the difficulties in feeding SMDI, which dimerizes at room temperature. Additionally, the use of a liquid MDI provides the fulfillment of the stoichiometric ratio that is critical to obtaining high molecular weight polyurethane. The reactive blending studies with the different MDIs resulted in blends with different properties and phase morphology, but similar thermal properties.

The kinetics of TPU polymerization was studied in a rheometer and in a home-made vessel under various conditions of shear and pressure, respectively. This study revealed that pressure had negligible effect on the polymerization under the conditions studied, but that the shear rate influenced the rate of TPU polymerization appreciably. The effect of different polyols (PBA and PHA) and a variety of MDIs (SMDI, LMDI and
CDMDI) on the TPU polymerization was studied. It was observed that the kinetic parameters depended on the chemical structure, functionality and reactivity of the monomers. Lastly, the effect of the addition of the PVC on the kinetics of TPU polymerization was studied. It was observed that the PVC stabilizer works as a TPU polymerization catalyst. The kinetic equation obtained that includes the effects of temperature, pressure, and shear would be useful for applications in twin screw extruders.
DEDICATION

To Juan for his invaluable love and support during the last five years. To my parents Edgardo and Myriam, for inspiring and guiding me to always do better and look for a brighter future. To Jeronimo for enlighting my life since the day he was born. To Elsa, who reminded always me that there is a world out there. To Antonio Luis for pushing me to be better than he is. To my dear friends Mayela and Liliana who always support me, even from a distance or in busy times. To Antonio, Guillermo and his family, Manuela, and to Majid for being my second family here in Akron. Finally, to the Families Baena, Rivero, and Adames that cheered me from a distance.
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CHAPTER I
INTRODUCTION

Reactive blending is a unique and novel technique that combines chemical reactions and blending. This technique allows for the production of polymer blends in one single step without the limitations of other blending techniques, such as melt or solution blending. Additionally, when reactive blending is compared to other blending techniques, the final blend properties and performance are improved because of the milder processing conditions which cause less degradation and better mixing than conventional melt processing.

Blends of Poly(vinyl chloride) (PVC) and Thermoplastic polyurethane (TPU) have demonstrated excellent properties as several researchers have delineated\(^2,3\). At the same time, PVC is a low cost yet versatile thermoplastic whose properties can vary from flexible to rigid as the need arises by adding plasticizers\(^1\). Conversely, TPU is a high cost thermoplastic elastomer that can be tailor-made by varying its segmental structure and available variety of monomers. Therefore, the resultant PVC/TPU blends can be considered to be impact modified PVC or permanently plasticized by TPU. PVC/TPU blends are said to exhibit permanence, low temperature flexibility, and remarkable abrasion and impact resistance. They have also been recognized as ideal candidates for cable jacket, tubing, hose, and shoe sole applications\(^2,3\).
Blends of PVC with TPU have been produced by melt and solution blending which has problems associated with PVC thermal degradation and solvent recovery, respectively. As a consequence, the reactive blending process of PVC with TPU appears to be a suitable blending technique to eliminate such problems. The melt blending of PVC and TPU causes severe PVC degradation even in the presence of thermal stabilizers at the elevated temperature required for melting PVC and TPU. Additionally, the use of TPU's is limited to low molecular weight to avoid excessive viscous dissipation and elevated melting temperatures. On the other hand, solution blending requires a costly solvent recovery process which has been found to be harmful to the environment.

However, the reactive blending of PVC with TPU overcomes the problems encountered with melt and solution blending because the reactive blending requires a lower temperature and is solvent free. In the first stage of the reactive blending, the PVC forms the miscible mixture with the polyol monomers of the TPU which have a plasticizing effect on the PVC. The addition of these low molecular weight monomers to the PVC requires a low mixing temperature and results in reducing the thermal degradation of PVC. Subsequently, the MDI is added to the plasticized PVC initiating the later stage of the reactive blending process. Both stages of the reactive blending occur at low temperatures and are solvent free processes thus, reducing PVC thermal degradation and environmental concerns.

This dissertation focuses on two thrust areas. The first investigates a novel reactive blending process of TPU by using in situ polymerization with PVC. The model studies in batch and continuous mixer were conducted to find the optimum processing conditions to be applied to the reactive blending process in a counter-rotating twin
screw extruder. The second area sought to develop the empirical, non-isothermal kinetic model of TPU including the effect of shear, pressure, and temperature.

In model studies in a batch mixer, the PVC was blended with various types of polyols to investigate the cause-effect relationship of their chemical structure on its miscibility with PVC. The polyols used in this study were selected to vary the number and structure of the carbonyl or ether groups.

Three different types of diisocyanate (MDI) were used in the model studies in the internal mixer to investigate the effect of their structure on the final properties of the reactive blends. The MDI affects the properties of the reactive blends because the addition of the MDI initiates the polymerization reaction and, consequently, the reaction induced phase separation. This phenomenon, attributable to the segmental character of the TPU, generates the complex morphology of the reactive blends and the properties in the products.

The studies of reactive blending performed in a twin screw extruder revealed the difficulty of feeding solid MDI and the necessity of controlling the molecular weight and structure during the course of the reactive blending. Therefore, it was critical to search for alternative modifications of MDI (liquid) for an accurate stoichiometric balance.

The miscibility of PVC with TPU monomers and the morphology of the reactive blends were characterized by means of several methods including differential scanning calorimetry, dynamical mechanical analysis, Fourier transformed infrared, and scanning and transmission electron microscopy. The thermal and infrared spectroscopy analyses revealed that the blends of PVC with polyester polyols and of PVC with TPU are partially miscible. As a consequence, the fine morphology was generated as revealed by TEM microscopy.
The investigation of the kinetics of TPU was carried out using adiabatic temperature rise (ATR), isothermal DSC, rheokinetic studies, and measurements of temperature rise under pressure in home-made vessels. The ATR and DSC techniques were complementary, because the ATR provides the information on early stages of the reaction, while DSC provides information on the reaction at its later stages. In the rheokinetic studies, a rheometer was used to determine the evolution of the dynamic properties (\(G'\), and \(G''\)) during the course of the reaction. Rheological studies during the course of a reaction will provide the effect of shear on the kinetics of TPU polymerization. Finally, the kinetic studies under pressure were conducted in a pressurized temperature rise experiment. The home-made vessels attached to the ATR set-up were used to follow the temperature rise while the reaction proceeded under pressure.

Based on the aforementioned experiments, the effects of the addition of PVC and types of polyol and MDI on the kinetic equation were investigated. The resultant kinetic equation, including the effects associated with the temperature, the concentrations, the shear, and the pressure, provided the empirical non-isothermal kinetic model applicable to the reactive blending process.
2.1. Poly(Vinyl Chloride)

Poly (Vinyl Chloride) (PVC) has been one of the most used plastics in the world for over half a century. PVC is widely accepted in the market because of its advantages, including low ingredient cost, processing versatility, and good overall performances in a variety of end use applications. It is important to mention that the versatility of PVC comes from the feasibility of compounding and blending it with a series of additives that allow the PVC to achieve any required property, processing, or cost. Its most notorious drawback is its low thermal stability; however, with the use of additives this problem can be overcome.

The history of PVC began when in 1872 Baumann\textsuperscript{11} polymerized it for the first time. PVC development was a consequence of the discovery of the vinyl chloride monomer in 1835 by Von Liebig, when ethylene dichloride and potassium hydroxide reacted. Hoffman detected the first vinyl halide polymer in 1860 when a vinyl bromide monomer was transformed into a white mass without compositional change occurring.

The development of this polymer continued over the next century. In the 1910s several patents on PVC polymerization initiated by light, heat, and free radicals were filed\textsuperscript{12} in the search to find a viable replacement for celluloid. In the 1930s, companies in the U.S. initiated the production of flexible PVC on a large scale.
Despite this, several years and a war had to pass before PVC became a major thermoplastic resin replacing rubber, linseed oil, cellulose acetate, synthetic fibers, and leather in flexible products\textsuperscript{13}. Then, the production and knowledge of PVC grew rapidly, not only for flexible PVC, but also for the rigid PVC. PVC has become one of the polymers used in the widest range of applications in the polymer industry. Currently, PVC is used in different markets, such as construction (e.g. pipe fittings, and siding), packaging, and container industries\textsuperscript{14}.

2.1.1. Synthesis

Commercial PVC is produced by the polyaddition of the free radical polymerization of the vinyl chloride monomer; this synthesis can be carried out in suspension, bulk, emulsion, and microsuspension systems. Suspension polymerization is the most commonly used method, in which droplets of a vinyl chloride monomer polymerize with the aid of agitation and suspending agents while suspended in an aqueous dispersing media. This polymerization process is temperature activated, meaning that once a certain level of temperature has been achieved, and the free radical initiator, which is present in the monomer, decomposes, the polymerization reaction starts. The polymer and monomer are completely miscible until the conversion of the polymerization reaction is approximately 2%; consequently, above this conversion limit, PVC macromolecules precipitate and separate from the monomer phase, forming aggregates, nucleating the formation of larger polymer primary particles. During the polymerization, the precipitated PVC flocculates until the PVC grains reach a final diameter of approximately \(100-150\mu m\)\textsuperscript{15,16}.

During the vinyl chloride polymerization, the polymerization processing conditions, including pressure, temperature stirring conditions, and phase distribution
influence the chains configurations of the PVC obtained. In the commercial production of PVC by suspension polymerization\textsuperscript{17}, there is a preponderance of the head-to-tail arrangement over the tail-to-tail or head-to-head configurations, which results in one chloride atom bonded to every other carbon atom along the PVC molecule. The conventional commercial production of PVC at temperatures of 45 to 70\degree C\textsuperscript{18} yields conformational and configurational irregularities. Producing stereoregular PVC is not economically justifiable. Even though syndiotactic PVC has been successfully produced, the result was an infusible and insoluble (and hence, useless) PVC\textsuperscript{19}.

Due to the lack of significant long-range stereoregularity, commercial PVC is predominantly amorphous, having a crystalline fraction of only 5 to 10\%. Short syndiotactic sequences in the main chains\textsuperscript{20} are responsible for the occurrence of this crystallinity. As this fraction of syndiotactic sequences increases, polymerization temperatures must be lowered in order to increase syndiotacticity\textsuperscript{21}. However, this is not desirable since high crystalline PVC can have melting temperatures in the order of ca. 400\degree C, and the polymer decomposes before it melts, making its processing an impossible task\textsuperscript{19,22}. Natta and Corradini\textsuperscript{23} reported that a PVC crystalline unit cell is orthorhombic with dimensions: $a=10.6$ Å, $b=5.4$ Å, and $c=5.1$ Å. It is generated by an all \textit{trans} planar zigzag conformation with a repeat distance corresponding to the four main chain carbon atoms\textsuperscript{23}.

2.1.2. Grain Morphology

Due to the immiscibility of the polymer with monomer during the aforementioned suspension polymerization, the PVC grains form a microstructure originating from the precipitation and agglomeration of the polymer during the polymerization. Figure 2.1. shows a detailed schematic grain morphology. As shown in
Figure 2.1., the interior of each grain has a significant amount of porosity created by the volume contraction during polymerization, as PVC ($\rho \sim 1.4 \text{ g/cm}^3$) is denser than the vinyl chloride monomer ($\rho \sim 0.9 \text{ g/cm}^3$). In detail, these particles consist of many small particles of approximately 1 µm in diameter called primary particles.

According to Geil’s and Allsopp’s studies on the use of SAXS and TEM, primary particles are nearly spherical and are partially fused together forming agglomerates of approximately 10 µm in diameter. The primary particles consist of smaller particles or “domains” of approximately 0.1 µm in diameter, spherical as well. These domains are also made of even smaller entities called “microdomains” of approximately 0.01 µm in diameter.

Geil proposed that the microdomains were unstable aggregates of approximately fifty polymer chains formed during the early stages of PVC polymerization, though its identity is still controversial. Inside these microdomains, syndiotactic sequences of PVC may form microcrystallites, as was mentioned earlier. These microcrystallites contribute to the crystalline fraction encountered in commercial PVC resins. Munstedt and Summer proposed that these microcrystallites act as...
physical cross-links and impart the desired physical properties to commercial PVC resins\textsuperscript{27,28}.

Differing from other types of PVC, the presence of a thin skin (0.5 µm) called the pericellular membrane that surrounds each grain creates the unique morphology of the PVC obtained by the suspension method. It has been postulated that during polymerization, the vinyl chloride monomer grafts onto the suspending agent and forms small particles. These particles migrate under centrifugal forces of agitation to the vinyl chloride-water interface and form the pericellular membrane\textsuperscript{29}.

2.1.3. Compound Formulation and Processing

It is difficult to process unmodified PVC resin due to its degradation at an elevated temperature and light. Conventional processes degrade neat PVC at an elevated temperature, producing hydrogen chloride gas that causes discoloration and damage to the processing equipment. Therefore, compounding PVC involves mixing it with additives that allow for it to be processed into a finished product with the desired properties and at minimum cost. These additives may be classified into two types: those that aid the processing of the PVC, and those that change the properties of the final product. Thermal stabilizer, plasticizers, and lubricants are additives of the first type; fillers, impact modifiers, and colorants of the second.

PVC compounding starts with a blending step, such as dry blending, followed by more processing steps to produce dry blends, plastisols, organosols, blended latexes, or solutions. Most unplasticized and plasticized PVC is compounded by dry blending in an intensive mixing device (e.g. an extruder) and then processed by another operation, such as injection molding, into the final product. In some cases, a melt processing operation is sufficient to compound and shape the PVC simultaneously.
Compounding allows PVC to be used in a variety of finished products, including electrical insulation, medical tubing, food wrapping, outdoor furniture, swimming pool liners, electrical conduit, pressure piping, garden hoses, house siding, bottles, flooring, and clothing. In the following sections, each important step of the compounding operations is described.

2.1.3.1. Stabilization

As has been mentioned, PVC’s principal drawback is its degradation under the influence of heat and light resulting in a loss of properties, discoloration, and the generation of hydrogen chloride. Therefore, PVC compounds require stabilizers prior to processing. The most frequently used stabilizers are organometallic compounds, such as dialkyltin mercaptides and dialkyltin carboxylates. The effect of these stabilizers is usually enhanced by the inclusion of alkali or alkaline earth metal salts, e.g. barium and calcium stearates. Other compounds that have a synergistic effect on organometallic compounds include weak organic acids, phosphite esters, epoxides, polyhydric alcohols, and antioxidants.

PVC degradation is set in motion by the evolution of hydrogen chloride (HCl), or dehydrochlorination, chain scission, and crosslinking. The degradation causes discoloration and poor physical and chemical properties. The HCl evolves by its elimination from the backbone; discoloration occurs because of the formation of conjugated polyene sequences of 5 to 39 double bonds. Subsequent reactions of highly reactive conjugated polyenes crosslink or cleave the polymer chain and form benzene and condensed and/or alkylated benzenes in trace amounts, depending on the temperature and available oxygen.
The causes of PVC degradation are not clear. In their studies, Ashina and Onozuka\textsuperscript{31,32} found that low molecular weight analogues of PVC, including 2,4-dichloropentane and 2,4,6-trichloroheptane, were relatively stable organic compounds that degraded at temperatures above 300ºC. Consequently, pure PVC should be more stable than it actually is. However, its degradation starts at temperatures below 150ºC. The instability of PVC, as compared to low molecular weight analogues, may be explained by irregularities in its structure and the increase in the number of conformations. The reactions to produce PVC molecules are more numerous than those which produce low molecular weight analogues. Then, contrary to what is found in small molecules, the randomness of the reactions necessary for obtaining high molecular weight PVCs can cause structural defects, such as head to head structures, double bonds, branching, the presence of tertiary (allylic) chlorine atoms, and the presence of groups with oxygen from oxidation reactions during synthesis and processing. The structural defects of PVC may cause its premature degradation with the release of HCl or dehydrochlorination.

Braun et al.\textsuperscript{33} showed that unstabilized PVC exposed to heat, ultraviolet light, or gamma radiation dehydrochlorinated via radical intermediate formation. The reactions involved the elimination of hydrogen chloride and the formation of sequences of double bonds or polyenes. Sometimes intramolecular and intermolecular crosslinking accompanied the elimination reaction. It is probable that crosslinking occurs by the Diels-Alder condensation of polyenes. As a result, the PVC properties deteriorate rapidly. Ambient oxygen intensifies these effects, making it necessary to use stabilizers.

Several researchers\textsuperscript{31-35} studied the effect of stabilizers on PVC degradation. These studies revealed that most of the stabilizers avoid the formation of hydrogen
chloride by coordinating with chlorine atoms in the chains to form a complex. The ligand (e.g. carboxylates, mercaptides, etc.) not only avoids the abstraction of the chlorine atom to which it is complexed, but also of close chlorine atoms in the chain. Because of this extended action, the stabilizer avoids the dehydrochlorination that initiates the formation of polyenes and crosslinks. Baker and Grossman\textsuperscript{34} have suggested that the effective selection of the stabilizers should be based on the ability to coordinate rapidly with the polar carbon-chlorine bond. This implies a polar-nonpolar molecule. Most organometallic stabilizers fit this description, but they are extremely toxic, react violently with air or water, or have high reactivity with polar substrates. Exceptions are the relatively inert, alkyltin derivatives, such as dialkyltin mercaptides and dialkyltin carboxylates, in which the tin in the +4 oxidation state is covalently bonded to two alkyl groups and to two ligands capable of reacting with labile chlorine\textsuperscript{34}.  

2.1.3.2. Plasticization

The mechanical properties of PVC have been tailor made to suit products with uses from rigid to flexible by adding plasticizers. The plasticized PVC compound increases its flexibility, workability, and densability. According to ASTM standard D-833\textsuperscript{36}, plasticizers interrupt strong intermolecular interactions existent in polar polymers such as PVC, increasing chain mobility and lowering the $T_g$. Plasticizers of either a monomeric or polymeric nature have been studied by many researchers\textsuperscript{37-39}. According to the monograph by Krauskopf\textsuperscript{37}, monomeric plasticizers are categorized into five major chemical families, including phthalates, aliphatic dicarboxylic acid esters, phosphates, epoxies, and others. Phthalates are the most versatile and widely used plasticizers because of their good compatibility, excellent processing behavior, low temperature flexibility, low volatility, heat and light stability, and relatively low cost. The other
plasticizers, such as aliphatic diesters, as well as phosphates and esters of phosphoric acid, are used for low temperature flexibility and flame resistance, respectively.

The addition of plasticizers to PVC has two goals: to change the processability of the resin, and to modify the long term physical and mechanical properties. Thus, the term “permanence” was introduced to represent the ability of a plasticizer to remain within the PVC, while retaining its plasticizing effectiveness under various conditions. Monomeric plasticized PVC exposure to high temperatures, extractive fluids, or other polymers can result in the loss of plasticizer due to volatization, extraction, or migration. Consequently, polymeric plasticizers were introduced. They exhibit long term permanence, but are required to have low glass transition temperatures and must be thermodynamically miscible with PVC.

Polymeric plasticizers are typically synthesized from the polycondensation of dihydric alcohols and dicarboxylic acids, resulting in oligomeric ($M_n \approx 1000 - 4000$) and high molecular weight polyesters. Control of the stoichiometry and the polymerization process yields hydroxyl terminated polyesters (carboxyl terminated polyesters are rare in PVC plasticizers) of the required molecular weight. Terminating agents, such as monohydric alcohols or monocarboxylic fatty acids, are frequently added in stoichiometric amounts to control molecular weight and viscosity and to change the terminal groups from hydroxyl to alkyl. Polyester plasticizers are noted for their improved permanence relative to standard low molecular weight monomeric plasticizers. Polyester plasticizers have made possible the successful use of flexible PVC in applications, such as refrigerator gasketing, pressure sensitive tapes, and oil resistant electrical insulation for high temperature appliance wiring -- all of which require plasticizer permanence. The drawbacks of such polymeric plasticizers include high
viscosity, low rates of solvation, poor low temperature properties (i.e. flexibility), and relatively high cost\textsuperscript{[37]}. 

2.1.3.3. Processing Methods

As mentioned, a typical PVC formulation with different ingredients requires various compounding steps. The first compounding is a dry blending, in which the PVC is mixed with additives (liquids, powders, waxes, etc.) in a high intensity mixing device. The objective of the first compounding stage is to have a free flowing powder that contains all the necessary additives to comply with the consecutive compounding, processing, and property requirements\textsuperscript{[40]}. According to Roesler and Shah\textsuperscript{[41]}, it is common practice to compound PVC with its additives with intensive mixers, such as two-roll mills, internal mixers, and extruders. When properly used, these mixers avoid late melt processing operations that could thermally dehydrochlorinate the PVC.

The effect of dry blending on the PVC grains depends on the blending temperature. At room temperature, the plasticizer fills the grain pores but it does not interact with the primary particles. The filling is irreversible because of strong surface interactions between PVC and the plasticizer. The plasticization at room temperature is a physical process determined by the geometry of the system. No chemical factors affect it.

In dry blending at high temperature (ca. 130 °C), the plasticizer diffuses into the grains and interacts with the primary particles. The plasticizer is absorbed into the primary particles making the plasticization time dependent. The role of the pericellular membrane is not yet clear. However, it is generally accepted that its presence does not affect the plasticization process.
As mentioned above, the plasticization of the PVC at scale of a grain depends on particle geometry and chemistry. However, effective plasticization on an industrial scale requires intensive mixing in the proper processing equipment.

Continuous mixers such as extruders are generally preferred as compounding devices in the PVC industry, due to higher production rates and reduced cost. Intermeshing twin screw extruders are particularly useful for compounding PVC. Relative to single screw extruders at comparable L/D ratios, twin screw extruders mix PVC with its additives more effectively at lower screw speeds and processing temperatures. To achieve the same level of mixing, single screw extruders must operate with high screw speeds, backpressure, and the high temperatures (often ≥ 200°C). As a result, thermal degradation of PVC becomes more probable in single screw extruders. In conclusion, intermeshing twin screw extruders (especially the co-rotating type) are more convenient continuous mixing devices for compounding PVC, especially if heat sensitive rigid compounds of PVC with other polymers are to be produced.

2.1.4. PVC Blends

The limited properties and processing difficulties of PVC compounding can be improved with the addition of high molecular weight polymeric modifiers to the PVC compounds. The blends of PVC with other polymers have commercial significance but are difficult to blend as well as to handle on conventional equipment used to process PVC. One of the oldest successful commercial blends of PVC with polymers is the blend of PVC and butadiene acrylonitrile rubber (NBR). The addition of NBR to PVC improves its permanence, tear strength, abrasion resistance, and compression set. Therefore, this low cost blend has held a unique position for many years as the only high molecular weight permanent plasticizer for PVC.
Even though the blend of PVC/NBR has been available commercially for a long time, the miscibility of PVC with NBR has not been well understood. Most of the studies of the miscibility of PVC with NBR were done by dynamic mechanical analysis, tear strength, and abrasion resistance tests. Based on these mechanical tests, the blends of PVC and NBR were believed to be completely miscible until morphology studies changed the opinion. The general concept of the miscibility of polymers with high polarity, such as PVC with non-polar or polar polymers, were examined for various polymer-polymer blends.

Several studies\textsuperscript{43,44} have suggested that in the case of polar polymers, specific interactions such as hydrogen bonding or electron donor/electron acceptor influence the miscibility of the polymers. In these studies, $T_g$ determination by DSC was used in conjunction with IR spectroscopy to determine miscibility. They found that in such blends, PVC chlorines act as electron acceptors and carbonyl, ether, acrylonitrile, sulfonyl, and phenyl ring groups present in the other polymer as electron donors. Therefore, polymers containing these groups exhibit miscibility with PVC. Specifically, Ziska et al.\textsuperscript{43} and Prud’homme\textsuperscript{44} studied the miscibility of polymers containing PVC with carbonyl containing polymers by means of IR spectroscopy. They reported that the interaction between the $\alpha$-hydrogen of the PVC and the oxygen present in the carbonyl group might cause the miscibility. Other possible mechanisms of interactions were proposed involving $\beta$-hydrogens and dipole-dipole interactions between the C-Cl and carbonyl groups\textsuperscript{45-49}.

Apart from NBR rubber, other polymers have been blended with PVC, including copolymers of ethylene and vinyl acetate, poly(methyl methacrylate) (PMMA) and copolymers of methyl methacrylate, block copolymers of poly(butylene therephthalate)
and poly(tetramethylene oxide), thermoplastic elastomers, hydroxyl terminated polyester oligomers and thermoplastic polyurethanes.

Elmqvist and Svanson\textsuperscript{50} and Hammer\textsuperscript{51} studied the miscibility of the copolymers of ethylene and vinyl acetate with PVC using DSC and torsion pendulum studies. They found that the miscibility of EVA copolymers with PVC was dependent on the EV content. The blends of PVC and EVA copolymers with the EV content of 65-70 \% exhibit miscibility. Below concentrations of 45 \%, the blends showed less miscibility. Schurer et al.\textsuperscript{52} studied the blends of PMMA and the copolymers of methyl methacrylate. They found that the $T_g$ of the blends was increased with respect to the $T_g$ of neat PVC. They also found that the miscibility of PVC/PMMA is a function on the tacticity of PMMA.

The block copolymers of poly(butylene terephthalate), poly(tetramethylene oxide), and Hytrel\textsuperscript{®} (thermoplastic elastomers based on random copolymer of poly(butylene terephthalate) and poly(tetramethylene oxide)) work as excellent permanent plasticizers of PVC. The blends of PVC with Hytrel and polyester based TPUs were at least partially miscible. Therefore, the $T_g$ shift of PVC was limited by its hard block content\textsuperscript{53-56}. Chen et al.\textsuperscript{57} patented a blend of PVC with Hytrel\textsuperscript{®} which exhibited excellent permanence, abrasion resistance, low temperature flexibility, impact resistance, and improved scratch resistance.

Hydroxyl terminated polyester oligomers used as PVC plasticizers have been cited in various patents\textsuperscript{58-60}. These publications suggest miscibility between the polymers. Bonk et al.\textsuperscript{2} reported that thermoplastic polyurethanes (TPUs) of the polyester type worked as polymeric plasticizers of PVC. They found that the blend properties combine the wear resistance and toughness of the TPU with the stiffness and high modulus of PVC. Brookman\textsuperscript{4} suggested that PVC blends with TPUs have good
abrasion and fatigue resistance and can be used in cable jacketing and shoe soling. In conclusion, Hytrel® and TPUs improved the abrasion resistance, fatigue resistance, and surface properties of PVC. However, their efficiency as plasticizers is low, due to their hard block content, high cost, and compounding difficulties.

2.2. Thermoplastic Polyurethanes

Polyurethanes are block copolymers containing blocks of low molecular weight polyesters or polyethers covalently bonded by a urethane group. In 1937, Otto Bayer and his coworkers of I.G. Farberindustrie at Leverkusen, Germany (now Bayer AG) produced the first polyurethane when trying to duplicate or improve the properties of synthetic polyamide fibers, thus opening the door to a new class of high performance polymeric materials suitable for coatings, adhesives, elastomer, fibers, and foam applications. By the 1940s Polyurethanes had been produced on an industrial scale and by the 1960s TPUs were already commercialized in Germany and the United States.

Thermoplastic polyurethanes (TPUs) are biphasic materials, usually called multiblock copolymers, that combine the properties of a glassy or semi-crystalline thermoplastic and a soft elastomer, enabling rubbery materials to be processed as thermoplastics. The TPUs consists of hard segments that form rigid domains linked covalently to rubbery segments providing a soft matrix in which the hard domains reside. These hard segments consist of a short-chain diol (chain extender) and a diisocyanate, while the soft segments consist of long-chain diols. The block structure of a molecule of TPU is represented in Figure 2.2.

At room temperature, the soft (low melting) and hard (polar high melting) segments are thermodynamically immiscible, resulting in a microphase separation. At
At room temperatures, the hard segments form crystalline domains, while the soft segments form the amorphous phase. At a temperature below the melting temperature of the crystalline domains, they act like a physical crosslink similar to the chemical crosslinks in cured rubbers\textsuperscript{10,64-68}. When TPUs are heated above the melting temperature of the crystalline domains, a homogeneous viscous melt is formed. In the melt, the TPU can be processed by a conventional thermoplastic technique (e.g., extrusion, injection molding, calendaring, etc.). When the TPU is cooled down, phase separation occurs again. It is expected that this cycle can be repeated indefinitely, displaying its thermoplastic character. The morphology of a TPU at both low and at high temperature is shown in Figure 2.3.

![Figure 2.2. Schematic representation of a TPU composed of: diisocyanate, long chain diol, and chain extender](image)

**Room Temperature**  
**High Temperature**

![Figure 2.3. Representation of domains in TPU\textsuperscript{68}](image)

TPUs were the first homogeneous thermoplastic elastomers to be commercially developed in the polymer industry and still play an important role within the rapidly
growing family of thermoplastic elastomeric materials. TPUs are used in a variety of applications owing to their excellent abrasion resistance, high tensile and compressive strength, excellent tear strength, good low temperature properties, good chemical resistance, good thermal resistance, and low compression set. Currently, TPUs are used in hoses, shoe soles, exterior automotive body parts, mechanical goods, medical applications, etc.\textsuperscript{10,69}

2.2.1. Chemistry of Polyurethanes

The term polyurethane is used to designate those polymers that are produced by the diisocyanate polyaddition principle that is, made by the reaction of polyfunctional isocyanates and hydrogen bearing nucleophiles, as shown in the equation (2.1).

\[ \text{RNCO} + \text{R'}\text{OH} \rightarrow \text{RNHCOOR'} \]  

(2.1)

Polyurethanes are characterized by the presence of the urethane group in the chain. This group is formed during this reaction at elevated temperature (\( \geq 210 ^\circ\text{C} \) for MDI/BDO linkages\textsuperscript{70}). The urethane reaction is completely reversible, even at the solid state. TPUs are polyurethanes in which the polyaddition reaction occurs between the diisocyanate and chain extender to form the hard segment, and simultaneously a reaction between hard and soft segments occurs among the hydroxyl end groups of the macrodiol and the isocyanate groups in the ends of the hard segments.

Even though the presence of urethane groups in the chain characterizes a polyurethane, its proportion in the chain compared to all the other functional groups also present in the chain is very small. Therefore the term polyurethane comprises a multitude of polymers that contain the urethane group. Due to the variety of monomeric building blocks available and the possibility of stable intermediates (i.e. prepolymers) during synthesis, the number of possible compositions and different
properties obtainable gives to polyurethanes a versatility that cannot be surpassed by any other polymer\textsuperscript{6,10,67}. Even if only the raw materials are considered, the great variety of diisocyanates and hydrogen bearing nucleophiles available, the number of building blocks to synthesize a PU is almost unlimited; hence, it is possible “tailor-make” PUs according to a required application.

In the following section, the raw materials required to produce a PU and hence a TPU are discussed in more detail.

2.2.1.1. Isocyanates

Isocyanates have been known as the most important components in polyurethane chemistry since the middle of last century\textsuperscript{71}. They have high reactivity, especially with nucleophilic co-reactants, such as polyesters or polyethers. Isocyanates include a large group of compounds that can be aromatic, aliphatic, or cycloaliphatic. They are produced by the phosgenation of amines. In the polymer industry, the aromatic diisocyanates are most commonly used to produce polyurethanes. Among these the 2,4- and 2,6- isomers of toluene diisocyanate (TDI) and isomers of methylene diphenylene diisocyanate (MDI) are the two more important reactants. Both monomers are toxic. TDI has higher vapor pressure that makes it far more dangerous to handle than MDI. At room temperature, MDI (m.p.\textsuperscript{\textdegree}C=42) is in the solid state and slowly dimerizes. In what follows, the mechanism of reaction between the polyol and the isocyanate for polymerization of polyurethanes is described. First, the chemical structure of each monomer is explained, and then their chemical reactions. The chemical structure of MDI is depicted in Figure 2.4.

The reactivity of the isocyanate group can be explained by its electronic structure, as depicted below\textsuperscript{72,73}:
Such resonance structure suggests the possibility of a reaction with electron donors attacking the carbon and electron acceptors attacking either the oxygen or the nitrogen atom. The normal reaction ultimately provides an ionic addition to the carbon-nitrogen double bond by functional groups that contain an active hydrogen atom (i.e. one that is replaceable by sodium).

The more important reactions of isocyanates can be classified as primary and branching reactions\(^\text{10,72,73}\). Primary reactions include reactions with hydroxyl containing substances (alcohols), amines and water; while branching reactions are reactions with products generated in the primary reactions or reactions of the raw materials with themselves.

Reactions of isocyanates with hydroxyl containing substances such as alcohols are used for the production of polyurethanes, as shown in equation (2.1)

\[
\text{RNCO} + R^+\text{OH} \rightarrow \text{RNHCOOR}' \quad (2.1)
\]

At lower temperatures, this reaction is easier, as the nucleophilic character of the alcohol increases. Therefore, the order of reactivity of alcohols is as follows: primary alcohols, secondary alcohols, and phenols\(^\text{74}\). Wagner et al.\(^\text{75}\) suggested that when the polyurethane is subjected to high temperatures, the reaction reverses, resulting in alcohol and isocyanate. Consequently, the reaction is reversible at high temperatures. The reaction 2.1 can be influenced by the presence of acids and bases. Acids will prolong the reaction\(^\text{76,77}\), and basic compounds will catalyze it\(^\text{78}\).

Reactions of isocyanates with primary and secondary amines produce ureas, as shown in equation (2.3) below. The reactivity of isocyanate with amines is higher than with hydroxyl bearing compounds because of amines’ higher nucleophilic character.
RNCO + R’NH₂ → RNHCONHR⁺ (2.3)

The reaction between an isocyanate and water produces a carbamic acid, which is unstable and decomposes to form an amine and carbon dioxide, as shown in equation (2.4). This reaction is useful in the production of foams.

\[ \text{RNCO} + \text{H}_2\text{O} \rightarrow [\text{RNHCOOH}] \rightarrow \text{RNH}_2 + \text{CO}_2 \]  

(2.4)

Branching reactions might generate crosslinking in some polyurethane systems, especially in formulations containing excess isocyanate. The branching includes reaction with urethane groups (allophanate formation), or with urea groups (biuret formation) or the trimerization of the isocyanate. These reactions are represented in equations (2.5), (2.6) and (2.7) respectively.

\[
\begin{align*}
\text{RNCO} + \text{R’’NHCOOR’’} & \rightarrow \text{CONHR} \\
\text{RNCO} + \text{R’’NHCONHR’’} & \rightarrow \text{CONHR} \\
2\text{RNCO} & \rightarrow \text{RN} - \text{N} - \text{N} - \text{R}
\end{align*}
\]

(2.5)  

(2.6)  

(2.7)

Allophenate and biuret formation also occur with polyisocyanate. In this case the reactions produce polymer branching. Saunders et al.\textsuperscript{79} and Wright et al.\textsuperscript{73} found that branching occurs at an appreciable rate when temperatures exceed 100-120°C. However, Thiele\textsuperscript{80} suggested that this reaction occurs much less vigorously than
urethane or urea formation and that these structures have low thermal stability and
dissociate into their starting components above 150°C.

MDI is one of the most widely used isocyanates in the polyurethane industry due
to its high reactivity and isocyanate content. Its use produces high-strength elastomers,
as well as PU coatings with an excellent combination of tensile properties, tear strength,
and elongation at break\textsuperscript{81}. Nevertheless its use is limited due to its tendency to
dimerize during storage and the difficulty of handling it due to its solid nature at room
temperature ($T_m$: 38 °C). Thermodynamically, the dimer is more stable and its
formation can occur either in the molten or solid state; however, it can be minimized if
the MDI is stored at temperatures lower than 5 °C or slightly above its melting point
(42-45 °C). Industry had to face having an excellent quality monomer with a limited
shelf life without ease of handling. To solve this problem, several modifications to the
4,4′-MDI have been proposed to replace it, sacrificing as little performance as possible.
Several approaches have been found to produce a liquid modified MDI\textsuperscript{81,82}. One is to
blend 2,4′- and 4,4′-MDI, while another is a carbodiimide-modified MDI. Also urethane
and allophanate modifications have been made. All these modifications had been
reported to have better storage stability, as well as being easier to handle due to their
liquid nature at room temperature. In addition, their dimerization is reduced. Table
2.1. shows a comparison of the different MDIs and their properties. Figures 2.4.-2.7.
shows the different chemical structures of the modified MDIs.

\[
\text{Figure 2.4. Chemical Structure of 4,4′-MDI}\textsuperscript{10}
\]
Figure 2.5. Chemical Structure of 2,4'-MDI\textsuperscript{10}

Figure 2.6. Chemical Structure of Carbodiimide-Modified MDI\textsuperscript{83}

Figure 2.7. Chemical Structure of Allophanate-Modified MDI\textsuperscript{81}
Table 2.1. Properties of the Different Forms of the methylene diphenylene diisocyanate (MDI)\textsuperscript{81}

<table>
<thead>
<tr>
<th>Product</th>
<th>Name</th>
<th>%NCO</th>
<th>F</th>
<th>Viscosity (mPa.s/25 °C)</th>
<th>Tc (°C)</th>
<th>2,4' isomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4' MDI</td>
<td>SMDI</td>
<td>33.6</td>
<td>2</td>
<td>Solid</td>
<td>28</td>
<td>Trace</td>
</tr>
<tr>
<td>2,4'-/4,4' MDI</td>
<td>LMDI</td>
<td>33.6</td>
<td>2</td>
<td>10</td>
<td>18</td>
<td>~55%</td>
</tr>
<tr>
<td>Carbodiimide Modified MDI</td>
<td>CDMDI</td>
<td>29-30</td>
<td>2-2.5</td>
<td>40-50</td>
<td>8</td>
<td>Trace</td>
</tr>
<tr>
<td>Urethane Modified MDI</td>
<td>UMDI</td>
<td>23</td>
<td>2</td>
<td>650</td>
<td>10</td>
<td>Trace</td>
</tr>
<tr>
<td>Allophanate Modified MDI</td>
<td>AMDI</td>
<td>23-29</td>
<td>2-2.2</td>
<td>37-450</td>
<td>-8 - 19</td>
<td>-</td>
</tr>
</tbody>
</table>

The blends of MDI isomers (LMDI) maintain the high isocyanate content, are liquid at room temperature, and have a lower tendency to dimerize. However, the isocyanate group in the 2 position reacts more slowly, due to its hindered position, than the one in the 4-position by a factor of 20 at room temperature\textsuperscript{81,84}. The carbodiimide modified MDI (CDMDI) is produced by the reaction of MDI with itself using a specific catalyst. Then the carbodiimide group reacts with another MDI molecule to produce a uretonimine group. There is an equilibrium between the carbodiimide and the uretonimine, which could be affected by changes in temperature. The CDMDI has a lower NCO content than the pure MDI and a functionality higher than 2. The allophanates and urethane modifications are produced by reacting the neat MDI (SMDI) with a polyether glycol or a monoalcohol to produce the urethane or allophanate linkage. These products are liquid at room temperature, generally have higher viscosities than LMDI and CDMDI, but have lower contents of NCO and/or higher
functionalities. A wide variety of liquid modified MDIs are available on the market; however, limited research has been done with them\textsuperscript{81-87},

2.2.1.2. Polyols

Polyols are polyhydroxyl compounds of nucleophilic character. Polyols with various molecular weights represent the most important component that reacts with isocyanates. High molecular weight polyols are used in more than ten syntheses of PUs. The high molecular weight polyols can be classified into two types: polyethers and polyesters.

Polyether polyols are synthesized from the alkali catalyzed anionic chain growth polymerization of epoxides to low molecular weight diols or polyols, such as ethylene oxide and propylene oxide. The other epoxides synthesized from the cationic chain growth polymerization of tetrahydrofuran is poly(tetramethylene ether or oxide) glycols (PTME)\textsuperscript{10}. The chemical structure of a typical polyether polyol is shown in Figure 2.8.

Hydroxyl terminated polyester polyls are synthesized by the step growth polycondensation of multifunctional carboxylic acids and hydroxyl compounds. Since it is necessary to have hydroxyl group chain termination in the synthesis of PUs, a stoichiometric excess of the hydroxyl component is required. Relative to polyether polyols, these polyester polyols have a wide molecular weight distribution, resulting from intramolecular transesterification reactions\textsuperscript{88}. In general, polyester polyls have an average molecular weight of 400 to 6000, hydroxyl numbers from 28 to 300 mg KOH/g, and acid numbers less than 1 mg KOH/g for the production of PUs. For example, typical polyester polyls used in the synthesis of TPU's would result from the direct esterification of adipic acid and an excess of ethylene glycol, 1,4 butendiol, 1,5 hexanodiol, neopentyl glycol, or mixtures of these diols. Branched polyester polyls are
obtained using a hydroxyl compound with a functionality greater than 2, such as trimethylpropane. Other processes for the synthesis of hydroxyl terminated polyesters include the ring opening polymerization of cyclic lactone esters, such as ε-caprolactone\textsuperscript{10}. The structure of a typical polyester polyol is depicted in Figure 2.9.

\[ \text{HO-CH-CH}_2\text{-}[\text{O-CH-CH}_2]_n\text{-CH}_2\text{-CH- OH} \]

Figure 2.8. Polyether Polyol Structure\textsuperscript{10}

\[ \text{HO-R-O[-CO-R'-CO-O-R-O]}_n\text{-H} \]

Figure 2.9. Polyester Polyol Structure\textsuperscript{10}

2.2.2. Synthesis

Thermoplastic polyurethanes can be synthesized by various methods of preparation, such as bulk, solution, etc, according to the different addition sequences of the reactants. TPU\textsubscript{s}, along with foams and cast elastomers, are exclusively prepared by the one shot method and prepolymer process. The one shot method consists of mixing all components at once, while in the “prepolymer method” the polyol is first reacted with the diisocyanate to give a prepolymer. This prepolymer is then reacted with the chain extender to form the polyurethane. Both preparation methods can be performed batchwise and continuously either in a mixing chamber or in an extruder\textsuperscript{65,89-99}. Regardless of the process used, the stoichiometric ratio of hydrogen bearing nucleophiles to isocyanate should be close to 1. If it is less than 1 (c.a. 0.96\textsuperscript{69}), a low molecular weight product is obtained, while if it is greater than 1 (c.a. 1.1\textsuperscript{69}), a partially crosslinked product, difficult to process, is obtained. The sum of functionalities should be approximately 2 to lead to a high molecular weight linear chain or with just a few branches. The sum of functionalities of all reactants should not exceed 2. The stoichiometric deficient quantities of isocyanate or functionalities less than 2 lead to low
chemical cross linking (allophanate and biuret structures, in the case of excess isocyanate\textsuperscript{10,69}). To avoid undesirable side reactions and to maintain adequate stoichiometry, water should be removed, even if it is present only in small quantities.

In the one-shot method, the bulk polymerization of TPUs is carried out by simultaneously mixing all reacting components at temperatures between 60 and 120 °C. The reaction is highly exothermic and fast. Therefore, reactants must be mixed quickly at a molecular level. Depending on the catalyst used, the completion of the reaction is usually approached within 2 to 30 minutes. Then, the polyurethane is post cured. The final desired mechanical properties and molecular weight are achieved in several hours if the polyurethane is post cured at a relatively high temperature (e.g. at 110 °C\textsuperscript{100}). If the polyurethane is post cured at room temperature, the final desired mechanical properties and molecular weight are approached after 24 to 48 hours\textsuperscript{10}. The one-shot process requires all reactants to exhibit approximately the same reactivity, otherwise branching or incomplete reaction due to phase separation occurs\textsuperscript{10}. The chemical reaction of the one shot process is shown in Figure 2.10.

In the prepolymer process, isocyanate terminated intermediates, often termed prepolymers, are synthesized from the polyaddition of polyols with a stoichiometric excess of isocyanates. The prepolymer is then reacted with other low molecular weight polyol or hydrogen bearing chain extenders to complete the reaction and to obtain a high molecular weight PU product. The prepolymer process makes it possible to synthesize isocyanate terminated intermediates with a desired average molecular weight, giving more control over the final chemical structure of the block copolymer. It also allows for the complete conversion of low reactivity reactants in the absence of catalysts\textsuperscript{10}. 
2.2.3. Kinetics of Polymerization

2.2.3.1. General

In the polymerization of polyurethanes, the primary reaction is the formation of PUs from active hydrogen bearing compounds and isocyanate. The secondary reactions generate undesired by-products. Among these by-products, allophanates can act as intermediates during the production of PU\textsuperscript{101,102}.

The previous mechanisms\textsuperscript{76,103-109} suggested the major reactions of PU formation in two steps. First, a complex is formed between the isocyanate group and the active hydrogen compounds, as depicted in Figure 2.11. Second, the conversion of the complex is changed to the product by reacting with a free molecule of the active hydrogen compounds. These two-step reactions can proceed with or without catalysts. The rate of the catalyzed reactions is faster than the uncatalyzed reactions. Robbins et al.\textsuperscript{108} proposed the following two-step mechanism for metal ion catalyzed formation of urethanes, as shown in Figure 2.8. The kinetic of PU reactions has been studied for 50 years. In the late 1940’s, Baker et al.\textsuperscript{78,103-105} studied the isocyanate reactions with
active hydrogen compounds with monofunctionality in solution. They found that the alcohol behaves as a reagent and as a base catalyst. They proposed a mechanism in which the isocyanate and the alcohol produced a complex that reacts further with the alcohol to form the polyurethane. It was discovered that the urethane group autocatalyzed the polyurethane formation reaction.

![Figure 2.11. Mechanism a PU catalyzed reaction](image)

The catalyzed and uncatalyzed reactions of aromatic\textsuperscript{101-105,109-115}, aliphatic\textsuperscript{110,116-118} and furan\textsuperscript{119} based isocyanates with alcohols in different solvents\textsuperscript{101,102,109-112,117,120}, as well as in bulk\textsuperscript{6,106,107,121,122} have been investigated. Most of the studies mentioned above focused on the reaction in solution states. Therefore, these results are not applicable for the reactive processing of PUs, such as the reactive extrusion of TPU or reactive injection molding. Ephraim et al.\textsuperscript{111} studied the reactions of polyurethane synthesis in different solvents. They found that the order of reaction depended on the H-bonding strength of the solvent. They proposed three mechanisms of reaction that included three different intermediate complexes, depending on the strength of the H-bonding with the solvent. Van Der Weij\textsuperscript{109} reported the different mechanism for the catalyzed reaction of dibutyltin diacetate. The reaction with the solvents with low polarity (e.g. dibutyl ether) proceeded via ionic intermediates when the concentration of
the ions was small. Later, Rand et al.\textsuperscript{113} found that the use of polar solvents decreased the activity of catalysts by hindering the complex formation.

The isocyanates and alcohols have different reactivity\textsuperscript{106,107,117,120,121}. In the case of diisocyanates, the aryl diisocyanates are the most reactive, while the alkyl the least. The furan-based diisocyanates have reactivity between those of aryl and alkyl diisocyanates. However, the reactions with furan-based diisocyanates are more complex and the modeling of the kinetics is difficult. Other studies conducted by Kogon\textsuperscript{112} and Burkus et al.\textsuperscript{110} revealed that different substitutions on the phenyl ring decreased the reaction rate as well as the kinetic parameters. The study of isocyanate groups with unequal reactivity\textsuperscript{106,110,120,123} found deviations from second order kinetics. These authors proposed that those deviations were due to steric hindrance. For Toluene diisocyanate (TDI), it was found that at room temperature the groups NCO react at different rates. The group in the para position reacts 100 times faster than the one in the ortho position at room temperature. However, at 125ºC the rates were almost the same. If the reaction was catalyzed, the difference in reactivity between the NCO groups was less. Thus, at room temperature the difference is less than 100, and no effect of the catalysts on the reaction rate was detected at 125ºC.

The functions of a catalyst are to increase the electrophillic character of the isocyanate group by coordinating either the oxygen or the nitrogen of the isocyanate, as well as to bring the OH and NCO to closer proximity\textsuperscript{124}. Hence, there was a difference in mechanism and rate of reaction between the catalyzed and uncatalyzed reactions due to the interaction of the components with the catalysts\textsuperscript{125}.

Frisch et al.\textsuperscript{126} have confirmed that the probability of the formation of isocyanate-catalyst complexes is very low. He also found that the combination of catalysts could
have a synergistic effect to form metal bonds and hydrogen bonding. Abbate et al.\textsuperscript{127} proposed a template-type mechanism for an organometallic catalyzitation. The catalysts could have complexed both reactants, but the complexion with isocyanate was unfavorable.

The most frequently used catalysts were amine catalysts and organotin compounds\textsuperscript{101,102,110,112,113,117,127,128}. These catalysts were found to be very effective in increasing the rate of reaction in comparison to the uncatalyzed systems\textsuperscript{115,118,128}. However, the organotin compounds have been found to favor selectively the primary reaction over the secondary reactions\textsuperscript{120}. Rand et al.\textsuperscript{113} found that the type and concentration of metal catalysts, as well as the structure of the alcohols and the type of solvents (if any) played an important role in the reaction rate and kinetic parameters. Gambiroza-Jukic et al.\textsuperscript{129} and Rand et al.\textsuperscript{113} found that the metal catalysts, including lead naphtenate, dibutyltin dilaureate, or ferriacetylacetonate increased the reaction rates of the formation of primary and secondary alcohols formation in different proportions.

Smith\textsuperscript{130,131} found the effect of different catalysts, such as tertiary amines and metal salts, on the reaction rates of mono or poly functional alcohols with mono or poly functional isocyanates. One of his studies\textsuperscript{130} revealed that the activities of the catalysts with monofunctional alcohols followed an order inverse to the order followed for the reactions with polyfunctional alcohols. With the monofunctional compounds, the order was cobaltous stearate > stannous 2-ethylhexoate > triethylendiamine. In his second study, Smith\textsuperscript{131} concluded that the amount of urethane catalyst was dependent on the type of catalyst and alcohol and the interaction between them.

Sojecki\textsuperscript{128,132-135} conducted a series of studies of the reaction of TDI with several unsaturated polyesters with various solvents to determine the interaction between
solvents and reactants. He found that the reaction rate increased as the dielectric constant of the solvents increased, as shown in Figure 2.12., and that higher temperatures favored selectivity. Sojecki proposed that the reaction of isocyanates with saturated polyesters\textsuperscript{106,124} followed a different mechanism than that for the reaction with unsaturated polyesters, because of the interaction between protons of hydroxyl groups with double bonds.

Figure 2.12. Effect of Dielectric Constant on the Rate Constant of Urethane Reaction\textsuperscript{135}

The studies mentioned above focused on both the mechanism and kinetics from the characterization of initial and final products with methods such as titration and dielectric constant measurements. They neglected a variety of intermediates formed during the reaction. However, by using modern analytical techniques including chromatography and spectroscopy it is possible to detect various intermediates, as well as the final reaction products\textsuperscript{101,102,136,137}. Wong et al.\textsuperscript{101,102} used High Performance Liquid Chromatography, HPLC, to determine the reaction mechanism by screening initial, intermediate, and final products. In their research, Wong et al. were able to
prove that allophanate products were an intermediate stage in the production of certain polyurethanes.

2.2.3.2. Kinetic Models

The mechanisms of reaction and the influence of different reaction conditions on the process were described in the previous section. To obtain kinetic models, there have been two general approaches used in previous studies, namely, phenomenological and "kinetic". The former approach is based on empirical results, according to which an empirical correlation is suggested in order to describe the whole reaction process. The latter "kinetic approach" has been developed on the basis of the detailed mechanism of reaction.

The kinetic approach is specific for the system that is being studied. It cannot be generalized to other systems under different conditions, and generally complex kinetic expressions are obtained even when important phenomena, such as branching, crosslinking, phase separation, and diffusional effects have been excluded. For this reason, most researchers$^{6,72,101,102,117,138-142}$ have proposed phenomenological kinetic models that can be generalized for the different polymerizing systems.

Camargo$^{72}$ produced a compilation of polyurethane formation kinetic data obtained by different authors, and found that most data followed the general kinetic expression shown below.

\[
\frac{d[NCO]}{dt} = -k[NCO]^a[H]^b
\]  

(2.8)

where \( k \) is the rate constant and \([NCO]\) and \([H]\) are the concentration of isocyanate and hydrogen bearing compounds, respectively. The superscripts \( a \) and \( b \) represent the order of reaction of each component. Several authors$^{6,72,101,102,117,138-145}$ have proposed that the rate constant for the catalyzed reaction be modified as follows.
$k = k_o + k_{cat}[Cat]^c$  \hspace{1cm} (2.9)

where $k_o$ is the rate constant for the uncatalyzed reaction, $k_{cat}$ is the rate constant for the catalyzed reaction, $[Cat]$ is the catalyst concentration, and $c$ is the order of reaction with respect to the catalysts.

Most of previous studies\textsuperscript{72,73,78,93,103-105,107,111,113,120,122,143-151} found that the classical overall second order reaction rate equation fit the experimental data best. However, some deviations from second order kinetics were found by several researchers. The disagreement was attributed to a variety of factors including the catalytic effect of the urethane group\textsuperscript{78,116,141,151}, secondary reactions\textsuperscript{118,120,141,152}, to the catalytic effect of the solvent\textsuperscript{117}, or to a change from a kinetic to a diffusion-controlled regime (gel formation)\textsuperscript{6,140,142,152,153}. The change from a chemical controlled regime to a diffusion controlled regime is generally caused by two situations. The first one happens when a monomer with a functionality greater than 2 is used, limiting the accessibility of the reactive groups by the introduction of crosslinks and consequent hindrance on the movement of the chains. The second situation occurs from the thermodynamic immiscibility of the TPU segments that results in the phase separation of them, hindering the accessibility of reactive groups. This phase separation occurs even when difunctional monomers are used.

In Greenshields’ et al.\textsuperscript{116} study, the reaction rate was found to increase with the dielectric constant and the nucleophillic character of the solvent. Additionally, Wagner and Murla\textsuperscript{76} showed that the chain length of the glycols did not influence the reaction rate constants. However, both investigations agreed that the functionality had an effect on the reaction rate; i.e. primary alcohols reacted faster than secondary ones. Another study accomplished by Rego et al.\textsuperscript{151} on the influence of macrodiol chain length on the
kinetics of PU formation showed that the helical structure, as well as the domain formation caused differences in the kinetic parameters of the reactions studied.

2.2.3.3. Effect of Temperature on Kinetic Models

In many of the studies mentioned above, the reaction rate constant (see equation 2.8) was assumed to follow the Arrhenius type dependence shown in the following equation.

\[ k = A_o \exp\left(-\frac{E_a}{RT}\right) \]  

(2.10)

Where \( A_o \) is the pre-exponential factor, \( E_a \) is the activation energy, \( T \) is the temperature, and \( R \) is the universal gas constant.

According to the Arrhenius expression, it is expected that increasing the temperature will increase the reaction rate. However, since the PU polymerization reactions are reversible, the rate of dissociation of the urethane groups is higher than their rate of formation at high temperature (i.e. 240ºC). Thus, polyurethane of low molecular weight is obtained. Ando\textsuperscript{138} discussed the effect of the temperature on increasing the molecular weight by controlling the temperature.

The phenomenological kinetic equation mentioned in the previous section is expressed more easily in terms of the conversion rather than concentration. The advantage is that conversion is normalized and that the relation between this variable and DSC and the spectroscopic measurements is direct. The kinetic equation 2.8 in terms of conversion is:

\[ \frac{d\alpha}{dt} = k[C]^n(1 - \alpha)^n \]  

(2.11)
where $\alpha$ is the conversion and $[C]_0$ is the initial isocyanate concentration, or active hydrogen compound concentration in the case of equal stoichiometry, and $n$ is the overall reaction rate.

This model has been successfully used by different authors with a variety of systems and experimental techniques including titration\cite{78,104-106,110,111,113,115,117-119,128,132-135,139,154}, infrared spectroscopy (IR)\cite{103,107,109,112,115,125-127,130,141,151}, Raman spectroscopy\cite{6,136}, high performance liquid chromatography (HPLC)\cite{101,102,109}, gel permeation chromatography (GPC)\cite{137,138}, differential scanning calorimetry (DSC)\cite{6,73,123,136,138,146-148,155}, ultraviolet spectroscopy (UV)\cite{109,126}, nuclear magnetic resonance (NMR)\cite{126,156}, and adiabatic temperature rise (ATR)\cite{93,107,122,124,139,153,157}. Most of the kinetic parameters were determined by fitting experimental data to the overall kinetic expression using several experimental of the techniques mentioned above. Therefore, the kinetic parameters are not readily available and are only provided for the systems studied. Some of the experimental techniques such as DSC, Raman, titration, etc. could capture only the extent of reaction at its later stages. The examples of kinetic parameters determined by various experimental methods are listed in Table 2.2.

2.2.3.4. Effect of Pressure and Shear Rate

The kinetic under pressure has scarcely been studied. As noted by Dutta et al.\cite{158}, the effect of pressure on chain polymerization has been studied more than the effect of pressure on step polymerizations, due to a greater difficulty in removing the by-product generated during the reaction. Nevertheless, it is expected that the step polymerizations show more similar behavior under pressure than a chain polymerization.
<table>
<thead>
<tr>
<th>Isocyanate</th>
<th>Hydrogen Bearing Compound</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>( k_1 ) Units</th>
<th>( A_1 ) Units</th>
<th>( E_{a1} ) Units</th>
<th>( k_2 ) Units</th>
<th>( A_2 ) Units</th>
<th>( E_{a2} ) Units</th>
<th>( n )</th>
<th>( c )</th>
<th>Ref.</th>
</tr>
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<tr>
<td>4,4-MDI</td>
<td>Polyoxyethylene adipate and ethylene glycol</td>
<td>-</td>
<td>-</td>
<td>0-100</td>
<td>8.52E07 kg/mol/eq</td>
<td>1.51E01 mol/L</td>
<td>1.61E03 J/mol/mol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>138</td>
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<tr>
<td>MDI</td>
<td>Subarin based polyglycol</td>
<td>dibutyltin diurate</td>
<td>THF</td>
<td>23</td>
<td>- 2.04E01 mol/L</td>
<td>- 2.62E01</td>
<td>- 1.61E03 J/mol/mol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>MDI</td>
<td>Polyoxyethylene glycol</td>
<td>-</td>
<td>-</td>
<td>60-100</td>
<td>9.35E02 mmol</td>
<td>- 2.07E02</td>
<td>- 3.50E02 J/mol/mol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.0</td>
<td>155</td>
</tr>
<tr>
<td>MDI</td>
<td>Polyoxyethylene glycol adipate</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td>9.65E-02 mmol</td>
<td>- 1.63E-02</td>
<td>- 3.08E-02 J/mol/mol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>148</td>
</tr>
<tr>
<td>MDI</td>
<td>Polyoxyethylene glycol adipate</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td>1.24E-01 mmol</td>
<td>- 1.40E-01</td>
<td>- 6.04E-03 J/mol/mol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>148</td>
</tr>
<tr>
<td>MDI</td>
<td>PBA and BDO</td>
<td>-</td>
<td>-</td>
<td>100-150</td>
<td>5.62E02 mol/L</td>
<td>- 3.87E02</td>
<td>- 6.55E10 J/mol/mol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.7</td>
<td>6</td>
</tr>
<tr>
<td>MDI</td>
<td>PBA and BDO</td>
<td>-</td>
<td>-</td>
<td>100-150</td>
<td>5.95E02 mol/L</td>
<td>- 3.87E02</td>
<td>- 6.55E10 J/mol/mol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.7</td>
<td>6</td>
</tr>
<tr>
<td>MDI</td>
<td>BDO-PFO-EO2000</td>
<td>dibutyltin diurate</td>
<td>-</td>
<td>100-150</td>
<td>-</td>
<td>-</td>
<td>- 4.35E06 mol/L</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>72</td>
</tr>
<tr>
<td>MDI</td>
<td>BDO-PFO-EO</td>
<td>dibutyltin diurate</td>
<td>-</td>
<td>100-150</td>
<td>-</td>
<td>-</td>
<td>- 3.24E06 mol/L</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>72</td>
</tr>
<tr>
<td>MDI</td>
<td>BDO</td>
<td>dibutyltin diurate</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>- 1.03E10 mol/L</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.85E10</td>
<td>20</td>
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<tr>
<td>MDI</td>
<td>Polyoxyethylene glycol 200</td>
<td>dibutyltin diurate</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>- 8.50E-01 mol/L</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.87E10</td>
<td>20</td>
</tr>
<tr>
<td>MDI</td>
<td>Polyoxyethylene glycol 400</td>
<td>dibutyltin diurate</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>- 9.80E-01 mol/L</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.53E10</td>
<td>20</td>
</tr>
<tr>
<td>MDI</td>
<td>Polyoxyethylene glycol 600</td>
<td>dibutyltin diurate</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>- 8.50E-01 mol/L</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.91E10</td>
<td>20</td>
</tr>
<tr>
<td>MDI</td>
<td>PCL</td>
<td>dibutyltin diurate</td>
<td>-</td>
<td>30-210</td>
<td>-</td>
<td>-</td>
<td>- 5.49E+04 mol/mol/eq</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.20E+01</td>
<td>20</td>
</tr>
</tbody>
</table>
Few studies have been conducted in relation to the effect of pressure on the step polymerization of PU\(^{154,158-160}\). However, for REX, the reactive extrusion conditions such as pressure and shear rate may influence the kinetic of PU polymerization.

The pressure effect on the reaction is associated with the value of the viscosity. If the viscosity is low, an increase on pressure decreases the diffusion rate, but simultaneously increases the number density of reacting molecules in the liquid and, therefore, the probability of reaction. Hence, an increase of the reaction rate is observed. If the viscosity reaches a certain high value, and the polymerization reaction becomes diffusion-controlled, an increase in pressure is expected to decrease the diffusion rate and thereby the rate of the reaction. In the transition region from a mass controlled to a diffusion-controlled reaction, two phenomena compete. An increase in pressure increases the number density of reacting molecules; however, this effect is compensated by the decrease in the diffusion rate because of the higher viscosity of the reaction mass. Then, in the transition region, no effect of pressure on the reaction rate is observed\(^{154,158-160}\).

The influence of the pressure on the equilibrium constant \(k\) of a chemical reaction is given by:

\[
\frac{d \ln k}{dP} = -\left(\frac{\Delta V}{RT}\right)
\]  

(2.12)

where \(k\) is the equilibrium constant, \(P\) the pressure, \(T\) the absolute temperature, \(R\) the universal gas constant, and \(\Delta V\) the change of reaction volume as the reaction proceeds. This latter factor is negative since the product is denser than the reactants.

From equation 2.12, several researchers\(^{154,158-160}\) proposed that the equilibrium constant increases upon an increase in the hydrostatic pressure. However, they found
that the kinetics also play an important role that affects greatly whether or not pressure influences the reaction. If the polymerization reaction is fast enough, complete conversion may be achieved by the time pressure is applied, influencing the rate very little; and if the reaction is slow, the effect of pressure is less than expected due to the phase separation. Finally, they concluded that the overall effect of pressure on the reaction kinetics is a combination of its effect on the viscosity and its effect on the reaction constant.

Wasylyshyn et al.\textsuperscript{159,160} studied the changes in the reaction regime from mass-controlled to diffusion controlled during the polymerization of amines and epoxides. This variation of the dielectric constant with the extent of reaction was measured. They concluded that the reaction rate increased with pressure.

Park et al.\textsuperscript{154} performed an experimental study on the effect of pressure for PU bulk polymerization under high pressure. They designed and constructed a “high-pressure” chamber that consisted of a lead capsule inserted into a cylindrical cavity of a mold made of steel alloy. Pressure was applied through a piston rod connected to a hydraulic press. The kinetic parameters were calculated by a conventional chemical characterization method (titration) in order to determine the unreacted isocyanate. The rate of polymerization at 300 MPa was three times faster than at atmospheric pressure, as shown in Figure 2.13. The activation energy of the polymerization decreased as the pressure increased. They also demonstrated that the increased temperature enhanced the effect of the pressure.

They found that the $T_g$ of the soft segment of the PU polymerized under high pressure shifted toward a higher temperature and the hard segment $T_m$ shifted to the lower temperature as pressure was increased. This behavior was explained as a
depression in the microphase separation of the soft and hard segments because of a reduced mobility of the chain segments under high pressure. Despite the hard segment $T_m$ depression, the increase of the synthesis temperature shifted the $T_m$ to higher temperatures, due to the higher mobility of the chains at higher temperature. They concluded that the pressure did not influence the molecular weight and molecular weight distribution.

![Figure 2.13. Effect of Pressure on Reaction Rate](image)

The effect of shear rate on the kinetics of linear polyurethane formation was studied by Navarchain et al.\textsuperscript{161} Their study was conducted by using a cone and plate rheometer for two polyurethane systems in a steady state. They found that the viscosity buildup at a constant shear rate depended exponentially on the rate constant of the polymerization. Navarchain et al. concluded that the shear enhanced the mobility of polymer chains and the diffusion of functional groups, resulting in an increased rate of polymerization. Additionally, they found that the system that was able to form a high hard segment displayed irregularities on the viscosity buildup that affected the
measurements. This behavior was attributed to the formation of the hard segment of TPU and the consequent phase separation.

Since the final product is biphasic, there is a time when phase separation occurs. It is very important to determine the phenomena between chemical controlled reaction and the diffusion control reaction\(^6\). It is desirable that the chemical control governs most of the reaction because otherwise a low molecular product would be obtained. The presence of any nucleophillic and electrophillic compounds affects the kinetic mechanism leading to early phase separation. A recent study in the non-isothermal kinetics study of polymerization using DSC and Raman spectroscopy was conducted by Parnell et al.\(^{6,136,162}\) He demonstrated that the presence of any material different from the reactants during the reaction should be controlled carefully to avoid reaching the diffusion-controlled type of reaction.

2.2.4. Morphology and Properties

As mentioned previously, linear TPUs consist of two segments, hard and soft segments (HS and SS, respectively). During polymerization, separation and congregation of soft and hard segments into separate phases occurs due to SS/HS thermodynamic immiscibility. As shown in Figure 2.3. (section 2.2.), the resulting morphology can be visualized as a separated HS domains dispersed phase in a coherent SS matrix.

At room temperature, the low \(T_g\) SS sequences are mobile and often in an amorphous conformation. Thus, they impart high flexibility and deformability to the resulting material. In contrast, the high \(T_m\) HS sequences are quite polar and fixed by intermolecular bonding (e.g. Van der Waals and interurethane hydrogen bonding). Because of their rigidity and covalent bonding to the SS, HSs inhibit thermoplastic flow
of the matrix. Thus, the HS domains act as a filler as well as “physical crosslinks” for the SS matrix imparting high elasticity and strength to the resulting TPU. An increase in the temperature and use of a solvent can eliminate HS domains aggregation and thus thermoplastic elastomers can be processed\textsuperscript{10}.

The covalently linked microphase structure present in TPUs contributes to many superior properties. The following sections will describe the relationship between phase-separated morphology and properties.

2.2.4.1. Soft Segment and Hard Segment Phase Separation

TPU phase morphology and properties are highly dependent on SS/HS phase separation. The degree of SS/HS phase separation is defined as the percentage of HS dissolved within the SS matrix and is dependent on soft and hard segment chemical structure, composition, average segmental molecular weight, polymerization conditions, and thermal history. This degree of phase separation is often determined simply by measuring the changes in the $T_g$s of the respective segments. Of the variables influencing TPU SS/HS miscibility and physical properties, SS chemical structure is probably the most significant. Due to their relatively high polarity, polyester SSs typically exhibit more phase mixing with high polar HSs (e.g. MDI/BDO) than do polyether SSs\textsuperscript{163-166}. In fact, TPUs containing polyethers with large $\text{CH}_2/\text{O}$ ratios\textsuperscript{167} or polybutadiene\textsuperscript{10} as their SS exhibit the most phase separation due to increased immiscibility between soft and hard segments.

HS chemical structure also influences SS/HS phase separation. Generally, HSs with symmetrical diisocyanates\textsuperscript{10}, longer chain extenders\textsuperscript{100}, amine based chain extenders\textsuperscript{168}, or aromatic chain extenders\textsuperscript{169} are less miscible with typical TPU SSs and lead to higher symmetry and organization within HS domains. Increased phase
separation\textsuperscript{165,170} usually results in lower SS \( T_g \)s, more HS domain ordering and crystallinity, higher tensile strength, and increased elongation at break. The use of different forms of the same isocyanates, as is the case of pure MDI and its modified versions, results in different mechanical properties, showing the effect the isocyanate has on them. LMDI produces a softer elastomer due to the reduced reactivity of the NCO in the 2-position\textsuperscript{81}, while CDMDI or polymeric MDIs usually outperform the pure MDI based TPUs, due to their higher functionality\textsuperscript{87}.

The composition or HS content of a TPU will also affect domain morphology. Prior to phase inversion (ca. 50-65 wt.\% HS\textsuperscript{171-174}) increasing the HS wt.\% in a TPU formulation will lead to an increase in phase mixing, an increased SS \( T_g \), increased HS ordering and crystallinity, and higher \( T_m \)s\textsuperscript{165,175-181}. Since HS domain concentration and size increases with increasing HS content, tensile strength, tear strength, and modulus also improve\textsuperscript{165,175-180}.

The other important factors that influence SS/HS phase separation in TPU structure are the molecular weight and molecular weight distribution of the segments. Chen et al.\textsuperscript{182} found that TPUs with more uniform, or monodispersed distribution of HS lengths exhibited better HS aggregation and phase separation, higher moduli, lower SS \( T_g \), and sharper high temperature DSC endotherms. Similarly, an increase in the molecular weight of the SS at constants HS content causes a decrease of the SS \( T_g \)s due to less SS/HS interaction and increased SS mobility\textsuperscript{149,165,170,173,183-185}. Such an increase in SS/HS phase separation is accompanied by more HS domain ordering and crystallinity\textsuperscript{149,165,176-181,183}, and results in an improvement of the tensile strength, tear strength, and modulus\textsuperscript{165,176,178,180,181,183,186}.
The polymerizations such as fast exothermic reactions with high catalyst content also affect the phase separation. Camargo et al.\textsuperscript{72,143} reported that the speed and temperature of reaction influenced the extent of phase separation achieved in an MDI based TPU polymerization. Similar investigations\textsuperscript{143-145} demonstrated that thermal history during polymerization played an important role in determining the final phase separated morphology and properties.

To produce a phase separated morphology with good properties, the kinetics of polymerization should be faster than the kinetics of phase separation. Therefore, the reactivity of the different functional groups towards the isocyanate should also be similar. In practice, post-polymerization phase separation and similar functional group reactivity are achieved by select temperature control and/or preferential catalysis of the urethane reaction using organotin catalysts that lead to the formation of coherent materials. The use of a monomer with different reactivities will result in an overall reduced reactivity and the final product will have a different phase separation and domain ordering, as is the case of LMDI based TPUs, due to the presence of the 2,4'-MDI\textsuperscript{91}.

The morphology of a TPU is also dependant on the annealing temperatures and thermal history. The previous studies\textsuperscript{137,167,171,187-193} conducted by using SAXS, WAXDS, DSC and FTIR have demonstrate that the overall SS/HS phase separation decreased, while HS inter-domain distances increased with an increasing annealing temperature ($T_{\text{ann}} \geq T_g$ of HS). Koberstein and Stein\textsuperscript{194} explained these behaviors based on a lamellar HS domain model that predicts fewer and thicker non-crystalline or crystalline lamellae at higher temperatures on a thermodynamic basis.
2.2.4.2. Soft Segment and Hard Segment Domain Structure

The HS domain structure of TPU was elucidated by the previous researchers\textsuperscript{167,172,188,189,195,196} using DSC, SAXS, WAXD, and FTIR. As shown in Figure 2.14., a typical TPU thermogram shows the $T_g$s of SS and HS and multiple endotherm transition temperatures associated with the HS, regardless of the nature of the SS (polyester or polyether). The $T_g$ of a HS at 90-100$^\circ$C for MDI/BDO HS\textsuperscript{167} is difficult to detect due to the low magnitude of the change in the heat capacity. The $T_g$ of the SSs is different from the $T_g$ of the polyols that form them. Cooper et al.\textsuperscript{197} suggested that the variability of soft segment $T_g$ is a result of the mixing of HS in the SS matrix, as well as a dispersion of SS material in the HS domains; consequently, the restricted mobility due to constraints imposed by the HS and the phase separation morphology are responsible for this difference. These authors\textsuperscript{167} also found that having long hard and soft segments will result in a more perfect phase separation and, hence, a low soft segment $T_g$. The perfection of the HS domain decreases with the decrease in the HS chain length regardless of the SS. The use of modified isocyanates results in a decrease in the purity of the isocyanate; consequently, a lowering on the melting point of the polyurethane hard segment occurs\textsuperscript{85}. Additionally, the introduction of crosslinks results in the molecular chains being kept apart from each other, disrupting the perfection of HS ordering\textsuperscript{83}.

A TPU annealed at a temperature near the HS’s $T_g$ shows one endothermic peak (peak 1) that corresponds to the disruption of long range (non-crystalline) HSs domain ordering and the transition of a completely phase mixed state with SS domains. In the literature, this transition was termed the microphase separation temperature (MST). Another minor endotherm (peak 0) appears at ca. 150$^\circ$C and is usually attributed to the
dissociation of short range HS order, induced by annealing at room temperature. Thermal annealing at higher temperatures (above 120°C) produces a second endothermic peak at temperatures near 200°C, which corresponds to the melting of a crystalline MDI/BDO polymorph. When the annealing temperature approaches 200°C, all non-crystalline HS domain endotherms (MSTs) disappear and only high temperature endotherms (peaks IIA and IIB) corresponding to MDI/BDO HS polymorphs of varying crystal size populations exist. When the annealing or processing temperatures exceed a certain critical value (somewhere from 190 to 230°C depending on the material), all crystalline structures melt and one type of MDI/BDO polymorph preferentially forms upon cooling to room temperature, resulting in one endotherm (peak III). Any type of annealing below this critical temperature afterward will result in recrystallization to produce more thermodynamically favored polymorphs represented as IIA and IIB endotherms.\textsuperscript{188,189,195,196}

Figure 2.14. DSC Thermogram of a Polyether and Polyester based MDI/BDO TPU with different HS and HS content.\textsuperscript{197}
A number of models for the TPU HS domain crystal structure proposed by various researchers\textsuperscript{198-201}. Most of the models are based on the model of Bonart\textsuperscript{201}. He suggested the model based on the HSs rigid rods with favored orientations resulting from strong hydrogen bond interactions. Blackwell et al.\textsuperscript{198-200} studied the effect of chain extender length on the HS domain crystal conformation of the polyether TPU by WAXD. They determined that even and odd diols formed different structures with BDO. Even diols had fully extended conformations with all \textit{trans}. On the other hand, the odd diols formed contracted conformations, in which both \textit{trans} and \textit{gauche} bonds were present. Both the even and odd series of TPUs demonstrated a triclinic unit cell with tilted basal planes. This crystalline arrangement and their respective conformation favored a hydrogen bonded network.

2.2.4.3. Hydrogen Bonding

TPUs have hydrogen bonds that play an important role in the formation and stabilization of the HS domain structure; therefore, a series of domain models of the HS has been proposed by the previous researchers\textsuperscript{198-200}. Hydrogen bonds are very strong dipole-dipole attractions between hydrogen atoms and small strongly electronegative atoms. The hydrogen bonding forms between a hydrogen donor atom and an hydrogen acceptor atom. In TPU H-bonding, the N-H group of the urethane linkages serves as the hydrogen donor, while the H-bond acceptor may be in either the HS (the carbonyl group or adjacent oxygen\textsuperscript{202} of the urethane linkage) or the SS (an ester carbonyl or ether oxygen). The relative amounts of the two types of H-bonds are determined by the degree of SS/HS phase separation, with increased phase separation favoring inter-urethane H-bonding. Studies of H-bonding in TPUs have shown that it is SS/HS thermodynamic immiscibility, and HS’ mobility and symmetry that control H-bonding
rather than the opposite case\textsuperscript{140,203}. The presence of H-bonding thus serves primarily to enhance SS/HS phase separation, but is not the cause.

The H-bonding is easily characterized by N-H and C=O (amide I) stretching vibrations observed in the spectra of IR and Raman spectra\textsuperscript{204}. Changes in the H-bonding can be followed by measuring frequency and/or intensity changes in these bands. In IR spectra, the major N-H band occurs approximately at 3320 cm\textsuperscript{-1}, which is characteristic of H-bonded N-H groups. Free N-H occurs ca. 3440 cm\textsuperscript{-1}, appearing as a weak shoulder on the high frequency side of the H-bonded band. Participation in H-bonding also splits the C=O vibration into two bands, though the effect is much smaller for the acceptor than for the donor (30 cm\textsuperscript{-1} vs. 125 cm\textsuperscript{-1}). In urethane C=O vibrations, bands at about 1730 cm\textsuperscript{-1} and 1700 cm\textsuperscript{-1} represent free and H-bonded urethane C=O groups respectively. An intermediate band sometimes observed at 1715 cm\textsuperscript{-1} and it is attributed to irregularly H-bonded urethane C=O\textsuperscript{145,234}. In both N-H and C=O vibrations, free and bonded bands can be resolved and their relative intensities can be used as a measure of the degree to which that functional group participates in H-bonding.

Investigations concerning the development of structure-property relationships for TPUs have frequently focused on elucidating the influence of H-bonding on morphology or vice-versa. Consequently, there have been many attempts to correlate the already mentioned IR spectral features of H-bonding to TPU domain morphology. More specifically, H-bonding was used to investigate the interaction between hard and soft segments in TPUs. Under the assumption that donor groups dissolved within the SS do not form H-bonds, many researchers have related changes in bonded and free N-H and C=O vibrational bands to the degree of SS/HS phase separation\textsuperscript{167,177,183,205,206}. Cooper and coworkers\textsuperscript{197,207,208} applied this analysis to several systems based on
polyether SSs and MDI/BDO HSs and found that the difference between N-H and C=O H-bonding correlated well with the degree of phase segregation measured by other techniques, such as DSC.

A number of studies have reported substantial changes in TPU H-bonding with annealing time or temperature. Brunette et al. studied the effect of annealing time on the frequency, bandwidth, and intensity of N-H bonded stretching vibrations in model, solution cast MDI/BDO copolymers with FTIR. As evidenced by DSC, annealing created more organized and strongly H-bonded HS domains with higher, uniform melting temperatures. In another fascinating study, Koberstein et al. showed that temperature dependent morphological changes can occur within TPUs, which may also influence local H-bonding environments. Upon heating a polyether based MDI/BDO TPU, complete SS/HS mixing coincided with rapid H-bonded dissociation. In addition, it was discovered that H-bonding was not significantly affected by morphological changes associated with the melting of HS crystallites in TPU HSs.

Modified versions of an isocyanate compared to the isocyanate result in different hydrogen bonding behavior. The introduction of crosslinks in the TPU structure results in reduced intermolecular attractive forces (i.e. hydrogen bonding) in the HS as well as the HS and SS due to the hindrance caused by the chemical reaction.

Vibrational spectroscopy is an extensively used tool in following reaction kinetics and phase separation dynamics during reaction induced phase transformations. Specific to TPUs, it can be used to determine reaction kinetics from changes in the isocyanate stretching vibration and to dietermine H-bonding dynamics from subtle changes in C=O vibrations. In most cases, the detection of TPU H-bonding is related to the onset of phase separation. For example, Camargo et al. followed the C=O band of reacting
polyether based MDI/BDO TPUs with FTIR and found that phase separation coincided with an increase in H-bonded C=O bands and a decrease in free C=O bands. In addition, other independent SAXS studies attempting to reproduce FTIR experiments have shown that SS/HS phase separation determined directly by SAXS may actually precede H-bonding. In an investigation utilizing simultaneous SAXS and FTIR on reacting TPUs, Bras et al. and other researchers confirmed that the driving force for structure development in TPUs was the thermodynamics of phase separation rather than H-bonding. Put another way, TPU polymerization pushes the system into a two-phase regime, resulting in the formation of long range order before the development of H-bonding can occur.

2.3. Blends of Poly(Vynil Chloride) and Polyurethanes

Polyurethanes exhibit excellent mechanical properties and good low temperature properties. The versatility of PU chemistry allows thermoplastic polyurethanes (TPUs) to be tailor made for various polymer blends. The blends of PVC and TPU obtained by melt-blending have been used for the production of coated wire, cable, tubing, hoses, upholstery, apparel fabric, film, etc. Soft grades of TPU are often used as polymeric plasticizers in PVC. Such blends tend to have better plasticizer permanence than conventional plasticized PVC. One of the serious problems to blend PVC with TPU is the narrow processing window to avoid thermal and mechanical degradation during blending in the processing device.

As mentioned, TPUs are synthesized from different constituents, or building blocks, which are a diisocyanate, a chain extender (short chain diol), and a polyol. However, the major portion of PU is polyether or polyester oligomeric polyols. Their miscibility with the other polymer will greatly influence the final properties of the blend.
Therefore, numerous studies of the effect of the chemical structure of polyester and polyether on the miscibility with PVC have been conducted.

2.3.1. Poly(vinyl chloride)/Polyol Blends

As mentioned above, the interaction between polyester and polyether polyol with PVC is a determining factor in the preparation of PVC/TPU blends. Therefore, the influence of the structure of the polyol has been the subject of several studies. In relation to polyethers, it is expected that because polyethers are proton acceptors, they exhibit miscibility with a polymer containing an acidic hydrogen, such as PVC. However, little research has been published on the topic of PVC/polyether blend miscibility. Margaritis et al.\textsuperscript{212,213} conducted two studies. Four different polyether polyols with PVC were studied using DSC and DMTA. The polyethers had different CH$_2$/O ratios: poly(methylene oxide) (PTMO), poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO) and poly(tetramethylene oxide) (PTMO). The polyethers were mixed with PVC in solution, and the melting point depression was measured. In their research, Margaritis et al. found that PMO and PPO based blends showed absolutely no phase mixing, as measured with DMTA. However, the thermograms of the blends based on PEO and PMTO showed broadening, indicating at least some level of phase mixing. They also determined the thermodynamic interaction parameter from the melting depression measurements. A value of -0.01 was found for PVC/PMO blends, while a value of -0.03 was obtained for PVC/PEO blends. A similar study by Neiro et al.\textsuperscript{214} also yielded negative interaction parameters (e.g. $\chi_{12} = -0.028$ to -0.102 depending on the molecular weight of PVC used in the blend) for the PVC/PEO blend pair. However, SEM revealed inhomogeniety at macroscopic level. Unfortunately, determining a thermodynamic interaction parameter for the PVC/PPO blend was not possible since PPO is not
crystalline; however, data for PVC/PTMO blends yielded a thermodynamic interaction parameter of -0.15.

From the results shown above, the miscibility of polyethers with PVC increases with increasing CH<sub>2</sub>/O ratios for linear polyethers. The studies of Margaritis et al.<sup>212,213</sup> concluded that the optimum CH<sub>2</sub>/O ratio was about 4, even though polyethers with larger CH<sub>2</sub>/O ratios had never been investigated. This lack of miscibility observed in PVC/PPO blends was attributed to the shielding of the ether oxygen with the bulky pendant methyl groups. Nonetheless, none of the PVC/polyether blends studied exhibited complete miscibility, as it is usually indicated by a single blend T<sub<g>.

Blends of polyester polyols have been the subject of many studies. Polyester polyols are expected to be miscible with PVC, since many polymers containing carbonyl groups have shown miscibility with PVC. Most linear, aliphatic polyesters are semi-crystalline with low melting points of approximately 50-60°C. For this reason, PVC/aliphatic polyester blend systems have limited commercial applications; nevertheless, the miscibility of certain kinds of aliphatic polyesters with PVC is a source of considerable academic and industrial interest. For industrial applications, polyesters are blended with PVC to achieve improved impact strength<sup>215</sup> or permanent plasticization<sup>37</sup>. Several polyesters have been reported to be completely miscible with PVC; however, some polyesters apparently highly miscible with PVC show heterogeneity with PVC at the molecular level when studied with SEM<sup>216</sup>.

An extensively studied polyester completely miscible with PVC is polycaprolactone (PCL). Several researchers<sup>44,175,217-228</sup> using different techniques, including DSC, DMTA, FTIR, and X-rays, have found that PCL is miscible through the whole range of composition with PVC. Other polyesters, such as α,α--substituted
poly(β-propiolactone)s, polyvalerolactone,\textsuperscript{48,229-231} and polyesters based on the condensation polymerization of dicarboxylic acids and diols, such as poly(butylene terephthalate)\textsuperscript{227} and poly(neopentyl adipate)\textsuperscript{232}, have been found to be miscible with PVC.

Several researchers\textsuperscript{45,48,220,221,228,233-235} have studied the blends of PVC with polyesters using FTIR in order to elucidate the specific interactions responsible for the miscibility with PVC. In these studies, it was concluded that the miscibility of polyesters with PVC involves interactions through carbonyl groups, even though the precise mechanism is not yet clear. There is no consensus in the interpretation of the interaction as a relatively weak hydrogen bond between the carbonyl group and the α-hydrogen of PVC, a dipole-dipole interaction involving the carbonyl group and the C-CL bond of PVC, or a more general Lewis acid-base type of interaction\textsuperscript{143,233,236-238}

Ziska et al.\textsuperscript{43} studied the miscibility of polyesters with PVC using DSC. They investigated the thermodynamic analysis based on the Flory-Huggins equation to determine the effect of the concentration of ester linkage in the polyester backbone on their miscibility. Melting point depression analysis was used to determine the interaction parameter. They found that polyester with CH\textsubscript{2}/COO ratios of less than 3 yielded immiscible blends (positive interaction parameters and two T\textsubscript{g}s), while polyesters with CH\textsubscript{2}/COO ratios greater than 12 were also estimated to be immiscible. Between 3 and 12, complete miscibility was expected.

Prud’homme\textsuperscript{231} studied the miscibility of polyesters, not only with PVC, but also with other chlorinated polymers. In his study, he analyzed the miscibility using melt point depression obtained from DSC data with the Flory-Huggins theory. It was demonstrated that miscibility was dependent on the CH\textsubscript{2}/COO ratio. If the CH\textsubscript{2}/COO...
ratio was between 3 and 10, complete miscibility was observed. Out of this range, the blends were immiscible. The rigidity of the chain was postulated as the cause of the immiscibility at ratios below 4, but the low concentration of COO groups was the reason for immiscibility at high CH$_2$/COO ratios. With the aid of the Gordon-Taylor equation, it was shown that the interaction between chlorinated polymers and polyesters increased with an increasing chlorine content of the chlorinated polymer. Prud’homme’s studies suggested that specific dipole-dipole interactions between carbonyl and C-Cl groups were responsible for polyester/chlorinated polymer miscibility, as opposed to hydrogen bonding between carbonyl groups and $\alpha$-hydrogens of PVC.

Woo et al.$^{239}$ studied the miscibility of aliphatic polyesters with PVC using melting point depression analysis based on the Flory-Huggins theory with a correction for finite lamellae thickness. As with previous studies of these systems, DSC and DMTA data revealed that polyesters having CH$_2$/COO ratios in the range of 4-14 were miscible with PVC. The cloud point analysis also showed that polyesters with CH$_2$/COO ratios between 4 and 14 were miscible with PVC. When the CH$_2$/COO ratios were over 10, the phase separation occurred at elevated temperatures (temperatures prior to degradation of the PVC). The system exhibited LCST behavior. They concluded that strong unfavorable intramolecular interactions between the -CH$_2$- and –COO- groups of the polyesters were responsible for the miscibility window. The most negative interaction parameter was found at a ratio of 7. They also demonstrated that the immiscibility at low CH$_2$/COO ratios ($\leq$ 3) had not originated from chain rigidity, as had been suggested earlier.

Aubin et al.$^{236}$ studied the miscibility of semi-aromatic polyesters with PVC. They found that a window of miscibility existed for blends of linear aromatic polyesters with
PVC, chlorinated PVC, and chlorinated polyethylene. With an increasing chlorine content, those blends became more miscible. They suggested that the miscibility might be attributed to hydrogen bonding between $\alpha$-hydrogens and $\beta$-hydrogens of the chlorinated polymer and carbonyl groups of the polyester, as well as to dipole-dipole interactions between the chlorine and the carbonyl groups.

These authors suggested that the miscibility of PVC with the polyesters was determined by the polyester $\text{CH}_2/\text{COO}$ ratio. An increase of the $\text{CH}_2/\text{COO}$ ratio results in lower LCSTs and immiscibility, since polyethylene is immiscible with PVC. In the systems studied, a decrease of the $\text{CH}_2/\text{COO}$ ratio also resulted in conditions unfavorable for miscibility. This is contradicted by the idea that increasing carbonyl density in polyesters should result in more interactions and thus enhance the miscibility.

Paul and Barlow$^{240}$ introduced the concept that intramolecular interactions may be important in realizing the exothermic heats of mixing rather than specific intermolecular interactions, as has been usually assumed. They proposed a simple binary interaction model usually applied to study copolymers. Essentially in some homopolymers, polymerization results in residual stresses within the macromolecule. These stresses can be reduced if favorable molecular interactions with another polymer are introduced. An alternative way to reduce the stresses is by also reducing unfavorable intramolecular interactions present in one or both blend constituents. The authors then applied this model to the case of PVC/polyester miscibility in which polyesters were thought of as copolymers consisting of $-\text{CH}_2-$ and $-\text{COO}-$ segments. The model described the miscibility window observed for PVC/polyester blends and revealed that a net exothermic heat of mixing for driving miscibility can exist even when intermolecular interactions lead to positive polymer-polymer interaction parameters.
Thus, it was shown that miscibility in these systems might result from an appropriate consideration of both intermolecular and intramolecular interactions rather than a specific intermolecular mechanism, such as H-bonding. Incidentally, this model has been successfully used in predicting the homopolymer/copolymer miscibility of PVC/SAN$^{240}$ and PVC/EVA$^{241,242}$.

2.3.2. Poly(vinyl chloride)/Polyurethane Blends

As has been discussed, TPUs are synthesized from different constituent building blocks: a diisocyanate, a chain extender (short chain diol), and a polyol. However, the major portion of PU is polyether or polyester oligomeric polyols. Thus, the miscibility of PU with PVC is determined by the chemistry of this component. In what follows, the blends of polyether based polyurethanes and polyester based polyurethanes with PVC are discussed.

Various researchers$^{243-247}$ studied the miscibility of TPUs based on PPO and PTMO with PVC. Such TPUs are usually chain extended with MDI/BDO hard segments, resulting in TPUS with relatively low hard segment content. Using the DMTA measurements of storage modulus and tan δ, Xiao et al.$^{247}$ showed that solution cast PPO based TPU/PVC blends exhibited two distinct $T_g$s representative of the constituent components, while solution cast PTMO based TPU/PVC blends exhibited one, broad $T_g$. Thus, they concluded that TPUs synthesized from PPO were immiscible with PVC, while PTMO based TPUs were partially miscible with PVC. The DSC experiments on the same blends resulted in similar observations. The blends based on polyether TPUs showed only partial miscibility. The mechanical property measurements of both PPO and PTMO based TPUs with PVC blends revealed that substantial interaction existed between blend components. For instance, Ha et al.$^{244}$ studied the fracture toughness and properties of
TPU plasticized PVC blends. It was observed that melt blending a polyether based TPU elastomer with PVC increased low temperature flexibility and toughness the same way as NBR rubber or conventional plasticizers did. However, the tensile strength of the TPU was not sacrificed. Wang et al.\textsuperscript{248} and Yano et al.\textsuperscript{249} noted a similar trend in analogous blends.

Several attempts have been made to enhance the miscibility of polyether based TPUs with PVC\textsuperscript{250,251}. One was to introduce attractive interactions between polymer components. This was accomplished with ionomer blends, in which Coulombic interactions enhanced the miscibility of the components or with polymer pairs capable of forming inter-polymer complexes with certain specific interactions between them. Al-Salah and Al-Raheil\textsuperscript{250} attempted to create an inter-polymer complex through the specific interaction of divalent transition-metal-neutralized TPU carboxyl with PVC. In this study, the hard segments of the polyether TPU contained free carboxylic acid groups which were subsequently neutralized with zinc acetate. It was proposed that the neutralized carboxylic groups on the TPU could enhance the TPUs miscibility with PVC via stronger ion-dipole interactions with the chlorine atoms of PVC. DSC analysis revealed one \( T_g \) in all compositions that approximately followed the Fox equation. This led the authors to conclude that ion pair-dipole interactions of the type used in their studies were sufficient to achieve significant miscibility. In a similar study, Kim et al.\textsuperscript{251} also observed differences in the miscibility of polyether and polyester based TPU/PVC blends when a neutralized carboxylic acid group was introduced onto TPU chains.

It was concluded from the studies mentioned above, that the miscibility of polyesters with PVC is caused by specific interactions between the carbonyl group of the polyesters and the PVC. Even though the nature of these interactions is not clear, the
strong enthalpic interactions do not exist in polyethers/PVC blends to the extent that they do in polyesters/PVC blends. Then polyethers are less miscible with PVC than polyesters. Consequently, most studies of PVC/PU have focused on polyester based PUs.

Piglowski et al.\textsuperscript{252} conducted one of the first comprehensive studies in this area. They presented different methods for determining miscibility in blends composed of PVC and a PEA based MDI/BDO chain extended TPU. Among the various methods used, one included Gee's\textsuperscript{253} equation applied to the swelling of a TPU. The solubility parameters measured by them were of approximately 10.8, compared to a solubility parameter of 9.52 for PVC. The authors concluded that the blend system was immiscible using this method. DMTA measurements on blends prepared in the melt revealed the presence of the constituent polymers $T_g$'s, indicating immiscibility. They concluded that the free energy of mixing was positive in this system and, as a result, the blends were thermodynamically immiscible.

In another study Piglowski et al.\textsuperscript{254} studied the effect of the stoichiometric excess of diisocyanate in PEA based MDI/BDO chain extended TPU on the PVC/TPU blend properties. The TPU acted in the PVC/TPU blend as does the NBR in PVC/NBR blends. The NBR acted as an impact modifier because of its rubbery nature and the phase separation. In previous studies\textsuperscript{255} DMTA results demonstrated that all blends had two $T_g$'s, which corresponded to a two-phase structure. The slightly shifted $T_g$'s suggested some phase mixing and perhaps miscibility. Adding TPU and increasing TPU NCO/OH ratios enhanced the Charpy impact strength of blends of PVC and TPU. The tensile experiments showed similar trends except that the tensile strength of blends was less than the tensile strength of pure PVC. In addition, in the melt processing of these
blends, TPU acted as an external lubricant for PVC and increased the dynamic (i.e. during processing) thermal stability of PVC. However, the thermogravimetric analysis of such blends showed that the effect of adding TPU to PVC/TPU blends was to decrease the thermal stability of PVC.

Several researchers\textsuperscript{253,256,257} have blended TPUs based copolymers of PEA and poly(butylene adipate) (PBA) with PVC. In these studies, the miscibility of these blends was less than that of blends based on pure PBA or PCL based TPUs. Nevertheless, the miscibility of PBA or PCL TPUs with PVC was better than that observed in PEA based TPUs. Their results for DSC, DMTA, and dielectric measurements showed two $T_g$s shifted from those of the constituent polymers. This shift was especially notable for high TPU content in the blends. These observations suggested that phase separation existed in all compositions and that each phase contained a certain amount of the other polymer. This is evidence for partial miscibility. The SEM micrographs and photographs revealed that at low TPU concentrations the TPU acted as a binder for PVC primary particles and at high TPU concentrations the PVC formed globules dispersed in a TPU matrix. In the case of high PVC contents, tensile tests\textsuperscript{253,257} showed that elongation at break increased and yield strength decreased with increasing TPU content in the blends. These results corresponded to the dispersed phase with a low content of TPU (i.e. below 30\%). Finally, at 35 to 40 wt\% TPU, a phase inversion occurred.

Zhu et al.\textsuperscript{258,259} conducted comprehensive studies of the blend of polyester based TPUs with PVC using three different types of polyesters. The polyesters used included PEA, PBA, and PHA. The hard segment consisted of MDI/BDO. The studies conducted by DSC and dynamic mechanical testing demonstrated that PBA and PHA based TPU/PVC blends were partially miscible, but PEA based TPU/PVC blends were
immiscible. Other investigations\textsuperscript{247,253} also concluded that polyester TPUs with relatively large CH\textsubscript{2}/COO ratios in their polyol SSs were more miscible with PVC than with PEA based TPUs or PPO and PTMO based polyether TPUs. Xiao et al.\textsuperscript{247} found that PBA and PCL based TPUs were quite miscible with PVC, as DSC and DMTA measurements indicated. Unlike PTMO and PPO based TPUs blended with PVC, PBA and PCL based TPUs blended with PVC storage modulus and tanδ measurements exhibited relatively narrow, single T\textsubscript{g}s. However, the PCL based TPU/PVC blend had a narrower T\textsubscript{g} shift than the corresponding PBA based TPU/PVC blend, possibly indicating higher system miscibility.

Xiao et al.\textsuperscript{247} used FTIR spectroscopy to study the miscibility of various PVC/TPU blends. The FTIR spectra showed two separate C=O stretching vibrations in all polyether TPU spectra at about 1730 cm\textsuperscript{-1} and at approximately 1700 cm\textsuperscript{-1}. The former vibration is attributed to ‘free’ C=O groups, while the latter is assigned to hydrogen bonded C=O groups. Given the well established two phase SS/HS domain morphology of TPUs, intense inter-segmental H-bonding in the HS domains is responsible for the peak at 1700 cm\textsuperscript{-1}. For polyester based TPUs, less HS domain segregation generated fewer H-bonded C=O groups. Also, the larger peak corresponding to ‘free’ C=O groups appeared due to the extra C=O groups residing in the SSs of polyester based TPUs.

In all blends, the quantity of H-bonded C=O groups decreases with increasing PVC with respect to the corresponding pure TPU. This was especially evident in blends synthesized from TPUs with polyester SSs. This behavior is consistent with PVC interrupting (i.e. mixing) the familiar TPU SS/HS domain morphology. Xiao et al.\textsuperscript{247} concluded that PVC/TPU miscibility decreased in the following order of TPU SS chemical structure types: PCL>PBA>PTMO>PPO. In addition, they proposed that for blends with
polyester TPUs, the PVC molecules might disperse in the SS phase with little microphase separation of the TPU at low PVC contents. Higher PVC contents lead to TPU HS mixing in the diluted SS matrix without segregation. In the case of polyether based PVC/TPU blends, PVC molecules might segregate to form an individual phase. In such blends, PVC constitutes the continuous phase and may penetrate into SS rich TPU domains or may be imbedded in both SS and HS domains. These findings suggested that it was possible to change the morphology of these blend systems significantly by choosing TPU SS with a different chemical structure. Further investigation\(^2\) yielded identical morphological models.

Ahn et al.\(^{260}\) and Gifford\(^{253}\) concluded that PCL based PUs were miscible with PVC at all compositions over a broad temperature range. Shilov et al.\(^{186}\) investigated the microphase structure of PVC/PU blends based on PCL prepared in solution. He determined the thermodynamic polymer-polymer interaction parameter close to zero by using melting point depression analysis. Their WAXD and SAXS studies suggested that 50 and 75 wt% PVC blends were within a binodal of a LCST, even though the proximity of blend \(T_g\)s to room temperature inhibited phase separation (blends were optically transparent). Their SEM studies agreed with the results of WAXD and SAXS. They concluded that the phase separation in amorphous PVC/PU blends (>50 wt% PVC) corresponded to spinodal decomposition.

Several researchers have investigated the miscibility of PUs with chlorinated polymers other than PVC. Utilizing DSC, DMTA, and TEM Garcia\(^{261}\) studied the miscibility of a PBA based PU with chlorinated PVC. Blends prepared in the melt exhibited a single, broadened \(T_g\) over the entire composition range and a co-continuous domain morphology with domain sizes ranging from 0.10 to 1.5 \(\mu\)m. As a result, the blends
were partially miscible. The study conducted by Ahn et al.\textsuperscript{260} showed that the PCL based TPUs were miscible with various chlorine containing polymers. The TPU/PVC blends exhibited single, composition dependent \( T_g \)s. The blends with high HS content did not show single \( T_g \)s. The Gordon-Taylor equation was applied to investigate the miscibility. Ahn et al.\textsuperscript{260} discovered that blends with higher chlorine content (e.g. poly(vinylidene chloride-vinyl chloride)) had stronger intermolecular interactions and, thus, higher miscibility.

There is very little literature concerning PUs polymerized in-situ with PVC. Alger and Karunanayake\textsuperscript{262} developed the method to polymerize a PCL based PU in the presence of melted PVC at 160ºC. They claimed that this in-situ method of blending overcame one of the major disadvantages of polymeric plasticizers, viz. the difficulty of compounding them with PVC. High PU conversions were achieved in the melt state. A few studies\textsuperscript{263,264} of interpenetrating polymer networks (IPNs) have been conducted by synthesing PU with PVC. Klempner\textsuperscript{263} polymerized a PCL/PPO based network PU in solution with PVC to produce a semi-IPN. In the aforementioned study, the incorporation of PPO into the PCL based PU lowered the miscibility with PVC. Then, a LCST behavior was observed that had not been observed in semi-IPNs based on pure PCL PUs. Their results for the DMTA measurements of the quenched samples showed that the phase separation of semi-IPNs with intermediate compositions occurred at temperatures below 200ºC, but all compositions exhibited single phase behavior at room temperature.

Based on the studies already mentioned, it was concluded that polyester based PUs are more miscible with chlorinated polymers than polyether based PUs. In addition, the experimental results suggest that the chlorinated polymer/polyester based PU
blends also displayed a window of miscibility. The miscibility was dependent on the chlorine content of the chlorinated polymer and the CH₂/COO ratio in the SS of the polyester based PU. However, several previous studies pointed out that with increasing urethane or HS content, PU’s miscibility with chlorinated polymers decreases\textsuperscript{186,253,260,265}. Thus, the qualitative trends observed in chlorinated polymer/polyester blend miscibility are useful in blends of chlorinated polymer with polyester based PU, if the urethane or HS content of the PU is low (e.g. ≤25 wt%). These findings suggest that the polyol component of the PU determines the miscibility and morphology of blends with PVC over a wide temperature range. Thus, permanent plasticized TPUs can be tailor made for almost any application.

2.4. Reactive Extrusion

Reactive extrusion (REX) may be defined as the process by which a polymer is synthesized or chemically modified simultaneously with its processing and shaping into a finished polymer product\textsuperscript{266}. Because of their ability to perform these operations, single and twin screw extruders have attracted attention for their ability to function not only as continuous melting, mixing, and pumping devices, but also for their ability to function simultaneously as continuous flow reactors.

For the preparation of polymeric materials the REX process has many advantages over conventional flow chemical reactors. Chemical reactions with polymeric materials with viscosities in the 100 to 100,000 Pa·s range are generally quite difficult in conventional chemical reactors, but can be easily accomplished with extrusion. Additionally, the REX process increases the degree of mixing, decreases residence time, and minimizes temperature gradients within reacting polymer systems and results in improved product quality, while performing the reaction in a single step.
continuous process. Finally, REX offers an effective means of performing polymer modification reactions through the multistage feeding of reactive agents. Tailor made polymeric materials containing the desired properties can be manufactured in an economical way. Given the chemical versatility of PUs and their inherent miscibility with a wide variety of polymers, the application of REX to the synthesis of PUs and to the reactive blending and/or modification of other polymers with PUs is of practical interest.

2.4.1. Reactive Extrusion of Thermoplastic Polyurethanes

Although REX is widely used for bulk polymerization and the chemical modification of various polymers, the number of patent publications on the subject of REX for polyurethane is limited due to the proprietary nature of the process developed. In one of the first patents, Frye et al. of Mobay described a one-shot process for producing TPUs by self-wiping twin screw extruders. They used polyester polyols and MDI. In their patent, all TPU reactants were premixed and then injected into the feed zone of an extruder with a downstream temperature profile of 177ºC, 149ºC, and 163ºC.

Ulrich et al. of Bayer described the continuous production of TPUs in co-rotating, self-wiping twin screw extruders. They analyzed the twin-screw extruders with high shear kneading elements to produce high quality TPUs without gel particles. In their patent, they claimed their invention was useful for a variety of diols, diisocyanates, and chain extenders. Reactants could be either added together in the extruder feed zone (one-shot process) or sequentially downstream (prepolymer process). In a typical procedure, all reactants, including polyol, chain extender, and diisocyanate were metered to a mixing head via separate gear pumps. The mixture was kept at a 95-120ºC and fed directly into the feed zone of an extruder operating at a rotational speed.
between 70-300 rpm. The temperature profiles were fixed at 95-105ºC near the inlet of the extruder, 180-260ºC in the middle of the extruder, and 100-180ºC near the exit of the extruder. Under these operating conditions, the residence times were between 0.8 and 4 minutes. A schematic of the screw configuration used in this patent is shown in Figure 2.15.

![Schematic of twin screw configuration](image)

**Figure 2.15. Co-rotating self-wiping twin screw configuration used in REX of TPUs**

In 1986, Zeitler et al.\(^9^9\) of BASF in Germany filed a patent for a two stage process for the production of TPUs using a single screw extruder. They claimed that the process was useful for a range of organic diisocyanates, polyhydroxyl compounds, and chain extenders. In the first stage of the process, the reactant mixture produced via the one-shot process was put on a steel conveyor belt and allowed to polymerize at temperatures between 100ºC and 180ºC in an insulated enclosure. Upon reaching a desired conversion, the TPU reactant mixture was introduced into a single screw extruder of 200 mm in diameter, whereupon the second stage of the process was done. In one example, the temperature profile was 160-170ºC, 170-200ºC, and 200-180ºC coupled with residence times of 1 to 6 minutes. In the patent filed by Lunardon et al.\(^3^8\) of Ausimont S.P.A., a co-rotating self-wiping twin screw extruder with a large number of homogenizing elements, composing up to 55% of the total length of the screw, was used to produce TPUs with the prepolymer technique. A relatively constant temperature profile was arranged from 200 to 220 ºC, along with screw rotational speeds of 150
rpm. The residence time was 1.5 minutes. Echols et al.\textsuperscript{268} of the Minnesota Mining and Manufacturing Company (3M) described a one-shot process for the production of radiation curable TPUs by a twin screw extruder. The 34 mm counter-rotating machine used in this patent was so effective for homogenizing TPU reactants that pre-blending TPU reactants prior to extrusion was not necessary. Instead, polyol/chain extender and diisocyanate reactant streams were pumped separately and directly to the feed zone of the extruder with two gear pumps. The screw configuration consisted of single and triple flighted helical screw elements with varying pitches. A relatively constant temperature profile was analyzed near 200ºC, and screw speeds of 25-50 rpm. The typical residence time was less than 10 minutes.

Oriani\textsuperscript{95} of the Dow Chemical Company also developed a patent involving the reactive extrusion of polyether based TPUs on counter-rotating twin screw extruders. In this process, a polyol/chain extender reactant mixture and a stoichiometric quantity of diisocyanate were metered separately into the feed port of the extruder. The twin screw extruder was operated at a screw speed of 450 rpm, with a typical downstream temperature profile of 220ºC, 215ºC, 180ºC, 180ºC, 180ºC, 180ºC, and 190ºC for each barrel zone.

In addition to the patent literature, the papers of application of REX to TPU synthesis were published. For example, Hyun and Kim\textsuperscript{92} studied the synthesis of a TPU on a single screw extruder by comparing numerical simulation with experimental results. These researchers used a small 19 mm extruder with single flighted screw elements of constant channel depth. TPUs were produced with the one-shot process, whereby all TPU monomers were premixed at 60ºC and taken to the feed port of the extruder. The extruder operated with a constant temperature profile of 100ºC and a screw speed of
15 rpm. To measure conversion, several samples were removed from various positions along the extruder. They developed the empirically polymerization kinetic model from data of adiabatic temperature rise experiments. From rheological experiments they determined the conversion-temperature-shear dependent viscosity model. The conservation equations were solved with two different finite-differences algorithms to obtain velocity, concentration, temperature, viscosity, and pressure profiles. Good agreement between experimental average conversion at the exit of the screw and simulated results was found.

Bouilloux and Macosko\textsuperscript{269} used a Leistritz 34 mm, counter-rotating, intermeshing twin screw extruder for the bulk polymerization of TPUs. A solution of diols containing the catalyst and the diisocyanate were metered into the first zone of the extruder. Constant temperature profiles of 200°C and screw speeds of 26 to 122 rpm, with output rates of 40 to 189 g/minute were used. The authors used a model developed by Stuber, who approximated a counter-rotating twin screw extruder as a series of continuous stirred tank reactors (CSTRs) with flight leakage inflows and outflows. They determined experimentally the parameters of a second order kinetic expression. The viscosity followed Arrhenius type dependence of temperature and a non-linear dependence on concentration. The dependence of viscosity on temperature and concentration was separable. The conservation equations were solved analytically to predict the flow parameters of the polymerizing TPU mixture throughout the extruder. Their simulation predicted the polymer molecular weight and extruder pressure profiles.

Other studies have focused on the REX of TPUs using twin screw extruders. Ganzeveld and Janssen\textsuperscript{270} polymerized a TPU in a counter-rotating twin screw extruder with a variable downstream temperature profile of 80 to 110°C. The authors focused
on adjusting extruder parameters to control distributive mixing, residence time, and conversion. Coudray et al.\textsuperscript{271} reported how acrylated PUs could be synthesized in a co-rotating, self-wiping twin screw extruder with a downstream temperature profile constant of 90°C. High shear kneading disks with screw elements of reversed pitch were used to promote effective mixing and inhibit gel particle formation. Using a co-rotating, intermeshing twin screw extruder, Cassagnau et al.\textsuperscript{272} found that extruder residence time controlled TPU polymerization in the bulk and dispersed mediums. They produced polyether based TPU, and used a constant temperature profile of 160°C in a corotating twin screw extruder. They found that the polydispersity of the TPU produced at the exit of the extruder approached a theoretical value of 2, irrespectively of the breadth of the residence time distribution.

2.4.2. Reactive Blending of Polyurethanes with Other Polymers

The REX process offers an effective means of blending and polymerizing PUs in-situ with other polymers, thanks to the possibility of sequentially adding reactants downstream. In fact, in many of the previously mentioned patents\textsuperscript{96,97,267,273}, describing the synthesis of TPUs via REX, the authors mentioned that other polymers, such as PVC, could be added to the extruder during TPU polymerization. In most cases, TPU reactants were added together with a base polymer, or TPU reactants were sequentially added to a base polymer downstream. As has been demonstrated a wide variety of compounding sequences and process conditions could be used to synthesis tailor made PU blends.

Goyert et al.\textsuperscript{91} of Bayer developed a process related to the modification of thermoplastics with PUs forming components. They claimed that a great variety of diols, chain extenders, and diisocyanates may be used with the process they invented.
The patent intended to develop rigid, elastic materials from thermoplastics of moderate hardness and strength. The REX process configuration was identical to that described by Ulrich et al.\textsuperscript{267} except that the base polymer was fed into the feed zone of the twin screw extruder and the PU reactants were added downstream. One example of the process modified a polyester based TPU using a downstream temperature profile of: 100ºC, 150ºC, 190ºC, 220ºC, 175ºC, 120ºC, and 110ºC.

In their patent of Heidingsfeld et al.\textsuperscript{274} of Bayer suggest a process for the preparation of polymer blends containing TPUs. Previous methods of producing TPU blends relied on conventional melt blending techniques in an extruder. However, processing of this type exposed the TPU at high temperatures and high shear, resulting in a loss in properties. To avoid this problem, TPUs with unreacted hydroxyl groups along with other polar polymers were charged into the feed port of a self-wiping twin screw extruder. Stoichiometric quantities of diisocyanate were added downstream to complete the in-situ TPU polymerization reaction which resulted in high molecular weight TPU blends. The blends of polycarbonate with TPU were produced with operating temperatures of 220 to 250ºC and residence times of 0.5 to 4 minutes.

Due to problems associated with the conventional production of high molecular weight polyesters, A.E. Brink and J.T. Owens\textsuperscript{89} of Eastman Chemical Company created a simple and effective method of increasing polyester molecular weight by the REX process. In their patent, a polyester with at least one hydroxyl group was melt blended with common TPU in a twin screw extruder. Using TPU compositions of 1 to 1.5% by weight, high temperature extrusion (ca. 240ºC) depolymerized the TPU to produce isocyanate intermediates in-situ, which in turn reacted with the isocyanate reactive hydrogen bearing polyester. This ultimately resulted in chain extension of the polyester,
thereby increasing its molecular weight. The patent also claimed that this process was useful in the chain extension of polycarbonates.

According to Khatib’s dissertation, the REX of a PVC/TPU blending in a single screw extruder was modeled and the results compared to the experiments. A one-shot process in terms of TPU synthesis was used. The PVC formulation along with TPU monomers and additives were fed together into the feed port of the extruder. The entire mixture was then processed at an extruder temperature of 140°C to produce a PVC/TPU blend wherein the TPU polymerized in-situ with PVC. He concluded that the PVC stabilizer catalyzed the PU reaction.

In his dissertation, Parnell studied the polymerization of TPU monomers in-situ with PVC sequentially in an intermeshing counter rotating twin screw extruder. He studied the effect of the PU monomers on the kinetics of the in-situ synthesis of TPU. He elucidated the effects of different nucleophilic and electrophillic compounds on the kinetics. He compared the properties of blends obtained by REX with those of melt blends. The melt blending process caused PVC degradation at the required temperatures. His research also confirmed the catalytic effect of PVC stabilizer on the in-situ polymerization of PU and its effect on reaction induced phase separation onset.

Cassagnau et al. studied the REX of a polyethylene oxide based TPU in-situ with PE in a co-rotating intermeshing twin screw extruder. They found that the residence time distribution of TPU monomers limited the degree of PU polymerization. Cassagnau et al. attributed this effect to the miscibility of TPU diisocyanate of diol monomers with the molten PE phase.
3.1. Reactive Blending of PVC/TPU Blends

The reactive blending of Thermoplastic Polyurethane (TPU) with PVC involves two phenomena that occur simultaneously. The first event is the PVC compounding with some of the TPU monomers, namely polyol and chain extender. The second event, also known as in-situ TPU polymerization, takes place simultaneously with the blending of diisocyanate and compounded PVC. The process just described is intended to overcome the compounding difficulties associated with the most common alternative blending processes, specifically melt blending. The disadvantage of the melt blending of PVC/TPU is the elevated temperature required (ca. 190°C) which causes PVC degradation. Consequently, the reactive blending process appears as an attractive alternative technique to the conventional melt blending of PVC and TPU.

This in-situ blending technique in both batch and continuous process was studied by Parnell et al. in our research group. They demonstrated its advantages over melt blending by reducing mixing times and with much less PVC degradation without sacrificing the mechanical and thermal properties of the blends. Based on this previous study, various monomers of TPU, monomer components, and processing methodologies were explored to improve the final properties of products and the processing scheme.
3.1.1. Materials

Suspension polymerized poly(vinyl chloride) of injection molding grade was used in the experiments. This PVC is manufactured by the Oxy Vinyls Company, and it has a number average molecular weight of 30,000 g/mol ($M_n$). Dibutyltin bis(2-ethylhexyl mercaptoacetate) (T31), supplied by Arkema, was used as the PVC stabilizer and as the catalyst of the TPU polymerization. The stabilizer and PVC were dry blended in a domestic Waring blender prior to compounding at a proportion of 1% of T31 by weight, as had been suggested by our previous studies.6

The TPUs used in this study consist of hard and soft segments. The TPUs’ soft segment was the product of the reaction between the hydroxyl terminated polyester or polyether, also known as polyol, with the diisocyanate. Four different polyols were used in this study to determine the effect of their miscibility with PVC and their impact on the TPU molecular structure. Poly (propylene adipate) (PPA), poly (butylene adipate) (PBA), and Poly (hexamethylene adipate) (PHA) are the polyester polyols. The polyether used was poly (propylene glycol) (PPG). These polymers were supplied by Ruco, Bayer, Crompton, and Aldrich Chemicals respectively.

The TPU hard segments were formed by the reaction between a diisocyanate and a short chain polyol or chain extender. The chain extender used in this study was 1,4-butanediol (BDO) supplied by ARCO Chemicals. In addition to this, four different isocyanates were used to determine the effects of isomer content, NCO content, functionality, and monomer appearance (solid or liquid). All of them are diphenylmethane based diisocyanates (MDIs) and were supplied by Bayer and BASF. The detailed description of the materials used in this study is shown in Tables 3.1 and 3.2.
Table 3.1. Materials used in this study and its characteristics

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Chemical Structure</th>
<th>Abb.</th>
<th>Supplier</th>
<th>Mn</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (Vinyl Chloride)</td>
<td><img src="image1" alt="Chemical Structure" /></td>
<td>PVC</td>
<td>Geon</td>
<td>30,000</td>
<td>N/A</td>
</tr>
<tr>
<td>Dibutyltin bis (2-ethylhexyl mercaptoacetate)</td>
<td>N/A</td>
<td>T31</td>
<td>Arkema</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Poly (Propylene Glycol)</td>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>PPG</td>
<td>Aldrich</td>
<td>2,400</td>
<td>2</td>
</tr>
<tr>
<td>Poly (Propylene Adipate)</td>
<td><img src="image3" alt="Chemical Structure" /></td>
<td>PPA</td>
<td>Ruco Polymers</td>
<td>2,400</td>
<td>2</td>
</tr>
<tr>
<td>Poly (Butylene Adipate)</td>
<td><img src="image4" alt="Chemical Structure" /></td>
<td>PBA</td>
<td>Bayer</td>
<td>2,000</td>
<td>2</td>
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<tr>
<td>Poly (Hexamethylene Adipate)</td>
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<td>PHA</td>
<td>Crompton</td>
<td>2,000</td>
<td>2</td>
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<tr>
<td>1,4 Butanediol</td>
<td><img src="image6" alt="Chemical Structure" /></td>
<td>BDO</td>
<td>ARCO</td>
<td>90</td>
<td>2</td>
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<td>2,4 Diphenylmethane Diisocyanate</td>
<td><img src="image7" alt="Chemical Structure" /></td>
<td>LMDI</td>
<td>Bayer</td>
<td>250</td>
<td>2</td>
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<td>4,4 Diphenylmethane Diisocyanate</td>
<td><img src="image8" alt="Chemical Structure" /></td>
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<td>Carbodiimide Modified 4,4 Diphenylmethane Diisocyanate</td>
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<td>BASF</td>
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<td>Carbodiimide Modified 4,4 Diphenylmethane Diisocyanate</td>
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<td>Bayer</td>
<td>248</td>
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75
Table 3.2. Characteristics of the MDIs used in this study

<table>
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<tr>
<th>Product</th>
<th>Name</th>
<th>%NCO</th>
<th>f</th>
<th>Viscosity (mPa.s/25 °C)</th>
<th>Tc (°C)</th>
<th>2,4’ isomer</th>
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<tr>
<td>4,4’ MDI</td>
<td>SMDI</td>
<td>33.6</td>
<td>2</td>
<td>Solid</td>
<td>28</td>
<td>Trace</td>
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<tr>
<td>2,4’/-/4,4’ MDI</td>
<td>LMDI</td>
<td>33.6</td>
<td>2</td>
<td>10</td>
<td>18</td>
<td>~55%</td>
</tr>
<tr>
<td>Carbodiimide Modified MDI</td>
<td>CDMDI</td>
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<td>2.2</td>
<td>50</td>
<td>8</td>
<td>Trace</td>
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<tr>
<td>Carbodiimide Modified MDI</td>
<td>CDMDIB</td>
<td>29.5</td>
<td>2</td>
<td>40</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The TPUs produced in this study were formulated with low hard segment content in order to have better miscibility between the PVC and the TPU\textsuperscript{258,259}. Equimolar quantities of Polyol and BDO were used, while the MDI was added in a 2 to 1 proportion (i.e. one molecule of MDI were present per one molecule of each one of the hydroxyl bearing compounds). The compositions of monomers used are shown in Table 3.3. An excess of 2% of MDI was used to compensate for any residual water present in the system.

Table 3.3. Compositions of the TPUs used in this study (Percentages)

<table>
<thead>
<tr>
<th>TPU</th>
<th>SMDI</th>
<th>LMDI</th>
<th>CDMDI</th>
<th>CDMDIB</th>
<th>BDO</th>
<th>PBA</th>
<th>PHA</th>
<th>PPA</th>
<th>PPG</th>
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<tr>
<td>SPBA</td>
<td>19.62</td>
<td></td>
<td></td>
<td></td>
<td>3.54</td>
<td>76.84</td>
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<tr>
<td>LPBA</td>
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<td></td>
<td></td>
<td></td>
<td>3.54</td>
<td>76.84</td>
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<td>CDPBA</td>
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<td>22.05</td>
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<td>3.43</td>
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<tr>
<td>CDPBAB</td>
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<td>21.75</td>
<td></td>
<td></td>
<td>3.45</td>
<td>74.80</td>
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<tr>
<td>SPHA</td>
<td>19.27</td>
<td></td>
<td></td>
<td></td>
<td>3.48</td>
<td>77.25</td>
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<tr>
<td>LPHA</td>
<td>19.27</td>
<td></td>
<td></td>
<td></td>
<td>3.48</td>
<td>77.25</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>CDPHA</td>
<td></td>
<td></td>
<td>21.65</td>
<td></td>
<td>3.37</td>
<td>74.98</td>
<td></td>
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<tr>
<td>SPPA</td>
<td>15.83</td>
<td></td>
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<td>2.83</td>
<td></td>
<td>81.31</td>
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<tr>
<td>SPPG</td>
<td>19.27</td>
<td></td>
<td></td>
<td>3.48</td>
<td></td>
<td>77.25</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
All the raw materials as supplied were dried to eliminate any residual moisture. The polyols were dried under a vacuum at 100ºC for a minimum of four hours. The BDO was dried over type 3A molecular sieves at room temperature for at least two weeks prior to the processing operations. The SMDI, supplied as flakes, was stored in a vacuum at 0ºC until the synthesis operation in order to avoid trimerization and wastage of the isocyanate groups. On the other hand, LMDI, CDMDI, and CDMDIB were stored in 1 L flasks under a nitrogen blanket until the synthesis. The PVC was dried under a vacuum at 60ºC for 12 hours prior to the experiments.

3.1.2. Processing Equipment and Procedures

One of the main objectives of this study was to develop the reactive blending technology in both a batch and continuous process. The first step in this development started on a batch internal mixer in a search for the optimal processing conditions for the different compounds. Then, the continuous experiments were conducted in a counter-rotating twin screw extruder. The detailed processing procedures and equipment are described in the following sections.

3.1.2.1. Model Studies of the PVC/TPU Reactive Blending: Batch Processing

All model studies were conducted by using an internal mixer (C. W. Brabender R.E.E. 6). The internal mixer has cam style rotors, an approximate volume of 82cm³ and is linked to a data acquisition system for the measurement of torque and temperature as a function of mixing time.

3.1.2.1.1. Stage 1: PVC Compounding and Plasticization

In these experiments, the first goal was to obtain the optimal conditions of the PVC PVC/Polyol blends at different compositions for the different polyols used. Different processing conditions were used, as shown in Table 3.4.
Table 3.4. Conditions for PVC/Polyol Blending

<table>
<thead>
<tr>
<th>Polyol</th>
<th>PVC/Polyol Composition (wt%)</th>
<th>Temperature (°C)</th>
<th>Mixing Speed (rpm)</th>
<th>Time of Blending (min)</th>
<th>Filling Factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALL</td>
<td>90/10</td>
<td>120</td>
<td>50</td>
<td>9</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>80/20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>70/30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPA</td>
<td>90/10</td>
<td>120</td>
<td>75</td>
<td>9</td>
<td>85</td>
</tr>
<tr>
<td>PBA</td>
<td>80/20</td>
<td>120</td>
<td>100</td>
<td>9</td>
<td>85</td>
</tr>
<tr>
<td>PHA</td>
<td>70/30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>90/10</td>
<td>120</td>
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<tr>
<td></td>
<td>70/30</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>ALL</td>
<td>90/10</td>
<td>120</td>
<td>50</td>
<td>20</td>
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<td></td>
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<td>90/10</td>
<td>120</td>
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<tr>
<td>PBA</td>
<td>80/20</td>
<td>120</td>
<td>50</td>
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<td>85</td>
</tr>
<tr>
<td>PHA</td>
<td>70/30</td>
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<td></td>
<td></td>
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<tr>
<td></td>
<td>90/10</td>
<td>120</td>
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<td>9</td>
<td>95</td>
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<tr>
<td></td>
<td>80/20</td>
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<td>95</td>
</tr>
<tr>
<td></td>
<td>70/30</td>
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<tr>
<td>ALL</td>
<td>90/10</td>
<td>120</td>
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<td>9</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>80/20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>70/30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Initially the stabilized PVC was added to the preheated internal mixer and mixed for 5 minutes. Then, the Polyol was added in the compositions of Polyol/PVC: 75/25, 50/50, 25/75, 30/70, 20/80, and 10/90% by weight. After being mixed under the different conditions, the samples were removed and inspected visually for thermal degradation (color change) and appearance.

Once the optimal conditions for this PVC/Polyol blend were obtained, the procedure was repeated and BDO was added in stoichiometric quantities to produce the corresponding PVC/Polyol/BDO blend compositions. The samples were mixed for six more minutes. Then the samples were removed for characterization for miscibility and morphology by DSC and SEM. Figure 3.1. exhibits the typical torque-time curve for the reactive blending process of the PVC/PBA/BDO/SMDI system.

![Figure 3.1. Torque-Time Characteristic Curve for PVC/TPU (PBA Based) Reactive Blend](image)

3.1.2.1.2. Stage 2: In-Situ Polymerization of the TPU with PVC

The second stage was the reaction of TPU polyols with the isocyanate in-situ with PVC. It can be seen in Figure 3.1. This stage began with adding the isocyanate to
the compound obtained in the first stage. Our previous studies revealed that the second stage took two to five minutes.

The experiment started with the compounding procedure described in section 3.1.2.1.1. to produce the PVC/Polyol/BDO blends that corresponded to the PVC/TPU blends with compositions of 25/75, 50/50, and 75/25% by weight. Then MDI was added until a maximum torque was observed (i.e. Figure 3.1. shows 5 minutes of mixing time), indicating that the TPU polymerization in-situ with PVC was complete. The PVC/TPU blends were removed from the internal mixer and characterized within one week.

Gel permeation chromatography (GPC) was used to measure the molecular weight and molecular weight distribution of the PVC/TPU reactive blends. SEM, TEM, DSC, and FTIR were used to characterize the morphology of the reactive blends. Finally, tensile testing was conducted for the mechanical properties of all the blends. A more detailed description of the characterization techniques will be presented in section 3.3.

The different properties of the reactive blends were compared to those of the neat polymers. To accomplish this, several neat TPUs of the same formulation present in the reactive blends were synthesized by the one shot method as follows. Heated PBA (90ºC) was gravimetrically metered into a 500 ml propylene beaker. Then BDO (at room temperature) was gravimetrically added and hand mixed for 10 s. Finally MDI was added to the mixture and rapidly hand mixed for 30 s. The resulting TPU reactant mixture was cast into a Teflon coated baking pan and fully polymerized at 110ºC for 16 hours in a convection oven.
3.1.2.2. Reactive Extrusion of TPU In-situ with PVC via a Twin Screw Extruder

The reactive extrusion process was carried out in a counter-rotating intermeshing twin screw extruder (Leistritz LMS 30.34). This extruder consisted of modular screws and mixing elements (kneading elements) in a segmented extruder barrel. Each barrel section was 120 mm long. The screw elements had different lengths for flexible assembly. The barrel diameter was 34 mm and the inter-screw centerline distance was 30 mm. The length to diameter ratio (L/D) of the extruder was 28.2 and the total length was 990 mm equivalent to eight barrel sections. Two barrel sections with feeding ports allowed for tailor-making the position of feeding the reactants and additives. In this study, two feeding ports were used, one to feed the PVC and the polyols, and the other (in the fifth barrel segment) to feed the solid or liquid form of MDI.

All barrel sections, except for the first one, had a heating electric resistance and a cooling fan to permit easy temperature control. Cylindrical die assembly was used for pelletizing. The die assembly consisted of three metal disks, which were aligned by pins. The first and second disks had a flow channel to homogenize the material. A breaker plate was located between them in order to remove impurities and foreign materials and to eliminate the polymer flow history. The final extrudate shape was given by a third disk that consisted of a convergent channel with three capillaries, each of 3mm in diameter, to produce polymer strings. The die was equipped with a heating band.

As previously mentioned, the reactive blending process used in this study has two stages. In the first, the polyols were blended with the PVC, and in the second, the MDI reacted with the polyols to polymerize TPU in-situ with PVC. To assemble the optimal screw geometry and to establish the operating conditions, it is important to
realize that both stages of the reactive blending process occur sequentially along the extruder. Therefore, the screw elements had to be selected to produce blends with processing histories similar as those found in batch model studies. Our previous studies\textsuperscript{6} established the operating conditions, the barrel and screw configuration, similar to the conditions used in the batch reactive blending. Figure 3.2. shows a schematic representation of the extruder apparatus with the screw configuration and the feeding equipment, as well as the processing conditions used. Additionally Table 3.5. shows detailed information and a list of the screw elements used.

![Figure 3.2. Schematic representation of the extruder apparatus, its screw configuration, and the stages of the blending process.](image)

Figure 3.2. Schematic representation of the extruder apparatus, its screw configuration, and the stages of the blending process.
Table 3.5. Detailed geometry of the elements in the counter-rotating, intermeshing twin screw extruder configuration.

<table>
<thead>
<tr>
<th>Illustration</th>
<th>Leistritz Designation</th>
<th>Length (mm)</th>
<th>Outside Diameter (mm)</th>
<th>Root Diameter (mm)</th>
<th>Flight Thickness (mm)</th>
<th>Pitch (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZD-26-R8</td>
<td>15</td>
<td>26</td>
<td>26</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>FD-1-20-R</td>
<td>120</td>
<td>34</td>
<td>26</td>
<td>9.3</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>FF-1-20-R2</td>
<td>60</td>
<td>34</td>
<td>26</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>KFD-120/20-R</td>
<td>120</td>
<td>34</td>
<td>26</td>
<td>3→9.3</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>FD-1-20-R2</td>
<td>60</td>
<td>34</td>
<td>26</td>
<td>9.3</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>ZS-33-R8</td>
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<td>33</td>
<td>26</td>
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<td>N/A</td>
</tr>
<tr>
<td></td>
<td>ZS-33-R8</td>
<td>15</td>
<td>33</td>
<td>26</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>ZD-26-R8</td>
<td>15</td>
<td>26</td>
<td>26</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>FD-1-20-R2</td>
<td>60</td>
<td>34</td>
<td>26</td>
<td>9.3</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Z2-26-R16</td>
<td>7.5</td>
<td>26</td>
<td>26</td>
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<td>N/A</td>
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<tr>
<td></td>
<td>ZS-2-R4</td>
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<td>33.5</td>
<td>26</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Z2-26-R16</td>
<td>7.5</td>
<td>26</td>
<td>26</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>FD-1-20-R</td>
<td>120</td>
<td>34</td>
<td>26</td>
<td>9.3</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>FF-1-30-R</td>
<td>120</td>
<td>34</td>
<td>26</td>
<td>4.5</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>FF-1-20-R2</td>
<td>60</td>
<td>34</td>
<td>26</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>ZS-26-R16</td>
<td>7.5</td>
<td>26</td>
<td>26</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>FF-1-20-R4</td>
<td>30</td>
<td>34</td>
<td>26</td>
<td>3</td>
<td>-20</td>
</tr>
<tr>
<td></td>
<td>ZS-26-R16</td>
<td>7.5</td>
<td>26</td>
<td>26</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>FF-1-20-R</td>
<td>120</td>
<td>34</td>
<td>26</td>
<td>3</td>
<td>20</td>
</tr>
</tbody>
</table>

To determine the optimal screw configuration and operating conditions for the reactive blending process required both theoretical analysis and testing. However, some insight was obtained from the nature of the phenomena that occur in the extruder,
namely mixing and reaction. In the first stage, the PVC is sheared to be melted and blended with the polyols to form a miscible blend. This stage requires high shear as well as dispersive and distributive mixing. While in the second stage, in which the TPU polymerization in-situ with PVC occurs, distributive mixing is critical to ensure the contact between the monomers for the reaction to take place. The extruder geometry used in this study consisted of closed meshed elements (FD) that provided a fast conveying of the materials to avoid allowing them to bridge in the feeding port. Next, a set of free meshing elements (FF) was mounted to homogenize the mixture, and a compression type element (KFD) was introduced to improve the distributive and dispersive mixing capability of the process using a variable increase in flight thickness. Then the PVC/Polyol/BDO mixture was transported by the FD elements into a section of no pumping elements that imposed a high amount of shear (shearing elements) and a negative pressure gradient (slit stowing elements) that enhanced the mixing of the blend.

In the second stage, MDI was added to the extruder to initiate the reaction with the polyols, and FD elements pumped the mixture away from the feeding port to avoid bridging. FF elements followed by reverse pitch FF elements created the distributive mixing required for the reaction to take place. Finally, the mixture was pumped out of the extruder into the die with a set of low pitch FF elements.

The different materials fed to the extruder had to be handled properly and metered for accurate stoichiometric balances as well as to avoid water absorption. In the first feeding port, stabilized PVC powder and the liquid polyols were fed simultaneously. For feeding PVC, a K-tron Soder volumetric feeder with twin corotating non-intermeshing screws was used. This feeder has reproducible conveying accuracy of better than ±1%
of flow. To feed the polyols, melting under an inert gas (dry nitrogen) atmosphere was required before pumping to avoid water absorption. The polyols required melting because they are solid at room temperature. In the previous study, Parnell\textsuperscript{6} designed and built a piston pump for feeding the polyols/BDO mixture. This pumping system device was used in this study, as shown in Figure 3.3. The MDI was fed as a solid in our previous studies in which the resultant reactive blends had low molecular weights due to problems with the feeding system and stoichiometry control. Using the SMDI and the conventional feeder resulted in dimerization of the MDI and its agglomeration on the feeder. To overcome the problems found in those studies, a new liquid feeding system was developed as follows. A home-made piston micropump was designed and built to feed the liquid MDI for stoichiometric balance accurately. Figure 3.4. presents a schematic representation of this LMDI feeding system. Photographs of the extruder setup and feeding systems are presented in Figure 3.5.

Figure 3.3. Schematic of home-made piston pump apparatus used to meter liquid mixtures of PBA and BDO into the first feed port of extruder
Figure 3.4. Schematic of home-made micropump apparatus used to meter liquid MDI into the second feed port of extruder
The characterization of the PVC/TPU reactive blends was carried out by the same methods used for the model batch studies. A more detailed description of the characterization techniques will be presented in section 3.3.
3.2. Kinetics Studies of TPU Polymerization

The reactive blending process includes the TPU polymerization in-situ with PVC. As a consequence, the kinetics of the polymerization will be different from the neat TPU polymerization due to the effect of the addition of PVC. It was important also to include the kinetics of neat TPU, as well as the reactive blends under the processing conditions, such as temperature, pressure, and shear.

The experiments were divided into three sections. In the first kind, isothermal and non-isothermal studies were performed to determine the kinetics of neat TPU polymerization under quiescent conditions, using different monomers. In the second, the effects of shear and pressure on the TPU polymerization were investigated. In the third, the effect of the addition of PVC was studied.

3.2.1. Materials

The TPU monomers used for these kinetic studies were:

- Long chain diol: Poly (butylene adipate) (PBA) and Poly (hexamethylene adipate) (PHA).
- Chain Extender: 1,4-butanediol (BDO).
- Isocyanates: Three different diphenylmethane based diisocyanates (MDIs): SMDI, LMDI and CDMDI.

PVC and its stabilizer (T31) were added to the TPU to study their effect on the polymerization kinetics.

For a more detailed description of the materials used in this study, refer to section 3.1.1. and Tables 3.1, 3.2 and 3.3. All the raw materials as supplied were dried to eliminate any residual moisture.
Equimolar quantities of Polyol and BDO were used, while the MDI was added in a proportion of 2 to 1 (i.e. two molecules of MDI were present per one molecule of each one of the hydroxyl bearing compounds). Except in the studies of TPU polymerization an excess of 2% of MDI was used to compensate for any residual water present in the system. All the other reactions were run at stoichiometry. Table 3.6. shows the details of the materials used for the different kinetic studies.

Table 3.6. TPUs used in the different Kinetic Studies

<table>
<thead>
<tr>
<th>TPU</th>
<th>Kinetic Study</th>
<th>Neat TPU Polymerization</th>
<th>In presence of PVC</th>
<th>Under Shear</th>
<th>Under Pressure</th>
<th>Reactive Extrusion of TPU</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPBA</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPHA</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LPBA</td>
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<td>X</td>
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<tr>
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</tr>
<tr>
<td>CDPBA</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2.2. Kinetics of neat TPU Polymerization

As has been mentioned, a phenomenological rate equation has been used to study the kinetics of the TPU polymerization, due to its flexibility and descriptive capability without knowledge of the reaction mechanism. Most of the previous studies have focused on developing an Arrhenius-type temperature dependency.

The kinetic equation used widely by various researchers is of the form:

$$- \frac{d[\text{NCO}]}{dt} = k_1[\text{NCO}]^n + k_2[\text{NCO}]^n[\text{Cat}]^c$$  \hspace{1cm} (3-1)

$$k_i = A_i \exp \left( \frac{E_{ai}}{RT} \right)$$  \hspace{1cm} (2-10)

where the variables were explained in section 2.2.3.2. If the equation (3-1) is expressed in terms of conversion ($\alpha$), the result is:
This kinetic equation (3-2) was used for the kinetic studies of neat TPU, and with varying conditions and starting materials, the different kinetic parameters were obtained.

3.2.2.1. Experimental Procedures

The effect of different chain lengths of the polyesters, as well as the effect of NCO, isocyanate content, and the functionality of the MDIs on the kinetic parameters was investigated. These kinetic studies were conducted by two dependent methods: the adiabatic temperature rise (ATR) that was used to measure the total heat of reaction, and the second one is isothermal DSC, intended to determine the kinetic parameters. The conditions of these experiments are shown in Table 3.7.

The TPUs produced for these studies have the same formulation as the TPUs present in the PVC/TPU reactive blends. For the isothermal DSC studies, the mixtures were prepared by metering the heated PBA (90ºC) into a 500 ml propylene beaker, and then BDO (at room temperature) was gravimetrically added. The mixture was stirred by hand for 10 s. Then MDI was added to the mixture and rapidly mixed by hand for 30 s. After this, the samples were removed, frozen rapidly with dry ice, for the immediate kinetic analysis. In the case of catalyzed mixtures the same procedure was used except the catalyst was added to the beaker containing the heated PBA at the beginning of the experiment.

For the ATR experiments, the procedure was the same as for the DSC studies except the polypropylene beaker was wrapped with a thermal insulator to avoid heat losses, and a type J iron-constant thermocouple was attached to the spoon inside the
reacting mass to measure the temperature rise with a homemade data acquisition system. Details of the experiment are presented in section 3.3.

Table 3.7. Kinetics of TPU polymerization – Experimental Conditions

<table>
<thead>
<tr>
<th>Experiment</th>
<th>TPU</th>
<th>Catalyst (%)</th>
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<td>SPBA</td>
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<td>N/A</td>
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<td>Temperature</td>
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<td>0.035</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.045</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.055</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.067</td>
<td>N/A</td>
</tr>
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<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.048</td>
<td>N/A</td>
</tr>
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<td></td>
<td></td>
<td>0.054</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.065</td>
<td>N/A</td>
</tr>
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<td>SPHA</td>
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<td>0.025</td>
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<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.047</td>
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</tr>
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<td></td>
<td>0.018</td>
<td>N/A</td>
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<td>0.038</td>
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<td>SPBA</td>
<td>0.0005</td>
<td>100</td>
</tr>
<tr>
<td>LPBA</td>
<td></td>
<td>0.002</td>
<td>120</td>
</tr>
<tr>
<td>SPHA</td>
<td></td>
<td>0.004</td>
<td>140</td>
</tr>
<tr>
<td>CDPBA</td>
<td></td>
<td>0.006</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.009</td>
<td>180</td>
</tr>
<tr>
<td>SPBA</td>
<td></td>
<td>0.0015</td>
<td>100</td>
</tr>
<tr>
<td>LPBA</td>
<td></td>
<td></td>
<td>120</td>
</tr>
<tr>
<td>SPHA</td>
<td></td>
<td></td>
<td>160</td>
</tr>
<tr>
<td>CDPBA</td>
<td></td>
<td></td>
<td>180</td>
</tr>
</tbody>
</table>

91
3.2.3. Kinetics of TPU Polymerization in the presence of PVC

The effects of the addition of PVC on the polymerization of TPU were investigated by using non-isothermal DSC of TPUs in-situ with stabilized PVC.

3.2.3.1. Experimental Procedures

Three different PVC/TPU reactive blends were prepared at 140ºC, 50 rpm, and 22 minutes of total mixing time, using the same compounding procedure as was described in section 3.1.2.1. In some instances, the PVC was stabilized with small amounts of T31. The MDI was added and incorporated into the blend for two minutes to produce a homogeneous PVC/TPU reactant mixture, in which the TPU polymerization was in its early stages. The samples were removed and prepared for immediate kinetic analysis. The 50/50 blend composition was studied under different temperature and stabilizer concentrations in order to obtain the kinetic parameters as a function of temperature and stabilizer concentration. The various conditions used for these studies are shown in Table 3.8.

3.2.4. Kinetics of TPU Polymerization under Shear

The effect of shear rate on the kinetics of TPU polymerization was investigated by using the following equipment and procedures.

3.2.4.1. Processing Equipment and Procedures

The TPU produced for these studies had the same formulation as the TPU present in the PVC/TPU reactive blends (Table 3.3). The one shot method was used, the heated PBA (90ºC) was metered gravimetrically into a 500 ml propylene beaker, and immediately the catalyst and BDO (at room temperature) were added gravimetrically. The mixture was stirred by hand for 10 s. Then MDI was added and stirred by hand for 30 s with a polypropylene spoon. After this, the samples were removed, frozen rapidly
with dry ice into the shape of a 25mm disk with an average diameter of 2mm, and prepared for immediate kinetic analysis.

Table 3.8. Kinetics of TPU polymerization in presence of PVC – Experimental Conditions

<table>
<thead>
<tr>
<th>Experiment</th>
<th>TPU</th>
<th>PVC Stabilizer (%)</th>
<th>PVC/TPU (wt%)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal DSC</td>
<td>SPBA SPHA</td>
<td>0.002</td>
<td>75/25</td>
<td>140</td>
</tr>
<tr>
<td>SPBA SPHA</td>
<td>0.009</td>
<td>50/50</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>SPBA SPHA</td>
<td>0.0005</td>
<td>75/25</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>SPBA SPHA</td>
<td>0.004</td>
<td>50/50</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>SPBA SPHA</td>
<td>0.006</td>
<td>25/75</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>SPBA SPHA</td>
<td>0.009</td>
<td>50/50</td>
<td>140</td>
<td></td>
</tr>
</tbody>
</table>

A Rheometric RMS-800 rheometer was used with disposable aluminum plates 25 mm in diameter, under a time sweep regime at a constant frequency and strain. After producing the samples, the rheometer was set to the specified isothermal temperature, and once it was stabilized, the sample was introduced. When the temperature was stabilized, after 1 min, the experiment was started. Measurements were made over a 30 minute period, with recordings every 30 s. Five different frequencies and three temperature levels were used. Table 3.9. shows the experimental conditions used in this study.

3.2.5. Kinetics of TPU Polymerization under Pressure

The effect of pressure on the kinetics of TPU polymerization was investigated by using a home-made pressure vessel as follows.
3.2.5.1. Processing Equipment and Procedures

As mentioned in the literature survey sections, the effect of pressure on the reaction kinetics is a combination of its effect on the viscosity and on the reaction constant. By increasing the pressure of the system, the reaction constant will increase as was shown in equation (2-12). Nevertheless the final effect of the pressure on the kinetics will depend on the viscosity of the system. If the viscosity of the system is low, the reaction rate increases due to the increase on the probability of reaction, but if the viscosity is high, the reaction rate decreases due to the diffusion controlled polymerization reaction and the limitation of the diffusion rate of the molecules introduced by the pressure.

Table 3.9. Kinetics of TPU polymerization under shear – Experimental Conditions

<table>
<thead>
<tr>
<th>TPU</th>
<th>Catalyst (%)</th>
<th>Temperature (°C)</th>
<th>Frequency (rad/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.015</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>0.015</td>
<td>120</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>0.015</td>
<td>140</td>
<td>5</td>
</tr>
</tbody>
</table>

In this study the effect of pressure on the kinetics was calculated by measuring the temperature rise of the polymerizing system under the application of different pressures on the cavities of the home-made pressure vessels. Figure 3.6. shows a schematic representation of these home-made chambers.
Figure 3.6. Schematic Representation of the Pressure Vessels used for the TPU polymerization under pressure kinetic studies
The TPU used in this study has the same formulation as the TPU present in the PVC/TPU reactive blends, as shown in Table 3.3. The heated PBA (90°C) was metered gravimetrically into the stainless steel chamber placed in a conventional oven at 80°C. Then the catalyst and BDO (at room temperature) were added gravimetrically. The mixture was stirred by hand for 10 s. Then the MDI was added and stirred by hand for 30 s with a polypropylene spoon with a J iron-constant thermocouple attached to it. Measurements were taken for 10 s. After that, the spoon with the thermocouple was removed from the chamber and the chamber lid with another thermocouple was inserted in the chamber. Different loads were placed on top of the chamber to give different pressure levels. The J iron-constant thermocouple of the spoon and the lid were connected to the data acquisition system and the temperature rise was carefully recorded every 5 seconds with a data acquisition system. Table 3.10. shows the experimental conditions used.

Table 3.10. Kinetics of TPU Polymerization under Pressure – Experimental Conditions

<table>
<thead>
<tr>
<th>TPU</th>
<th>Catalyst (%)</th>
<th>Vessel</th>
<th>Load (kg)</th>
<th>Pressure (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPBA</td>
<td>0.151</td>
<td>Small</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.5</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.5</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Large</td>
<td>8.5</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10.5</td>
<td>120</td>
</tr>
</tbody>
</table>

3.2.6. Reactive Extrusion Studies of TPU Polymerization

The reactive extrusion of TPUs in single or twin screw extruders is an efficient and economical alternative to more conventional processes such as the one shot/belt process. However, the previous literature revealed the difficulties of TPU polymerization
via twin screw extrusion associated with control of stoichiometry, as well as the selection of the appropriate processing conditions to obtain a high molecular weight. The principal objective of this area of interest was to observe the effect of the processing conditions (i.e. pressure, shear and temperature), as well as screw configuration on the extent of reaction of TPU polymerization, and on the final properties of the TPU.

3.2.6.1. Processing Equipment and Procedures

Kinetic studies of TPU in an extruder are divided in two parts. In the first part the effect of changes on the processing conditions such as rotor speed, number of holes on the die and temperature profile were studied. In the second part, the effect of different screw configurations on the kinetics of TPU polymerization was studied.

The two different screw configurations used in the study differ in their use of mixing elements and backpressure zones. The first screw configuration used one, named as screw 1, as the screw configuration for the reactive blending process, discussed in section 3.1.2.2. The second screw configuration, named screw 2, is a modified version of the screw configuration used by Macosko et al. Figure 3.7. shows a schematic representation of the extruder apparatus with the screw configuration, and Table 3.11. shows detailed information and a list of the screw elements used. The TPU monomers are added to the extruder in the first feeding port. The reacting mixture is conveyed by closed flighted transport elements (FD) except for a very short part in zone three (30 mm of length) that is open flighted (FF). The closed elements are fully intermeshing self-wiping with different pitches (i.e. 30, 20, 12 and 6mm).
Figure 3.7. Twin Screw Extruder Configuration- Second Screw Configuration
Table 3.11. Detailed geometry of the elements in the counter-rotating, intermeshing twin screw extruder configuration.

<table>
<thead>
<tr>
<th>Illustration</th>
<th>Leistritz Designation</th>
<th>Length (mm)</th>
<th>Outside Diameter (mm)</th>
<th>Root Diameter (mm)</th>
<th>Flight Thickness (mm)</th>
<th>Pitch (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Illustration" /></td>
<td>FD-1-30-R</td>
<td>120</td>
<td>34</td>
<td>26</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td><img src="image2" alt="Illustration" /></td>
<td>FD-1-20-R2</td>
<td>120</td>
<td>34</td>
<td>26</td>
<td>9.3</td>
<td>20</td>
</tr>
<tr>
<td><img src="image3" alt="Illustration" /></td>
<td>FF-1-20-R4</td>
<td>30</td>
<td>34</td>
<td>26</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td><img src="image4" alt="Illustration" /></td>
<td>FD-3-48-R</td>
<td>120</td>
<td>34</td>
<td>26</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td><img src="image5" alt="Illustration" /></td>
<td>FD-3-48-R</td>
<td>120</td>
<td>34</td>
<td>26</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td><img src="image6" alt="Illustration" /></td>
<td>FD-3-48-R</td>
<td>120</td>
<td>34</td>
<td>26</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td><img src="image7" alt="Illustration" /></td>
<td>FD-3-30-R</td>
<td>120</td>
<td>34</td>
<td>26</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td><img src="image8" alt="Illustration" /></td>
<td>FD-3-30-R</td>
<td>120</td>
<td>34</td>
<td>26</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td><img src="image9" alt="Illustration" /></td>
<td>FD-3-30-R</td>
<td>120</td>
<td>34</td>
<td>26</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

Changes on the screw rotation speed, number of holes used on the die, and temperature profiles were used to observe their effect on the melt temperatures and pressures at the end of the extruder, as well as on the shear rates of the extruder. In this study all the monomers were added to the extruder in the first feeding zone. Table 3.12. shows the processing conditions used.
Table 3.12. Operating Conditions for the Reactive Extrusion of TPUs

<table>
<thead>
<tr>
<th>TPU</th>
<th>Screw Configuration</th>
<th>Temperature Profile</th>
<th>Screw Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Screw Speed</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Screw 1</td>
<td>Flat 120°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Screw 2</td>
<td>Reactive Blending</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>50</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Flat 120</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>150</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>200</td>
</tr>
</tbody>
</table>

At the exit of the die, the TPUs were collected and characterized within a week with differential scanning calorimetry (DSC) and gel permeation chromatography (GPC). A more detailed description of the characterization techniques will be presented in section 3.3.

3.3. Characterization Techniques

The following sections provide a detailed description of the characterization techniques used in the studies.

3.3.1. Morphology and Miscibility Studies

3.3.1.1. Differential Scanning Calorimetry (DSC)

A Differential Scanning Calorimeter (TA DSC 2922) in the scanning mode was used to quantify the glass transition behavior, the melting point depression, and/or the presence of crystallinity in all the blends investigated. The samples were carefully weighed to 10±2 mg and sealed in aluminum hermetic pans and lids, placed in the DSC, and heated at a rate of 20°C/min. The temperature range was from -120°C to 150°C.
for PVC/Polyols blends and from -120°C to 200°C for PVC/TPU blends. The transition temperatures of PVC and TPU were influenced by the processing and thermal histories during processing. Therefore, first and second (quenching) scans were conducted to eliminate different thermal and/or processing histories of those blends and TPU.

3.3.1.2. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (Hitachi S-2150 microscope) was used to study the phase morphology of the TPU/PVC blends and TPU HS/SS morphology. The samples were immersed in liquid nitrogen and cryogenically fractured. Afterwards the samples were glued to aluminum mounts and coated with silver by a sputter coating machine (Emitech K575X).

3.3.1.3. Transmission Electron Microscopy (TEM)

A Transmission Electron Microscope (a JEOL model JEM 100 CX II) was used to observe the morphological characteristics of the blends produced via reactive blending. The ultrathin sections were obtained using an ultramicrotome under cryogenic conditions. The samples were subsequently placed on 300 mesh copper grids and analyzed at various magnifications. Due to the electron density of PVC (high) staining was not required as stated in our previous studies.⁶

3.3.1.4. Fourier Transform Infrared Spectroscopy (FTIR)

Hydrogen bonding behavior, specifically C=O stretching vibration of the blends (ca. 1700-1730 cm⁻¹), was investigated by the use of a Fourier Transform Infrared Spectrometer (Perkin Elmer, 16 PC) with 16 scans per sample at a resolution of 4 cm⁻¹. The samples were dissolved in tetrahydrofuran and cast on a KBr disk to form thin films. After the solvent had been removed, they were scanned in the FTIR in the 400 to 4000
cm⁻¹. For the insoluble samples, they were compression molded to produce thin strips of material that were subjected to the FTIR in the reflection mode over the same range.

3.3.2. TPU Polymerization Studies

3.3.2.1. Gel Permeation Chromatography (GPC)

The measurements of weight average molecular weight, number average molecular weight, and molecular weight distribution of the neat TPU and the reactive blends was performed with a Waters 150-C gel permeation chromatograph used in tandem with light scattering and solution viscosity equipment. Samples were prepared by dissolving the polymers in THF at a known concentration and then running them in the five Ultrastyragel columns with THF as the carrier solvent. Calibration was done with Polystyrene standards.

3.3.2.2. Isothermal Differential Scanning Calorimetry

A Differential Scanning Calorimeter (TA DSC 2922) in the isothermal mode was used to study the TPU polymerization of neat TPU, as well as the in-situ polymerization of TPU with PVC. The samples were carefully weighted to 10±2 mg and sealed in aluminum hermetic pans and lids. Upon placing the sealed sample into the preheated DSC at the specified temperature, the heat flow that resulted from the TPU polymerization was measured as a function of time. After 30 minutes of isothermal polymerization, the samples were rapidly quenched to 0°C and subjected to a temperature scan from 0°C to 200°C at a heating rate of 20°C/min. This temperature scan was performed in an effort to quantify any residual heat of reaction remaining after the isothermal polymerization as well as to ensure a complete polymerization. A second temperature scan was conducted immediately after the first to determine the baseline for the residual heat of reaction calculation.
3.3.2.3. Adiabatic Temperature Rise (ATR)

The TPU polymerization reaction is a fast exothermic reaction that begins as soon as the monomers come in contact. During the quantification of the polymerization kinetics by DSC, a certain amount of heat of reaction that occurred during sample preparation and equipment stabilization cannot be accounted for, making the quantification of a total heat of reaction impossible. Independent adiabatic temperature rise experiments were preformed to determine the total heat of reaction and to be able to account for the heat losses.

In these experiments, five different TPU mixtures were prepared for each one of the TPU formulations (as shown in Table 3.3). The heated PBA (90ºC) was metered into an insulated 500 ml propylene beaker. Then the BDO and catalyst (at room temperature) were added to the system, and the reactant mixture was stirred by hand for 10 s. Next, the MDI was added and stirred by hand 30 s, with a polyethylene spoon. A type J iron-constant thermocouple was attached to the spoon to take temperature measurements of the TPU reactant mixtures. This thermocouple was attached to the spoon in such a way that it was centrally located within the beaker during and after hand mixing. The temperature rise was carefully recorded every 5 seconds with a homemade data acquisition system. Measurements were terminated after 30 minutes of measured time. Figure 3.8. shows the schematic representation of the system used for the ATR experiments.

3.3.3. Mechanical Property Studies - Tensile Testing

The mechanical behavior of melt and reactive blends determined the tensile stress-strain curves. The samples were prepared by compressing the blends into 1 mm thick sheets at 180ºC for 2 minutes. Then in accordance with ASTM 412, die C
dumbbell shaped tensile specimens were cut out of each sheet. The measurements were performed following the testing procedure outlined in ASTM 412 using an Instron Tensile Tester with a 10 KN load cell at room temperature and a crosshead speed of 500 mm/min (neat TPU and PVC/TPU blends with compositions of 25/75, and 50/50 wt%) or 50 mm/min (neat PVC and PVC/TPU blends of 75/25 wt%) and a gauge length of 50 mm stress-strain. The mechanical properties determination includes, elastic modulus, yield stress, elongation at break and tensile strength.

Figure 3.8. Schematic Representation of the ATR experimental set up for the TPU polymerization under pressure kinetic studies

3.3.4. Thermal Stability Studies

3.3.4.1. Thermogravimetric Analysis (TGA)

A TA Thermogravimetric Analyzer was used to study the thermal stability of the PVC/TPU blends prepared during this study, in the range of 30°C and 500°C with a...
scanning rate of 20°C/min. The purpose of these studies was to analyze the influence of the components on the thermal stability of the blends, as well as to compare the thermal stability of melt and reactive blends. The temperature corresponding to a predetermined percentage weight loss served as a measure of thermal stability in all the blends studied.

3.3.5. Processability Studies

3.3.5.1. Rheological Characterization

A cone and plate rheometer (TA Instrument ARES) was used to study the rheological properties of the PVC/TPU blends based on CDMDIs prepared during this study. Three different temperatures and 5 different strain levels were used under frequency sweep experiments. The purpose of this study was to analyze the influence of the CDMDI on the rheological properties of the blends and to determine their processability for a further secondary operation after blending, such as extrusion, injection, or compression molding.

3.3.5.2. Dynamic Mechanical Characterization

A Rheometrics DMA was used to study the dynamic properties of some of the PVC/TPU blends based on CDMIs and LMDI prepared during this study under a given deformation condition in a temperature sweep. The purpose of this study was to determine the behavior of the blends under a compression oscillatory mode of deformation and to find the influence of temperature on the behavior.
CHAPTER IV

RESULTS AND DISCUSSION – REACTIVE BLENDING OF PVC AND TPU

4.1. Reactive Blending of PVC/TPU Blends

The reactive blending of PVC and TPU was carried out in the internal mixer and in the intermeshing counterrotating twin screw extruder. The relationship between processing conditions and their effect on the properties of the blends are presented in the following two sections. The reactive blending of PVC and TPU is a viable process that solves the problems associated with the melt blending, such as difficulty in homogeneous mixing, incorporation of additives, and PVC degradation.

4.1.1. Model studies of Reactive Blending of TPU in-situ with PVC in a Batch Mixer

The studies of the reactive blending of TPU in-situ with PVC consisted of three steps as follows: i) PVC compounding and plasticization with the polyol monomers, ii) the in-situ polymerization of TPU with PVC, and iii) the comparison of the properties of melt blends with those of reactive blends.

4.1.1.1. Stage 1: PVC Compounding and Plasticization

In the first stage of the reactive blending process, the PVC is compounded and plasticized with the TPU polyols including the chain extender and a long chain diol. The miscibility of PVC with the polyols depends on both processing conditions and the types of polyols. Therefore, these studies included two goals. The first is to determine the optimal conditions for PVC blending with polyols and the second is to determine...
the influence of the type of polyol on the miscibility with PVC and morphology of the blends.

4.1.1.1.1. Effect of Processing Conditions

PVC and Polyols blends have been extensively studied by researchers in industries and academia. Most of the previous studies were conducted by means of solution blending rather than melt blending processing because of the drawbacks of the melt blending, as mentioned earlier. The previous studies\(^6\) showed that the PVC/PBA melt blended at 120 °C, 50 rpm, and 85% fill factor produced miscible blends after 9 minutes for three blend compositions: 75/25, 50/50, and 25/75. The analyses showed that blends with low PVC content during mixing exhibited negligible torque, presumably caused by the low viscosity of PBA that constituted the continuous phase. On the other hand, blends with moderate to high PVC contents, showed that increasing PVC concentrations enlarged both the plateau torque and the time to reach that steady values.

From the previous paragraph, it can be concluded that it is more difficult to produce blends with high contents of PVC than blends with a high Polyester content. Consequently, PVC/Polyol blends were studied with PVC/TPU ratios of 70/30, 80/20, and 90/10 at various mixing temperatures, rotor speeds, mixing times, and fill factor. The blend conditions from the previous study\(^6\) were taken as the starting point for the next.

Table 4.1. presents the experimental conditions used in this study and the feasibility of the blends. The first 6 columns show the type of polyol, the ratio of PVC to polyol, the compounding temperature, the mixing speed, the blending time, and the fill factor, respectively. The last column indicates if the blending was viable or not. A viable blending produced a material that looks uniform and smooth at the processing
temperature. On the other hand, unviable blending yields a wet and incoherent powder with no integrity at all.

The blending of PVC and polyester with 70 wt% of PVC was possible under the conditions given in the previous study. However, increasing the concentration of PVC made the blending process impossible. A PVC concentration above 70 wt%, for instance 80 and 90 wt%, resulted in unplasticized PVC. Therefore, blending process conditions, such as temperature, mixing time, mixer's rotor speed, and fill factor must be modified in order to compound the PVC at the larger concentrations of 80 and 90 wt%. Each of these process variables was changed as follows.

The variation of the speed of the rotors did not improve the plasticization of the polyesters into PVC. Although increasing shear rates in polymer blending usually improves mixing, there were no blending improvements when PVC and polyester were blended in the internal mixer.

Previous studies suggested that an increased mixing time improves the incorporation of polyester to the PVC. However, mixing times exceeding 20 minutes, that is more than double the original time, did not show any effect on the compounding of polyester into PVC.

The temperature of mixing determines to a great extent if the polyester incorporates into the PVC. For instance, when the mixing temperature was 140 °C, the polyester was incorporated into the PVC at PVC concentration of 80%. An additional temperature increment to 160 °C permitted the production of smooth and uniform blends with 90 wt% of PVC. In Figures 4.1. and 4.2. the time-torque curves are presented for blending PVC and PBA at 140 °C and 160 °C.
<table>
<thead>
<tr>
<th>Polyol</th>
<th>PVC/Polyol ratio (wt%)</th>
<th>Temperature (°C)</th>
<th>Mixing Speed (rpm)</th>
<th>Blending time (min)</th>
<th>Fill Factor (%)</th>
<th>Blending viability</th>
</tr>
</thead>
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Table 4.1. Results of the PVC/Polyol Melt Blending - Continued

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Figure 4.1. Time-Torque Curve for PVC/PBA blending at 140 °C and 50 rpm for three different blend compositions.

Figure 4.2. Time-Torque Curve for PVC/PBA blending at 160 °C and 50 rpm for three different blend compositions.
The mixing temperature is an important factor in the blending process; however, a high mixing temperature causes PVC thermal degradation, even in the presence of a thermal stabilizer. In Figures 4.3., 4.4., and 4.5. the blends prepared at various processing conditions are shown. The blends obtained at high temperature (i.e. 140 °C) are yellowish in contrast to blends produced at lower temperature which are white. The discoloration may be attributed to the PVC degradation. Consequently, it is desirable to reduce the mixing temperature. Another processing variable will be the fill factor for mixing in an internal mixer.

Figure 4.3. Photograph of the 70/30 PVC/PBA blend (120 °C, 50 rpm, 10 min, 85% fill factor).

Figure 4.4. Photographs of the PVC/PBA blends (140 °C, 50 rpm, 10 min, 85% fill factor) for two different blend compositions. a) 70/30 and b) 80/20.
Increasing the fill factor from 85% to 95% at 120 °C and 50 rpm resulted in homogeneous blends of 80/20 PVC/Polyester. Increasing the fill factor by 5% in all three blends of PVC/PBA 90/10, 80/20 and 70/30 formed homogeneous blends. It is evident that increasing the PVC content, as shown in Figure 4.6., increased the torque and the time at maximum torque peak. These results are attributed to the increased viscosity with the lower concentration of polyester.

Visual observation during the blending process suggests that the polyester is not incorporated to the PVC until to the maximum torque is reached. Initially the blend was powdery and non-uniform. However, after the maximum torque, the blend becomes smooth and uniform.

Figure 4.7. shows the pictures of the blends obtained with 100% fill factor. The samples with high PVC content display a yellowish color, meaning that some degradation took place at a high PVC concentration. Nevertheless, the samples at a
higher fill factor and low temperature display less discoloration than samples at a lower fill factor but higher temperature. On the other hand, the effect of mixing time on blend appearance is shown in the Figures 4.7. and 4.8. Figure 4.8. displays blends obtained at double the mixing time compared to the samples shown in Figure 4.7., while all other compounding variables were kept the same. As a consequence, it becomes apparent that increasing the mixing time caused more degradation because of the increased discoloration of the samples in Figure 4.8. Finally, the rotor speed was increased, showing no effect on the discoloration of the samples. Therefore, it can be concluded that since the batch mixing is going to be scaled up to twin screw extrusion, the residence time in the extruder should be kept as short as possible in order to reduce PVC degradation, while providing enough time to complete the TPU polymerization.

Figure 4.6. Time-Torque Curve for PVC/PBA blending at 120 °C, 50 rpm and 100% fill factor for three different blend compositions.
As a consequence of the experimental results obtained from blending PVC with polyester polyols, the optimal conditions of the melt blending of PVC/Polyester are:

- Temperature: 120 °C
- Rotor speed: 50 rpm
- Mixing time: 9 minutes
- Fill factor: 100%

Blending PVC with polyether polyol was studied under varying conditions similar to the studies of the blends of PVC with polyester. However, in this case variation of temperature, rotor speed, mixing time, and fill factor did not affect the blending process for compounding PVC with a small amount of polyester. In all cases, the product was a
non uniform crumbly material. Consequently, it is difficult to find optimal blending conditions for the blends with a high content of PVC and with low content of polyester. It is noted that all the PVC/polyol blends prepared in this study will be processed under the optimal conditions presented in this section for the PVC/polyester listed above.

4.1.1.1.2. Effect of types of Polyol

As mentioned in the literature survey, PVC and polyols blends have been extensively studied by various researchers, who have concluded that polyester polyols are miscible with PVC because of the interaction of hydrogen bonding with polymers containing carbonyl groups. Ziska et al.\textsuperscript{43}, Prud’homme\textsuperscript{232}, and Woo et al.\textsuperscript{214} concluded that chains with ratios of CH\textsubscript{2} to COO between 3 and 12 were miscible with PVC. On the other hand, because of the proton acceptor nature of polyethers, polyether polyols would be miscible with polymers containing acidic hydrogen, such as PVC. Margaritis et al.\textsuperscript{213,214} found that the miscibility of polyethers with PVC increases with increasing CH\textsubscript{2}/O ratios for linear polyethers. However, PVC/PPO blends were found to be immiscible due to the hindrance of the ether oxygen by the bulky pendant methyl groups.

The aforementioned studies were based on the PVC/polyol blends produced by solution blending. Therefore, it is important to investigate the effect of the nature and structure of the polyols and the influence of melt blending conditions on the miscibility and final properties of the blends. Based on the previous studies, PVC/polyester blends are expected to be miscible with PVC under all compositions. Three blends will be studied: 75/25, 50/50, and 25/75 PVC/polyol.

Figures 4.9 – 4.12 show the time-torque curves for compounding of PVC with different polyols and BDO in internal mixer. The first two figures, Figures 4.9. and 4.11,
show the torque evolution curves for blending of PVC with polyester polyols, while Figures 4.12. for PVC with polyether polyol.

Figure 4.9. Time-Torque Curve for first stage of the PVC/TPU reactive blending PBA based for three different blend compositions.

Figure 4.10. Time-Torque Curve for first stage of the PVC/TPU reactive blending PHA based for three different blend compositions.
Figure 4.11. Time-Torque Curve for first stage of the PVC/TPU reactive blending PPA based for three different blend compositions.

Figure 4.12. Time-Torque Curve for first stage of the PVC/TPU reactive blending PPG based for three different blend compositions.
Figure 4.9. reveals that the torque does not increase appreciably for blending 25 wt% of PVC with PBA. In contrast, curves for 50/50 and 75/25 PVC/PBA blends show a noticeable increase in torque with respect to time upon the addition of PBA. The reason for the negligible increase in torque for the 25/75 PVC/PBA blend is that low viscosity PBA constitutes the continuous phase. In contrast, in the 50/50 and 75/25 PVC/PBA blends after adding PBA, the torque increased in proportion to the amount of PVC. For instance, adding PBA to the 50/50 PVC/PBA blend increased the torque for about 2 minutes, before subsequently reaching a steady value. On the other hand, PBA addition to the 75/25 PVC/PBA blend caused a sharp torque raise followed by stabilization to a smaller value. Another difference between the 50/50 and 75/25 PVC/PBA blends is that upon the addition of the PBA, the torque in the last blend reached a peak followed by a monotonically decreasing curve. This torque overshoot was not displayed in the blending of PVC and PBA with 50/50 PVC/PBA ratio.

The addition of the short chain diol, BDO, while blending PVC with polyols, caused a disruption of the time-torque curve. In the instance of the 50/50 PVC/PBA blend, the torque decreased abruptly, but rapidly recovered a steady value that was smaller than before the addition. On the other hand, in the 75/25 PVC/PBA blending, when BDO was added, there was an abrupt variation in torque, but the torque recovered immediately to the same value and slowly decreased to a lower value.

The time-torque curves revealed the plasticization effect of the PBA and the BDO. Both materials plasticize the PVC rupturing its grain structure and increasing the contact area for further interaction. The two polyesters showed similar behavior when mixed with PVC. However, the addition of PHA increased the torque more than PBA, and accelerated the stabilization to a constant torque.
The compounding process of PVC with PPA is depicted in Figure 4.9. In this instance, the 25/75 and 50/50 PVC/PPA blends showed behavior similar to that of the 25/75 PVC/PBA blend. In other words, there was no noticeable increase in torque with respect to time. Therefore, to have a better understanding of this behavior, three more blends with compositions of 40/60, 60/40 and 70/30 PVC/PPA were prepared. The time-temperature curves showed that blending PPA with low PVC content (40\%) did not increase the torque, which behaved similarly to the 25/75 and 50/50 PVC/PPA blends. Nevertheless, the torque increased when compounding PPA with 60 and 70 wt\% PVC. There was plasticizing effect of the PPA and BDO on PVC in the 60/40 and 70/30 PVC/PPA blends.

The time-torque curve corresponding to the blending process of PVC with the polyether, PPG, is shown in Figure 4.12. The difference between the mixing curve for PVC/PPG and those of the PVC/polyester is that the first one is not smooth. It display peaks originated in the non-uniformity of the blends, as confirmed by direct observation. Therefore, PVC was not plasticized because of the immiscibility of the PVC with the PPG because of the hindering effect of the pendant group on the ether oxygen. The blends obtained were not smooth and consisted of mostly unplasticized moistened PVC.

DSC was also used to study the miscibility of the blends. The DSC studies were carried out within two days after preparing the blends. Miscibility studies with DSC are based on the fact that miscible blends behave as a single and stable phase, showing one single glass transition temperature ($T_g$) that is dependent on composition. On the other hand, immiscible blends display two distinct $T_g$s revealing the coexistence of domains of the neat components of the blend.
Figures 4.13. through 4.28. show the DSC scans for PVC/polyol blends with BDO after blending for 15 minutes. Additionally, the DSC traces for PVC/polyol blends excluding the BDO are also shown for comparison with the blends without BDO.

The DSC scans for the PVC/PPA and PVC/PPA/BDO blends are shown in Figures 4.13., 4.14, 4.21 and 4.22. It is apparent that at compositions below 60/40 PVC/PPA the blends exhibit two \( T_g \)s corresponding to those of the PVC and PPA. Therefore, those blends are immiscible. On the other hand, PVC/PPA and PVC/PPA/BDO blends with a PVC concentration greater than 50 wt% exhibit a single broad glass transition. These blends are miscible. Therefore, the blends of PVC with PPA with and without PBA have a dual behavior that is correlated with the time-torque curves shown before. The immiscible blends appeared as non-uniform and powdery material, while miscible blends appeared uniform and smooth.

Figures 4.15. through 4.18. show the DSC scans for the blends of PVC with PBA and PVC with PHA, both without BDO. Figures 4.23. through 4.26 show the corresponding blends of PVC/PBA including BDO. The scans show that PVC is miscible with both BPA and PHA because the blends display one glass transition temperature in between those of the PVC and the corresponding polyester polyol. Nevertheless, for blends with 25 wt% of PVC for both PBA and PHA, the scan is not conclusive since the melting endothermic peak of the polyol appears in the temperature range of the occurrence of the glass transition of PVC.

The DSC scans of the PVC/PPG and PVC/PPG/BDO blends are shown in Figures 4.19.-4.20, and 4.27.-4.28. respectively. In all compositions, the blends exhibit two glass transition temperatures corresponding to those of the neat components, indicating that PVC is immiscible with PPG.
Figure 4.13. First DSC scan for the PVC/PPA reactive blends.

Figure 4.14. Second DSC scan for the PVC/PPA blends.
Figure 4.15. First DSC scan for the PVC/PBA blends.

Figure 4.16. Second DSC scan for the PVC/PBA blends.
Figure 4.17. First DSC scan for the PVC/PHA blends.

Figure 4.18. Second DSC scan for the PVC/PHA blends.
Figure 4.19. First DSC scan for the PVC/PPG blends.

Figure 4.20. Second DSC scan for the PVC/PPG blends.
Figure 4.21. First DSC scan for the PVC/PPA/BDO blends.

Figure 4.22. Second DSC scan for the PVC/PPA/BDO blends.
Figure 4.23. First DSC scan for the PVC/PBA/BDO blends.

Figure 4.24. Second DSC scan for the PVC/PBA/BDO blends.
Figure 4.25. First DSC scan for the PVC/PHA/BDO blends.

Figure 4.26. Second DSC scan for the PVC/PHA/BDO blends.
Figure 4.27. First DSC scan for the PVC/PPG/BDO blends.

Figure 4.28. Second DSC scan for the PVC/PPG/BDO blends.
The miscible blends of PVC with polyols display a single glass transition temperature that, as mentioned before, indicates miscibility and an extensive phase mixing of the components. Additionally, the scale of any phase separation and dispersion in these blends approaches the scale of cooperative segmental motion responsible for the glass transition. However, the broadness of the glass transition has been associated with miscible blends with a broad distribution of finely dispersed phases with varying compositions\(^{236}\). Consequently, the results of the DSC miscibility studies show that blends of PVC with polyester and BDO are miscible with heterogeneities at a very small scale as suggested by Parnell\(^6\).

The main difference between the PVC/Polyol blends with or without BDO is a narrower transition shifted little toward higher temperatures. This result reveals that BDO could have enhanced the miscibility of the PVC with the Polyol or that it plasticized the PVC more.

To study the influence of the PVC concentration of the \(T_g\) of the blends of PVC with polyester and BDO, \(T_g\) of the blends was plotted as a function of the PVC concentration as shown in Figures 4.29.-4.31. It is apparent that the \(T_g\) of the blends increases monotonically with an increasing PVC concentration for all the blends. Additionally, a negative deviation from the linear additivity (rule of ideal mixtures) was observed.

The Gordon-Taylor Equation could be fitted to the experimental \(T_g\) versus PVC concentration data. The fitted curves are displayed in Figure 4.32. by the dotted line. The Gordon-Taylor equation is given by:

\[
T_g = \frac{w_1 T_{g1} + w_2 T_{g2}}{w_1 + w_2}
\]

(4-1)
where $T_g$ and $T_{gi}$ are the glass transition temperatures of the blend and component $i$ respectively, and $w_i$ is the weight fraction of component $i$. The parameter $k$ is an adjustable parameter that expresses the degree of concavity of the curve. Parameter $k$ is usually less than 1, representing a positive free volume deviation. Nevertheless, for PVC/Polyester blends $k$ has been interpreted as a measure of the strength of the specific intermolecular interaction occurring between PVC and polyester. Higher values of $k$ have been correlated to stronger intermolecular interactions\textsuperscript{260}. Reported values of $k$ were given for completely miscible PVC/PCL blends by several researchers\textsuperscript{260,277}. Parameter $k$ was between 0.50 and 0.55\textsuperscript{260,277}.

In the equation of Gordon-Taylor, the $T_g$ of the BDO does not appear in the equation, since the BDO concentration is too small, the nature of its $T_g$ is unknown, and its influence on blends glass transition is negligible, as shown previously.

![Graph showing $T_g$ vs. PVC concentration for the PVC/PPA and PVC/PPA/BDO blends.](image)

Figure 4.29. $T_g$ vs. PVC concentration for the PVC/PPA and PVC/PPA/BDO blends.
Figure 4.30. Tg vs. PVC concentration for the PVC/PBA and PVC/PBA/BDO blends.

Figure 4.31. Tg vs. PVC concentration for the PVC/PHA and PVC/PHA/BDO blends.
The fitted Gordon-Taylor equation presented in Figure 4.32 provide k values of 0.42 for PVC/PPA and 0.45 for both the PVC/PHA and PVC/PBA blends. These values of k are smaller than the values reported in the literature for similar blends. The fact that the k constant is the same for PVC blends with PHA and PBA reveals that there is a negligible effect of the chain length between ester groups on the miscibility. On the other hand, the lower value of constant k for the PVC/PPA blend means that the interaction between PVC and PPA is less than for the PVC with the other two polyester polyol. This reduction is attributed to the hindrance effect of the pendant methyl group. Even more, blends with 50% or less PPA were immiscible. In conclusion, the introduction of a pendant group in the polyester decreased the miscibility with PVC, while adding two methylene groups to the chain in between ester groups caused no variation in miscibility of the polyester polyol with PVC.

Figure 4.32. Tg vs. PVC concentration for the PVC/Polyester blends fitted to the Gordon Taylor Equation.
The presence of microheterogeneities in the PVC/polyester blends is believed to be the reason for two results of the miscibility studies, namely, the broadness of the glass transition region and the lower values of constant k with respect to values reported in the literature. It is proposed that different phases coexist in the PVC/polyester blends. The origin of these phases is the semicrystalline nature of PVC. As mentioned in the literature survey, PVC is a semicrystalline polymer with 5 to 10% of microcrystals that act as physical crosslinks\textsuperscript{26,27} between amorphous domains. These microcrystals melt in a wide range of temperatures, from 120 to 210 °C\textsuperscript{1}. Consequently, the microcrystals that did not melt at 120 °C remained as hard domains reducing the molecular mobility of the components of the PVC/polyester blends. Additionally, the unmelted PVC domains restricted the mobility and ability of mixing of the amorphous regions of PVC with the Polyester and BDO.

Morphological studies were conducted by using scanning electron microscopy in order to observe the aforementioned heterogeneities. SEM micrographs are shown in Figures 4.33.-4.36. for the different PVC/Polyol/BDO blends. For the immiscible PVC/PPG/BDO and PVC/PPA/BDO blends at low PVC concentrations, the PVC grains appear surrounded by the polyol. Nevertheless as the PVC content decreases, the concentration of PVC decreases. In the blend with 25 wt% PVC the PVC grains have almost no contact with each other. All the micrographs shown here reflect the poor plasticization of PVC in immiscible blends because of the presence of PVC grains.

For the miscible blends, the results are somewhat different, as shown in Figures 4.34. and 4.35. The micrographs reveal the presence of a homogeneous continuous phase. The PVC grain structure is not observable at the magnification used. Therefore, it is presumed that PVC grains have been destroyed at all compositions to the level of
magnification achievable with SEM. This observation is expected for the blends with 75 and 50% PVC, because during mixing, the high torque indicated that the shearing was high enough to cause PVC particle breakage. On the other hand, the 25% PVC blend was not subjected to the same level of shearing since the viscosity was very low. As a consequence it was presumed that the primary grains of PVC were not significantly destroyed.

Figure 4.33. SEM Micrographs of the PVC/PPA blends. a) 70/30 b) 60/40 c) and d) 50/50 e) and f) 40/60
Figure 4.34. SEM Micrographs of the PVC/PBA blends. a) 75/25, b) 50/50 c) 25/75
Figure 4.35. SEM Micrographs of the PVC/PHA blends. a) 75/25, b) 50/50 c) 25/75
Figure 4.36. SEM Micrographs of the PVC/PPG blends. a) 75/25, b) 50/50 c) 25/75
To summarize the results of this section, it was found that the blends of PVC with PPG and PVC with PPG and BDO are immiscible because of the presence of the methyl pendant group on the PPG chain that hindered the ester groups. In contrast, it was found that the blends of PVC with Polyester (PPA, PBA and PHA) and PVC with Polyester and BDO are miscible at the proposed blending temperature of 120 °C. The only exception were the PVC/PPA blends with less than 60 wt% PVC which were immiscible. It was also discussed how the blending process was enough to break up the PVC particles to a scale smaller than the magnification scale of SEM. Nevertheless, PVC microstructure rupture was dependent on the composition of the blend and the apparent viscosity of the mixture.

4.1.1.2. Stage 2: In-Situ Polymerization of TPU with PVC

The in-situ polymerization of TPU takes place upon the addition of diisocyanate to the blend of PVC with polyol. The reactive blends of PVC with TPU are obtained from miscible and immiscible mixtures of PVC with polyol and PVC with polyol and BDO. The previous studies\(^6\) have shown that the optimal conditions for the reactive blending of a TPU from PBA, SMDI, and BDO were:

- Temperature: 120 °C
- Isocyanate index: 1.02
- T31 Concentration: 1% with respect to the PVC
- Rotor speed: 50 rpm
- Mixing time: 3 minutes (when torque reaches a steady value)

These conditions were used as the operating conditions for this study. Additionally, three different blend compositions (25/75, 50/50 and 75/25 PVC/TPU) were investigated.
During the in-situ polymerization of TPU, the reaction progressed simultaneously with the blending. The phenomenon that dominates this process is the reaction induced phase separation attributed to the immiscibility of the soft and hard segment structures of the TPU produced along the polymerization.

The results obtained from the study of the in-situ TPU polymerization are presented in two sections. The first one deals with the effect of changing the TPU soft segment in the final properties of the blend. The second presents the results of varying the diisocyanate on the properties of the final product.

4.1.1.1.3. Effect of the type of Polyol

The time-torque curves for the reactive blending process of PVC with TPU based on the four polyols and SMDI are shown in Figures 4.37 through 4.40. The Figures reveal that for almost all the reactive blends the torque rises upon the addition of the diisocyanate and stabilizes in about 3 minutes. At that point the reactive blending has ended, since the TPU has already been polymerized.

The curves of the different PVC/TPU reactive blends reveal that there is no significant difference in the time-torque curve once the SMDI is added. Even more, there is no difference between miscible and immiscible blends of PVC and polyols. Once the reactive blending ends, samples are collected and characterized within a week. The characterization methods determine their thermal and mechanical properties, as well as blend morphology and molecular weight.

The molecular weight of the PVC/TPU reactive blends was determined by GPC. It is important to notice, that the molecular weight measured corresponds to the PVC/TPU blend and not to the TPU only. This is because it was impossible to completely extract the TPU from its blend with PVC. Table 4.2. shows the molecular weights for
some of the blends determined from GPC. The number average molecular weight \( M_n \), the mass average molecular weight \( M_w \) and the polydispersity index are reported.

Figure 4.37. Time-Torque Curve for PVC/TPU reactive blending PPA based for three different blend compositions.

Figure 4.38. Time-Torque Curve for PVC/TPU reactive blending PBA based for three different blend compositions.
Figure 4.39. Time-Torque Curve for PVC/TPU reactive blending PHA based for three different blend compositions.

Figure 4.40. Time-Torque Curve for PVC/TPU reactive blending PPG based for three different blend compositions.
Table 4.2. shows that the PBA and PHA based reactive blends have higher molecular weights than those of the reactive blends based on PPA and PPG. Additionally, it is evident that the molecular weights of most of the blends lie between those of the neat polymer, i.e. PVC, and TPU.

Table 4.2. Molecular weights of the PVC/TPU reactive blends with different polyols and SMDI. *

<table>
<thead>
<tr>
<th>MDI</th>
<th>POLYOL</th>
<th>PVC/TPU</th>
<th>Mn</th>
<th>Mw</th>
<th>Pd</th>
</tr>
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<tr>
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<td>PPA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td>10,000</td>
<td>20,000</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>12,000</td>
<td>31,000</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100/0</td>
<td>30,000</td>
<td>63,000</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SMDI</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PBA</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>0/100</td>
<td>56,000</td>
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<td>150,000</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>38,000</td>
<td>83,000</td>
<td>2.2</td>
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<td>75/25</td>
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<td>PPG</td>
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<td>100/0</td>
<td>30,000</td>
<td>63,000</td>
<td>2.1</td>
<td></td>
</tr>
</tbody>
</table>

* Molecular weights based on Polystyrene Standards

The molecular weights can be related to the qualitative elastomeric behavior of the blends. For instance, the neat TPUs of PPG and PPA as well as their reactive blends with PVC do not exhibit elastomeric behavior. They appeared as waxes. Therefore, it is presumed that reactive blends based on PPG and PPA did not form high molecular weight TPU. As a consequence, these blends were not studied further because of a lack of elastomeric behavior.

One of the important structural characteristics of the reactive blends of PVC with TPU is the reaction induced phase separation resulting from the separation of the hard
and soft segments of the TPU. In order to characterize this phenomenon and its effect on the miscibility of blends of PVC with polyols DSC characterization is used.

Figures 4.41.-4.48. show the DSC scan traces of the different PVC/TPU reactive blends based on different polyols. For the sake of comparison, the DSC scan traces of neat PVC and neat TPU are also shown in the figures. Additionally, the first and second DSC scans are shown. The first scan corresponded to the untreated samples, while the second to the quenched sample from a temperature of 200 °C immediately before characterization.

Figure 4.41. First DSC scan for the PVC/TPU reactive blends – SMDI and PPA based.
Figure 4.42. Second DSC scan for the PVC/TPU reactive blends – SMDI and PPA based.

Figure 4.43. First DSC scan for the PVC/TPU reactive blends – SMDI and PBA based.
Figure 4.44. Second DSC scan for the PVC/TPU reactive blends – SMDI and PBA based.

Figure 4.45. First DSC scan for the PVC/TPU reactive blends – SMDI and PHA based.
Figure 4.46. Second DSC scan for the PVC/TPU reactive blends - SMDI and PHA based.

Figure 4.47. First DSC scan for the PVC/TPU reactive blends - SMDI and PPG based.
Figure 4.48. Second DSC scan for the PVC/TPU reactive blends – SMDI and PPG based.

The DSC for untreated and treated PVC/TPU blends based on PPA, PBA, and PHA are shown in Figures 4.41.-4.42., 4.43.-4.44. and 4.45.-4.46., respectively. These blends displayed a broad glass transition that correspond to partially miscible blends. In the case of PBA, this finding coincides with the behavior reported by other researchers, that showed how the miscibility of the PVC/polyol blend decreased along the TPU polymerization because of the immiscibility of the PVC with a TPU with increasing HS content. These results indicate that the polyether based reactive blends should be immiscible since the PVC/polyether blends were already immiscible. The confirmation of this assumption is shown in Figures 4.47. and 4.48. It is evident the presence in both scans of two Tgs, corresponding of those of the neat PVC and TPU.

The detailed analysis of the first scans show that all the blends exhibit small endothermic peaks at temperatures above 170 °C, decreasing in intensity as the PVC
content increases. The thermograms of neat TPU usually show multiple endothermic peaks associated with the HS ordering, regardless of the SS nature (polyester or polyether). The independence of the thermal transitions of the HS on the type of SS reveals that they are thermodynamically immiscible and then are phase separated. However, quantitative analysis of the intensity of HS/SS separation is difficult because of the small magnitude of the endothermic peaks, especially as the PVC concentration increases. Nevertheless, all the thermograms of the reactive blends show to some extent the endothermic peaks, being more evident in the PBA and PHA based blends. It is worth pointing out that on the second scan these peaks disappeared. This result is attributable to the effect of quenching from 200 °C because of hindering on the ordering of the molten HS.

The SS can apparently show ordering as well. The reactive blends based on PBA and PHA show SS crystalline melting endotherm at approximately 48 °C and 47 °C, respectively. Additionally, the PHA based reactive blend also displayed an exothermic peak around 0 °C. This peak indicates that the PHA segments are undergoing a cold crystallization process. The thermal transitions associated with the ordering of the SS disappeared after quenching for the PBA and were minimized for the instance of PHA based blends. The cold crystallization transition of PHA based blends was also invisible in the second DSC scan after quenching. These results are attributed to the rapid cooling process, which did not allow the reordering of the HS and, in the case of cold crystallization, eliminated the secondary nucleation required for this process to begin.

Comparing the first and second scans for PVC/TPU blends based on polyesters reveals that the glass transition region narrows in the second scan. Additionally, the
transitions shift to slightly higher temperatures. The scale of the phase separation decreases after quenching from 200 °C.

Figure 4.49. shows the $T_g$ as a function of the PVC concentration of the PVC/TPU miscible blends. It becomes apparent that the $T_g$ increases monotonically with increasing PVC concentration for all blends. The reactive blends based on PBA and PHA show similar glass transition dependence on composition. Conversely, PPA based blends show a different dependence on the PVC concentration than those of PHA and PBA based blends. Additionally, the glass transition temperatures of PPA based reactive blends are lower than the blends with PHA and PBA. The similarity between the $T_g$ of PHA and PBA based reactive blends indicate that the glass transition temperature of the PVC/TPU blends is not greatly affected by increasing the length of the chain between ester groups in the polyester polyol molecule. However $T_g$ is affected by the introduction of a pendant group in its backbone, as mentioned before.

The behavior of the PPA blend indicates that the PVC/TPU blends are miscible at all concentrations. The miscibility is attained even though the PVC/PPA blends were immiscible at PVC concentrations of 50 wt% or lower. However, upon the addition of the SMDI and TPU polymerization, the reactive blends exhibited partial miscibility at all the compositions studied. This can be attributed to the effect of a higher apparent viscosity that generates higher shearing, favoring the plasticization of PVC through the PVC microstructure destruction.

It is very difficult to detect the $T_g$ of the HS due to its low heat capacity. Nevertheless, the effect of the appearance of the HS in the glass transition behavior of the blend can be observed in Figures 4.50. through 4.52. These Figures show the dependence of the $T_g$ on the PVC concentration of the PVC/Polyol, PVC/Polyol/BDO, and
PVC/TPU blends. The curves corresponding to PVC/polyol blends show the plasticizing effect of the polyol, since at increasing content of polyol the blend's $T_g$ decreases. Similarly, if the BDO content increases, the $T_g$ of the PVC/Polyol/BDO blends decreases. These two trends indicate that the polyols and the BDO plasticized the PVC.

![Graph showing Tg vs. PVC concentration for different Polyols](image)

Figure 4.49. Tg vs. PVC concentration for the PVC/TPU Reactive Blends based on different Polyols.

In the case of PVC/TPU reactive blends, the addition of the diisocyanate to the plasticized PVC increases the $T_g$. This behavior is attributed to the HS formation. A comparison between the curves for PHA and PBA based reactive blends reveals that the increment in $T_g$ of the first blend was larger than that of the second blend. In the case of PPA, the analysis is not valid since PVC and polyol are immiscible at low PVC concentrations.
Figure 4.50. Tg vs. PVC concentration for the different blends PPA based.

Figure 4.51. Tg vs. PVC concentration for the different blends PBA based.
Figures 4.53.-4.54. show the FTIR spectra of the different PVC/TPU blends and neat polymers acquired at room temperature. The samples were dissolved in THF and then cast on KBr disks. No further thermal treatment was imposed on the samples. The bands assigned to the PVC and Thermoplastic Polyurethanes are listed in Table 4.3.

The intensity of the different band assignments vary with varying PVC and TPU composition, as shown in Figures 4.53. and 4.54. The intensity of the band assignment corresponding to the C-Cl vibration increases with an increasing PVC concentration. Similarly, the intensity of the known TPU band assignment corresponding to the C=O stretching vibrations of the TPU increases with an increasing TPU content. The interaction of the PVC with the TPU is studied through the changes in intensity in the carbonyl stretching region. Figures 4.55. and 4.56. show the carbonyl stretching
vibrations of the urethane and SS ester linkages of the TPU, respectively. At all blend compositions, two overlapping stretching vibrations at approximately 1700 and 1730 cm\(^{-1}\) were observed. The band at 1700 cm\(^{-1}\) is associated with hydrogen bonded carbonyls with adjacent N-H groups, while the band at 1730 cm\(^{-1}\) to the non bonded carbonyls, or in other words, carbonyls that are free of intermolecular interactions\(^{205,278}\).

Table 4.3. FTIR Band Assignments of PVC and TPU.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>TPU</td>
</tr>
<tr>
<td>3420</td>
<td>N-H non-bonded</td>
</tr>
<tr>
<td>3320</td>
<td>N-H bonded</td>
</tr>
<tr>
<td>2960</td>
<td>CH(_2)</td>
</tr>
<tr>
<td>1730</td>
<td>C=O non-bonded</td>
</tr>
<tr>
<td>1700</td>
<td>C=O Bonded</td>
</tr>
<tr>
<td>1610</td>
<td>C=C in benzene ring</td>
</tr>
<tr>
<td>1410</td>
<td>C-C in benzene ring</td>
</tr>
<tr>
<td>1180</td>
<td>C-O-C of ester</td>
</tr>
<tr>
<td>1080</td>
<td>C-O-C of ester in HS</td>
</tr>
<tr>
<td>695</td>
<td>C-Cl</td>
</tr>
<tr>
<td>636</td>
<td>C-Cl stretch</td>
</tr>
<tr>
<td>980</td>
<td>C-C</td>
</tr>
<tr>
<td>1500</td>
<td>C-H</td>
</tr>
</tbody>
</table>

The polyester based TPUs showed four major bands due to the presence of the carbonyl band in both the HS and SS. The first band occurs at 1700 cm\(^{-1}\) and as in the case of urethane, it represents the bonded carbonyl of the SS. The second band coincides with the bonded carbonyls present in the HS at 1730 cm\(^{-1}\). The other two bands are contributions to the band assignment corresponding to the non-bonded carbonyls in the SS and HS.
Figure 4.53. FTIR Spectra acquired at room temperature from the different PVC/TPU reactive blends PBA based.
Figure 4.54. FTIR Spectra acquired at room temperature from the different PVC/TPU reactive blends PHA based.
Figure 4.55. Carbonyl Stretching Region of FTIR Spectra acquired at room temperature from the different PVC/TPU reactive blends PBA based.
To find any specific interaction between PVC and the TPUs, the two bands at 1700 cm\(^{-1}\) and 1730 cm\(^{-1}\) are considered regardless of which segment is causing it.

Figures 4.55.-4.56. show that an increasing PVC concentration decreases the intensity of the 1700 cm\(^{-1}\) band with respect to the 1730 cm\(^{-1}\). This means that because of an increasing PVC presence in the blend, H-bonding decreases. Consequently the PVC is interrupting the intra H-bonding of the TPU because of preferred interaction between PVC and TPU. Additionally, this result shows that the phase mixing is occurring at the molecular level.
When comparing the effect of polyols on the interaction of PVC with TPU, it is observed that PBA based blends show gradual transition when PVC content rises from 25 to 50 wt%. For instance, the 25/75 and 50/50 PVC/TPU blends have an extremely similar degree of interaction, while 75/25 has a stronger interaction and less H-bonding. On the other hand, the PHA based blends show a sharp transition between H-bonded and less H-bonded behavior. The 25/75 blend has a higher degree of hydrogen bonding than the other two blends. However, the hydrogen bonding in the neat TPU is much more than those in the 25/75 PVC/TPU blend. Consequently, the PVC/TPU blends based on PHA show a higher degree of interaction between the PVC and the TPU than PVC/TPU blends based on PBA.

The morphology of the reactive blends was investigated with scanning electron microscopy. Figures 4.57. through 4.60. show the SEM micrographs of the blends obtained in the batch model studies.

The PPG based reactive blends of 75/25 PVC/TPU show that all of the PVC grain structure was completely destroyed, as compared to the PVC/PPG blend of the same PVC concentration. Therefore, a single phase is observed. The blend with 50/50 PVC/TPU content shows a reduced number of PVC grains, as compared to the 50/50 PVC/PPG blend. The micrograph of the 25/75 blend shows the presence of PVC grain in increased amount with respect to the 25/75 PVC/PPG blend. These results show that the mixing process was improved with respect to the PVC/PPG blending because of an increased viscosity upon the addition of the MDI, despite the result for the 25/75 PVC/TPU blend.
Figure 4.57. SEM Micrographs of the different PVC/TPU reactive blends PPA based.
a) 25/75 b) 50/50 c) 75/25
Figure 4.58. SEM Micrographs of the different PVC/TPU reactive blends PBA based.
a) 25/75 b) 50/50 c) 75/25
Figure 4.59. SEM Micrographs of the different PVC/TPU reactive blends PHA based. 
a) 25/75 b) 50/50 c) 75/25
Figure 4.60. SEM Micrographs of the different PVC/TPU reactive blends PPG based.  
a) 25/75  b) 50/50  c) 75/25

The polyesters based PVC/TPU reactive blends display homogeneous morphology regardless of the PVC concentration, as shown in Figures 4-57 through 4-59. These results reveal that the blends are homogeneous at the available level of
magnification of the SEM available. Of particular interest is the case of the former immiscible PVC/PPA blend. It is believed that high shear upon the addition of MDI on the second stage of the reactive blending process improved the melting of the PVC and eliminated any remnant PVC grain structure.

The SEM micrograph also reveals that when the PVC content is low, the samples had a ductile fracture revealing a smooth surface. This behavior is consistent with a rich TPU blend that fractured in a ductile manner because of the rubber-like behavior of this material. On the other hand, as the PVC content increases, the fracture surface tends to be rough. This is caused by the brittle nature of the PVC.

TEM experiments were performed on typical blends to reveal their structure of the blends at higher magnification than those attained with SEM.

TEM studies of PBA, SMDI, and BDO based TPUs reported in a previous study showed that the PVC/TPU blends exhibit two phase morphologies with domains of approximately 1 μm. The interface between the dispersed and continuous phase was diffuse, suggesting a significant phase mixing of the PVC and TPU. Additionally, the micrographs revealed a broad distribution of phase sizes originated by the in-situ polymerization of the TPU with the PVC. The TEM results from this study will be shown in the next section in which the different blends will be compared.

Thermogravimetric analysis (TGA) of the blends based on PBA and PHA was performed in order to determine how the thermal stability of the PVC was affected by the addition of the TPU. These results are presented in section 4.1.1.4.

Figures 4.61-4.62. show the TGA curves of the different reactive blends, as well as those of the neat polymers. The TGA curve for the neat TPU reveals that the stability of the neat TPU is high and that the degradation progress in one stage. In
contrast, PVC was less stable and had a two-stage degradation that started at a lower temperature (around 60 °C before the TPU) than TPU. The reactive blends showed the two-stage degradation process, and in general, with the exception of the 75/25 blend, they have more thermal stability than the neat PVC. A similar result has been obtained for the PHA/TPU blend.

Figure 4.63 shows the comparison of the temperature at 5 and 50% weight loss as a function of the PVC concentration for PBA and PHA based TPU. The temperature that corresponds to a 5% weight loss for a PBA based TPU is higher than the one for the PHA based TPU. However, this relation is inverse when the temperatures corresponding to 50% weight loss are compared, with the exception of the 75/25 PHA based TPU blend that does not follow the expected trend. These results indicate that the PBA based blends are more stable than those which are PHA based at a low degradation level. However, at high degradation (50%), the PHA based TPU decomposes faster than the PBA based TPU.

In Figure 4.63, the effect of PVC concentration on degradation behavior can be also derived. Increasing the PVC content in the PVC/TPU blends has a detrimental effect on the thermal stability of the blends. However, the effect is more dramatic at high degradation levels. This behavior may be attributed to the PVC degradation that follows an autocatalytic mechanism.

4.1.1.2.2. Effect of Isocyanate Structure

Four different diisocyanates were used to prepare PVC/TPU reactive blends based on PBA and PHA. The PBA based reactive blends were prepared with three types of MDI, while blends containing PHA based TPUs were polymerized with SMDI and LMDI. The properties and characterization results of the PVC/TPU blends based on PBA
and PHA with solid MDI were presented in the previous sections of this chapter. However, those results are used in this section to compare the effect of different types of MDI on blends properties.

Figure 4.61. Thermogravimetical Analysis for the PVC/TPU reactive blends - SPBA.

Figure 4.62. Thermogravimetical Analysis for the PVC/TPU reactive blends - SPHA.
Very few studies on TPU polymerization have used other forms of MDI, i.e. liquid MDI (LMDI) and CDMDI, besides SMDI. Even more, to the best of the author’s knowledge there is no information available on PVC/TPU blends based on LMDI or CDMDI. Consequently, the results obtained in this section are novel and were not compared to any published data to date.

Figures 4.64. through 4.67. show the time-torque curve for the reactive blending of PVC with TPU with three compositions. As explained previously, the reactive blending consisted of two stages. The PVC is compounded with the polyol and BDO, and then it is reactive blended with the MDI.

The time-torque curves reveal that there is a step rise of the mixing torque for almost all the PVC/TPU reactive blends. After approximately 3 minutes, the torque stabilizes and the reactive blending process is considered completed. The exception to
the time-torque behavior as described is the reactive blending of the 25/75 PVC/TPU reactive blend based on LMDI. Even for the 50/50 and 75/25 PVC/TPU reactive blends, the torque increases more slowly than that for all the other blends. This behavior can be attributed to the different reactivity of the two isomers present on the LMDI. One of them, the 2,4 MDI isomer reacts more slowly than the 4,4 MDI isomer; therefore, the total rate of reaction of LMDI may be smaller than for other MDIs. Additionally, the maximum torque that the LMDI based blends reach (~20 Nm) during reactive blending is smaller than the maximum torque attained by TPU polymerization with other MDIs (~25 Nm). This result implies that the reactive blending of PVC with TPU based on LMDI required less energy than the same blends based on other MDIs.

Figure 4.64. Time-Torque Curve for PVC/TPU reactive blending PBA and LMDI based for three different blend compositions.
Figure 4.65. Time-Torque Curve for PVC/TPU reactive blending PHA and LMDI based for three different blend compositions.

Figure 4.66. Time-Torque Curve for PVC/TPU reactive blending PBA and CDMDI based for three different blend compositions.
Once the blends are removed from the internal mixer, they are characterized within a week. Thermal and mechanical properties, as well as morphology and molecular weight were determined.

Gel permeation chromatography (GPC) was used to measure the average molecular weight of the PVC/TPU reactive blends. It is important to acknowledge that the molecular weight of the TPU in the blends is impossible to measure, because there is no way to extract them from the reactive blends. Table 4.4. shows the molecular weights and the polydispersity index of some of the blends. The molecular weights of the blends based on CDMDI and CDMDIB are not presented in Table 4.4. because they were insoluble in THF. The same behavior was displayed by the neat TPU s based on those MDIs.
Table 4.4  Molecular weights of the PVC/TPU reactive blends with different MDIs and Polyols.

<table>
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<th>Polyol</th>
<th>PVC/ TPU</th>
<th>Mn</th>
<th>Mw</th>
<th>Pd</th>
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<td>PBA</td>
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<td>108,000</td>
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</tr>
<tr>
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<td></td>
<td>50/50</td>
<td>38,000</td>
<td>83,000</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>38,000</td>
<td>83,000</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>30,000</td>
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* Molecular weights based on Polystyrene standards

The molecular weights of the blends lie between those of the neat components, PVC and TPU. However, the SMDI based blends have higher molecular weights than the LMDI based. This result as is expected due to the lower total reactivity of the LMDI. Nevertheless, if the molecular weights obtained with different polyols are compared, the blends based on SMDI with PBA showed higher molecular weight than the blends based on SMDI with PHA. This relation is reversed when the MDI is the LMDI. Therefore, there are differences in the way the polyols react with the various MDIs.

Miscibility studies of the reactive blends based on different MDIs were conducted using DSC, as shown in Figures 4.68. to 4.75. The first scan corresponded to untreated samples, while the second scan to quenched samples from a temperature of 200 °C immediately before characterization.
Figure 4.68. First DSC scan for the PVC/TPU reactive blends – LMDI and PBA based.

Figure 4.69. Second DSC scan for the PVC/TPU reactive blends – LMDI and PBA based.
Figure 4.70. First DSC scan for the PVC/TPU reactive blends - LMDI and PHA based.

Figure 4.71. Second DSC scan for the PVC/TPU reactive blends - LMDI and PHA based.
Figure 4.72. First DSC scan for the PVC/TPU reactive blends – CDMDI and PBA based.

Figure 4.73. Second DSC scan for the PVC/TPU reactive blends – CMDI and PBA based.
Figure 4.74. First DSC scan for the PVC/TPU reactive blends –CDMDIB and PBA based.

Figure 4.75. Second DSC scan for the PVC/TPU reactive blends –CMDIB and PBA based.
The DSC scans showed that all the blends have one single broad glass transition region between those of the neat PVC and TPU. This behavior was associated with a blend morphology characterized by a broad distribution of finely dispersed phases with varying compositions\textsuperscript{279}, demonstrating that the PVC and TPU are partially miscible. The first DSC scans exhibited small endothermic peaks at temperatures above 170 °C, as shown in Figures 4.68. and 4.70. The presence of these transitions was associated with the HS and SS phase separation and HS ordering\textsuperscript{197}. The blends based on LMDI did not show the endothermic peaks. This was credited to the low extent of HS ordering. In contrast, PVC/TPU blends based on SMDI and CDMDI show these endothermic peaks but at different temperatures. The endothermic peaks in the case of blends based on CDMDI occurred at lower temperatures than those of the peaks displayed on the instance of SMDI based blends. The reason may be a colligative effect because of the impurities present in the CDMDI based blends. Quantitative analysis cannot be completed due to the small magnitude of these peaks.

The endothermic peaks associated with the SS crystalline melting that were observed for all the PVC/TPU blends based on SMDI are evident only in the case of PVC/TPU blends based on PHA and LMDI. Additionally, this blend displays a cold crystallization transition near 0 °C. After quenching, the second scan revealed no peaks whatsoever. It is apparent from these results that different diisocyanates influenced the way in which the SS and HS arranged. In some instances, the type of MDI hindered the crystallization of the SS, in addition to the restricted mobility of the PVC molecules.

One thermal transition that is not present in neat TPUs based on any other MDI is evident in the TPU based on CDMDI. There is a melting peak around 10 °C that may be associated with the melting of the carbodiimide structure\textsuperscript{10}. This peak appeared in
both scans. In the case of TPU based on the CDMDIB, the peak is not present. The reason is the higher content of the carbodiimide structure on the CDMDI, as compared to the CDMDIB. Conversely, the PVC/TPU blends based on CDMDI did not show the peak. This could be attributed to two factors: the concentration of the carbodiimide was low and consequently not detectable, or the PVC interacted with the carbodiimide structure.

The comparison between DSC first scans and second scans revealed that narrower transitions occurring at higher temperatures are observed in second scans. As was mentioned in the case of PVC/TPU blends based on SMDI, this behavior is attributed to a smaller scale of phase separation, less HS ordering, and more phase mixing of the TPU and PVC.

Figures 4.76. and 4.77. show the $T_g$ as a function of PVC concentration for the PVC/TPU blends. The $T_g$ of all the blends increases monotonically with an increasing PVC concentration. The most remarkable result is the low dependence of $T_g$ on the type of MDI. At low PVC concentrations, the SMDI based blends have lower $T_g$ than blends based on LMDI or CDMDI. The difference is of 0.5 to 2 °C. According to previous results obtained by other researchers, lower $T_g$s are the result of better phase separation\textsuperscript{165,170} of the HS and SS. Consequently, SMDI based TPUs and the respective PVC/TPU reactive blends have a slightly higher degree of phase separation than the other blends. In conclusion, the type of MDI affected the ordering of the HS and SS even though the effect is minimal.

The characteristics of the HS and SS influence the way the polyols are chain extended upon the inclusion of the HS on the blend. For example, the blends based on PHA display lower $T_g$ that those based on PBA, because of the intensity of the interactions between the HS and SS and the mobility of the SS. In the case of PHA
based TPUs, the interactions between the SS and HS are lower than those in the PBA based TPUS. Owing to the increased length of the chain between ester groups in PHA that renders more mobile SS and less SS/HS interactions, thus lowering the T_g.

![Figure 4.76. T_g vs. PVC concentration the PVC/TPU Reactive Blends based PBA and different Polyols.](image1)

![Figure 4.77. T_g vs. PVC concentration the PVC/TPU Reactive Blends based PBA and different Polyols.](image2)
The FTIR spectra of the different PVC/TPU blends and neat polymers acquired at room temperature are shown in Figures 4.78. throughout 4.81. SMDI and LMDI based samples were dissolved in THF and solution cast on KBr disks without any further thermal treatment. The insoluble samples (CDMDI and CDMDIB based TPUs and their reactive blends) were compressed molded and characterized by the ATR technique. The FTIR stretching vibrations of interest for the PVC/TPU reactive blends were shown previously in the Table 4.3. Figures 4.78. to 4.81. show that an increasing PVC concentration increases the intensities of the C-Cl stretching vibrations. Additionally, increasing the TPU content makes the carbonyl stretching vibrations blend composition dependent.

Figures 4.82 through 4.85. show the effect of blend composition on the carbonyl stretching vibrations in the urethane and SS ester linkages of the TPU. The variations of intensity or shifting of these peaks can be related to the interaction between the PVC and the TPU. As was mentioned before for SMDI based reactive blends, the carbonyl vibration is composed of two bands, one at the 1700 cm\(^{-1}\) representing hydrogen bonded carbonyls and the other at 1730 cm\(^{-1}\) representing the non bonded carbonyls. Any variation on the peaks will mean an effect of the PVC in the hydrogen bonding of the TPU.

Figure 4.82. reveals that the LMDI based reactive blends with both PHA and PBA polyols behave as the respective SMDI based blends presented in the previous section. The intensity of 1700 cm\(^{-1}\) band decreases more than the 1730 cm\(^{-1}\) band with increasing PVC concentration. This is due to the effect of the PVC on the H-bonding of the TPU. Consequently, the PVC interferes with the intra H-bonding of the TPU showing that there is interaction between these two polymers.
Figure 4.78. FTIR Spectra acquired at room temperature from the different PVC/TPU reactive blends LMDI and PBA based.
Figure 4.79. FTIR Spectra acquired at room temperature from the different PVC/TPU reactive blends LMDI and PHA based.
Figure 4.80. FTIR Spectra acquired at room temperature from the different PVC/TPU reactive blends CDMDI and PBA based.
Figure 4.81. FTIR Spectra acquired at room temperature from the different PVC/TPU reactive blends CDMDIB and PBA based.
Figure 4.82. Carbonyl Stretching Region of FTIR Spectra acquired at room temperature from the different PVC/TPU reactive blends LMDI and PBA based.
Figure 4.83. Carbonyl Stretching Region of FTIR Spectra acquired at room temperature from the different PVC/TPU reactive blends LMDI and PHA based.
Figure 4.84. Carbonyl Stretching Region of FTIR Spectra acquired at room temperature from the different PVC/TPU reactive blends CDMDI and PBA based.
Figure 4.85. Carbonyl Stretching Region of FTIR Spectra acquired at room temperature from the different PVC/TPU reactive blends CDMDIB and PBA based.
Figure 4.86. Carbonyl Stretching Region of FTIR Spectra acquired at room temperature from the different PVC/TPU reactive blends CDMDIB and PBA based.

Comparing the FTIR stretching region of LMDI and SMDI based blends reveals that when TPU is based on PHA and SMDI, the transition from highly bonded to non-bonded hydrogen is more significant as PVC content increases. However, for PHA and LMDI based blends this transition is more gradual. If the polyester is PBA, the transition from highly bonded to non-bonded hydrogen is gradual for both LMDI and SMDI based blends, though, the peak is broader in the SMDI based blends.

The FTIR results for CDMDI based blends showed that the neat TPU had a narrower transition than any other TPU or their reactive blends. This revealed that there was less degree of hydrogen bonding in CDMDI based TPUs than in any other TPUs.
studied. The reactive blends based on CDMDI showed similar behavior to the SMDI and LMDI based reactive blends with, however, a much smaller variation of intensities. In the case of the CDMDIB based blends, the FTIR revealed that there was the same degree of phase separation at all compositions, and that inclusion of the PVC in the blends affected the level of hydrogen bonding in the TPU.

The various MDIs are compared in Figure 4.86. For the neat PVC/TPU 25/75 blend composition, it was observed that the SMDI based blends has the highest intensity compared to the other MDIs in the carbonyl stretching region. This was consistent with the higher degree of hydrogen bonding in these blends as compared to the blends based on other MDIs. Reactive blends based on other MDIs have either, crosslinking (CDMDI based) or stereochemical hindrance (LMDI). Figure 4.86. also reveals that the blends based on LMDI and CDMDI have a similar stretching band width, but narrower than for the SMDI and CDMDIB based blends.

Figures 4.87.-4.90. show the SEM micrographs of the different blends. Homogeneous blend morphology is observed regardless of the magnification of the measurement. Therefore, it was concluded that the SEM microscope was not capable of detecting the two phase morphology that is expected from the results obtained with other analytical techniques, i.e. DSC, DMA. The various MDI did not generate significant difference on the surface fracture of the samples.

Samples with low PVC content exhibited a smooth fracture surface, which is consistent with a rich TPU blend that has a ductile fracture. On the other hand, as PVC content increases, the fracture surfaces become rougher. This behavior showed how the brittle nature of the PVC influenced the fracture surface.
Figure 4.87. SEM Micrographs of the different PVC/TPU reactive blends PBA-LMDI based. a) 25/75 b) 50/50 c) 75/25
Figure 4.88. SEM Micrographs of the different PVC/TPU reactive blends PHA-LMDI based. a) 25/75 b) 50/50 c) 75/25
Figure 4.89. SEM Micrographs of the different PVC/TPU reactive blends PBA-CDMDI based. a) 25/75 b) 50/50 c) 75/25
Figure 4.90. SEM Micrographs of the different PVC/TPU reactive blends PBA-CDMDIB based. a) 25/75 b) 50/50 c) 75/25
The morphology of the reactive blends prepared in the internal mixer were investigated by using transmission electron microscopy (TEM). Figures 4.91.-4.93. show the TEM photographs of typical PVC/TPU reactive blends. Figure 4.91. show the TEM micrographs of the LPBA based blends with different compositions. For 25/75 PVC/TPU (sPBA) blend, the island domain dispersed in the TPU matrix are observed. The dark domains might represent PVC rich phases with the TPU SS separated from the HS rich domains which are of lighter color. The micrograph for the PVC/TPU(sPBA) 50/50 blend demonstrated the occurrence of phase inversion at 50/50 composition and the HS rich TPU domain dispersed in the PVC rich matrix. The boundary was very clear in comparison to that observed in Figure 4.91.a. The PVC-SS rich phases are the matrix and the white HS rich domains the dispersed phase. The HS rich domains have a broad distribution of sizes and the shape of the dispersed domains appear to be oval with the average size is of about 0.8 microns. In the TEM micrograph in Figure 4.91.c. of the 75/25 blend, there is a continuous phase with very small domains of acicular shape. In this TEM micrograph the presence of white colored domains which identified the phase of TPU HS rich phase is not visible, as it is in the other TEM micrographs. Therefore, it was believed that the distribution of HS rich domains is small and they are well dispersed in the PVC-SS matrix. In this micrograph, the dark domains of acicular shape may contain PVC primary particles in larger amount than that in the rest of the sample, as discussed in the previous literature.

Figures 4.92. and 4.93. show the TEM micrographs of the reactive blends with the 50/50 blend composition with the different polyols and MDIs. The TEM micrographs of Figure 4.92. show TPUs based on SMDI with different polyols. In the two micrographs it can be observed that they have a similar morphology with the islands of
PVC rich domains with SS of TPU dispersed in HS TPU rich domains with PVC matrix. It is important to point out that the boundaries are more diffuse in the PHA based blend. This means that there was better mixing between phases. In conclusion, it is possible to affirm that the change in polyol did not influence the sea-island domain morphology, and it could be correlated to the similar miscibility of both polyols in PVC.

Figure 4.93. show the micrographs of the blends of PVC and TPU (PBA and CDMDIs based). Both micrographs show the two phase morphology of PVC rich domain with blur boundary dispersed in the STPU rich matrix. However, the CDMDI based blend shows more distribution of a dispersed phase with more diffuse boundaries compared to the CDMDIB based one..

The micrographs for CDMDIS, SMDI and LMDI based blends reveal the occurrence of the phase inversion at 50/50 composition. However, it seems that the use of different types of MDIs delays the occurrence of phase inversion. The blends based on CDMDIs show elongated domains, while those in the LMDI are round, the SMDI ones are irregular. In the SMDI based blend, it is not easy to identify which is the continuous phase, while in the LMDI based blend it is clear that the continuous phase is composed of HS rich material. The observation of these micrographs lead to the conclusion that the use of different MDIs leads to different types of morphologies, generated from the different reactivities and functionalities of the MDIs.

It is interesting to note that the thermal properties of these blends, as shown before, exhibit similar glass transition temperatures and broad range of $T_g$. However, the different morphology of these blends corresponds to the mechanical properties shown in section 4.1.1.3. From the $T_g$ experiments in the characterization section, it is evident that the addition of PVC to the TPU drastically reduced the SS interactions. This
may create difficulty in identifying the change of $T_g$ due to different morphologies observed in this section.

Figure 4.91. TEM Micrographs of the different PVC/TPU reactive blends PBA-LMDI based. a) 25/75 b) 50/50 c) 75/25
Figure 4.92. TEM Micrographs of the different PVC/TPU reactive blends with 50/50 Composition based SMDI and different Polyols a)PBA b)PHA
Figure 4.93. TEM Micrographs of the different PVC/TPU reactive blends with 50/50 Composition based PBA and different MDIs a) CDMDI b)CDMDIB

The mechanical behavior of the PVC/TPU reactive blends based on CDMDI and CDMDIB were characterized by rheometry and dynamical mechanical analysis (DMA).

Figures 4.94. to 4.98 show the frequency sweep curves of the reactive blends based on CDMDIB. The strain was varied from 0.01% to 10% for each sample. Figures 4.94 to 4.96 reveal three important points. There is no significant difference on the modulae at different strains. The modulae and viscosity of all the blends follow the same trend namely, complex viscosity decreases with an increasing frequency while $G'$ and $G''$ slowly increase with an increasing frequency. Finally, elastic modulus is always
larger than the dissipation modulus for all the blends at all compositions. This latter behavior means that elasticity is predominant in the viscous part.

Figure 4.94. Rheological Characterization for the PVC/TPU reactive blend 75/25 based on CDMDIB and PBA.

Figure 4.95. Rheological Characterization for the PVC/TPU reactive blend 50/50 based on CDMDIB and PBA.
Figure 4.96. Rheological Characterization for the PVC/TPU reactive blend 25/75 based on CDMDIB and PBA.

Figure 4.97. Rheological Characterization for the PVC/TPU reactive blends at three different blend compositions - CDMDIB and PBA based.
The results mentioned above mean that the blends behave linearly in the range of frequencies tested (0.01 to 100 rad/s). Additionally, the similitude of rheological behavior implies that the PVC did not influence the behavior of the reactive blends. Nevertheless, Figure 4.97 indicates that increasing the PVC concentration increases the storage and loss modulus, as well as the complex viscosity. This result could be attributed to the rigidity of PVC as compared to neat TPU. It is worth pointing out that at a given frequency the variation of the loss modulus with blend composition is less evident than the difference of storage modulus. Therefore, the blends have similar viscous behavior but dissimilar elastic behavior, originating in the effects of PVC and crosslinks.

The effect of the temperature on the modulae and viscosity is depicted in Figure 4.98. It is apparent that the complex viscosity and the modulae increase with increasing temperature. Therefore, crosslinks of a physical and chemical nature are possible. In conclusion, the material is more processable at low temperatures.

Figures 4.99 to 4.104 show the results obtained from the dynamic mechanical analysis (DMA) of the reactive blends based on CDMDIs. Figures 4.99 and 4.100 show the tan δ transitions of the blends. The DMA curves show only one peak for each blend with a maximum that shifts to higher temperatures with higher PVC concentrations. The presence of one peak reveals that the PVC and the TPU based on CDMDIs is miscible, corroborating the results of DSC scans. Additionally, the peaks are broad, revealing that the blends have a wide distribution of phases, sizes and concentrations. DMA scans show narrower transitions for the blends based on CDMDIB in contrast to the wide transitions of blends based on CDMDI. Additionally, the peaks are shifted to higher temperatures. These differences were not observed in the DSC scans.
Figure 4.98. Rheological Characterization for the PVC/TPU reactive blend 50/50 at two temperatures - CDMDIB and PBA based.

Figures 4.101. through 4.104. show the loss and storage modulus of the blends. It is apparent that the modulus changes accordingly with PVC concentration. The modulae increases with increasing PVC concentration. Additionally the total variation of modulae from 25 °C to 175 °C decreases with increasing PVC content.

The concentration of PVC in the blends determines whether or not a rubbery plateau. exists For the blend with 25 wt% of PVC, the G’ shows a rubbery plateau region after the T_g transition, while, blends with 75 wt% PVC show no plateau, but instead a decreasing G’ with respect to temperature. The blends with intermediate PVC concentration behave in a range between the 25/75 and 75/25 PVC/TPU blends.
Figure 4.99. Tan δ for the PVC/TPU reactive blends –CDMDIB and PBA based.

Figure 4.100. Tan δ for the PVC/TPU reactive blends –CDMDI and PBA based.
Figure 4.101. $G''$ for the PVC/TPU reactive blends –CDMDIB and PBA based.

Figure 4.102. $G''$ for the PVC/TPU reactive blends –CDMDI and PBA based.
Figure 4.103. $G'$ for the PVC/TPU reactive blends –CDMDIB and PBA based.

Figure 4.104. $G'$ for the PVC/TPU reactive blends –CDMDI and PBA based.
The blends with high and intermediate PVC content show a sharp increase in modulae after 120 °C. This behavior may be attributed to a possible disruption of the HS ordering.

To make a final remark, the blends based on CDMDI showed larger differences in both $G'$ and $G''$ along the whole range of temperature than the respective CDMDIB based blends. Possibly because the blends based on CDMDIB have a lower degree of crosslinking than those based on CDMDI. This is consistent with the larger functionality of the CDMDI.

### 4.1.1.2. Mechanical Properties of the Reactive Blends

The mechanical properties of polymers are important in giving an understanding of how structural features determined their behavior. Additionally, the mechanical properties permit us to compare materials of a similar nature to elucidate or prove structural characteristics. Figures 4.105 through 4.110. show the stress-strain behavior of the different reactive blends obtained in this study, including the neat polymers.

The curves for the neat polymers reveal that PVC with a $T_g$ well above room temperature shows yielding behavior and failure at small strains. In contrast, the neat TPU with a $T_g$ well below room temperature shows elastomeric behavior and it fails only at large elongations and strains. The behavior of TPUs may originate in its structure, the HS acting as physical crosslinks to the deformable SS matrix. TPUs did not showed neither yielding nor necking.

The reactive blends, with the exception of the 25/75 PVC/TPU LMDI based, showed the stress-strain behavior between those of the neat PVC and TPU. It was observed that the blends with a 75 wt% of PVC have a similar behavior to the PVC, in terms of yielding behavior and stress hardening. However, these blends showed less
yield stress, less stress at failure, and a higher elongation at break than neat PVC because of the presence of the TPU on the PVC matrix.

Figure 4.105. Stress-Strain behavior for the PVC/TPU reactive blends - SMDI and PBA based.

Figure 4.106. Stress-Strain behavior for the PVC/TPU reactive blends - SMDI and PHA based.
Figure 4.107. Stress-Strain behavior for the PVC/TPU reactive blends - LMDI and PBA based.

Figure 4.108. Stress-Strain behavior for the PVC/TPU reactive blends - LMDI and PHA based.
Figure 4.109. Stress-Strain behavior for the PVC/TPU reactive blends –CDMDI and PBA based.

Figure 4.110. Stress-Strain behavior for the PVC/TPU reactive blends –CMDIB and PBA based.
The 50/50 and 25/75 PVC/TPU blends show elastomeric behavior similar to the neat TPU. They exhibited a monotonic increase of the stress prior to failure, without exhibiting any yielding or necking behavior. Nevertheless the elongation at break and tensile strength are lower than those of the neat TPU for two reasons. The presence of PVC that with the high $T_g$ restricts the molecular mobility of the TPU molecules and HS with weaker intermolecular interactions implies that the physical crosslinks are weaker than those in the neat TPU.

Comparing the reactive blends based on LMDI, SMDI, and CDMDI it is apparent that the blends based on LMDI showed lower tensile strength than the blends based on SMDI. But the blends based on CDMDIs showed higher tensile strength than the other two with lower elongation at break. Table 4.5. summarizes the mechanical properties of the blends and Figures 4.111. through 4.116. show each of the varying mechanical properties for different blends.

From Table 4.5. it is clear that the properties of the blends based on SMDI and PBA and PHA are between those of the neat TPU and PVC. Nevertheless, the PVC/TPU 25/75 blends based on PBA and PHA exhibited higher tensile strength and elongation at break than the neat TPU. This result showed that the reactive blending of PVC and TPU at this composition had a synergistic effect on the mechanical properties.

The reactive blends based on LMDI showed lower tensile strength than blends based on SMDI. However, the blend based on LMDI and PHA showed a higher elongation at break than for SMDI based blends. The different behavior of the LMDI based blends as compared to the SMDI based blends may be due to the higher reactivity of 4,4’-MDI isomer in contrast to the 2,4’-MDI isomer. Therefore, the total reactivity of the LMDI is not only smaller than the reactivity of the SMDI but different.
The faster reactivity of the 4,4'-MDI isomer in the LMDI produces an ordering of the HS because of the reaction with the chain extender and polyester polyol. Nevertheless, the 2,4'-MDI isomer also reacts with the polyester and BDO and contributes to the HS ordering; however, it reacts more slowly. Therefore, when the reaction becomes diffusion controlled, the 4,4'-MDI isomer would have formed long chains of significantly restricted mobility, rather than the chains formed by the 2,4'-MDI isomer, if any. Then, it would be easier for the more mobile chains and for the 2,4'-MDI isomer to react with the polyols. In this way, the 2,4'-MDI isomer is either, introduced in the SS, decreasing the concentration of HS or reacts to form another HS with decreased hydrogen bonding because of steric hindrance. These HS domains, however, are isolated from other HS regions formed at much earlier stages in the reaction because of reduced mobility due to diffusional restrictions. Additionally, the introduction at the early stages of the reaction of 2,4-MDI isomer molecules in the hard segment limits its ordering because of stereochemical hindrance. The consequence of the reaction scheme of the LMDI isomers is less physical crosslinks than SMDI based blends and lower strength.

It is also noteworthy to relate the mechanical behavior of the blend with 75 wt% of TPU based on LMDI with the time-torque curve of the corresponding reactive blending (Figures 4.64 and 4.65). This blend with both polyols shows lower tensile strength than the neat TPU. The reason may be in the behavior of the mixing curve. In the second step of the reactive blend, these blends took about 15 minutes to achieve a complete reaction. The longer time of reaction reflects the lower reactivity of the LMDI when compared to the SMDI. The effects of the reduced reactivity of the 2,4'-MDI isomer was mentioned in the last paragraph and it is responsible for the reduced tensile strength and longer in-situ polymerization times.
Table 4.5. Mechanical Properties of the different PVC/TPU reactive blends.

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Figure 4.111. Tensile Strength vs. PVC concentration for the PVC/TPU reactive blends - PHA based with different MDIs.

Figure 4.112. Elongation at break vs. PVC concentration for the PVC/TPU reactive blends - PHA based with different MDIs.
Figure 4.113. Tensile Strength vs. PVC concentration for the PVC/TPU reactive blends – PBA based with different MDIs.

Figure 4.114. Elongation at break vs. PVC concentration for the PVC/TPU reactive blends – PBA based with different MDIs.
Figure 4.115. Tensile Strength vs. PVC concentration for the PVC/TPU reactive blends - PHA and PBA based with different MDIs.

Figure 4.116. Elongation at break vs. PVC concentration for the PVC/TPU reactive blends - PHA and PBA based with different MDIs.
The neat TPU based on LMDI exhibited yielding that consists of an increase in elongation without an increase of the tensile strength. This behavior was not presented by the other neat TPUs and it could be explained as the effect of the lower reactivity of the 2,4’-MDI isomer that is making part of the long SS, or of a short HS embedded in a SS reach region. When the samples are stretched, the ordered HS (formed at early stages of the polymerization) act as physical crosslinks. At certain force and elongation HS domains cannot sustain the stress longer, and then they disarray and start moving as a part of the SS. The reactive blends based on the LMDI do not show this yielding behavior. This different performance shows the influence of the PVC on the TPU structure. PVC hinders TPU ordering.

With the exception of CDMDI at 25 wt% PVC concentration, the CDMDI and CDMDIB based blends show a higher elongation at break than the respective SMDI and LMDI based blends. As was to be suspected from the insolubility of the blends in THF, some crosslinking occurred during the reactive blending process, because the uretoneimine reaction is reversible at high temperatures as has been shown in the technical literature$^{85}$, however the results are showing that at some point along the reaction TPU polymerization, the carbodiimide modified MDI reacts with the polyols before reversing its production reaction and going back to the original structure. Consequently crosslinks in the TPU structure that impart the mechanical properties exist.

The CDMDI has a much higher tensile strength than the CDMDIB, as shown in Figure 4.113. and 4.114. This is consistent with the higher functionality of the CDMDI. Nevertheless, as the PVC content increases, the difference between the tensile strength of the two CDMDIs based blends decreases, reaching a similar tensile strength when the
PVC concentration is 75%. The elongation at break of both CDMDIs is lower than that of the SMDI and LMDI with the exception of the blends with 75% of PVC. In this last case the presence of the PVC on the CDMDIs could not affect the formation of chemical crosslinks. However, it decreased the interaction of the physical crosslinks of the SMDI and LMDI, as was shown from the FTIR results.

Finally, if the different polyols are compared (Figure 4.115-4.116.) a dual behavior can be observed. In the case of SMDI based blends, the properties of PBA based blends are better than those of blends based on PHA. They display higher tensile strength and elongation at break at all the concentrations of PVC. However the difference decreases with an increasing PVC content increase. For the example LMDI, it can be observed that the PHA based blends show better behavior than those based on PBA. Once again, the difference decreases with increasing PVC content. From these results the different behavior of the blends based on SMDI and LMDI may be attributed to the TPU itself and the way the polymerization takes place. Additionally, the molecular weight greatly influences the final properties. The SMDI blends based on PBA have a higher molecular weight that reflects the creation of better interconnection of TPU segments. The same reasoning applies to the PHA and LMDI based blends that displayed higher molecular weights than PBA based blends with LMDI. In conclusion, the TPU polymerization process and the final molecular weight of the samples play a determining role in the final mechanical properties of the blends.

Figures 4.117. and 4.118. show the mechanical properties of the PVC/TPU blends based on PPG and PPA. The samples not shown were impossible to form into tensile bars. They did not exhibit any elastomeric behavior whatsoever. The reactive blends that were characterized exhibited very low mechanical properties, which are not
comparable to the properties of other reactive blends. These and the molecular weight results indicated that in these blends the TPU polymerization did not generate a TPU polymer.

Figure 4.117. Stress-Strain behavior for the PVC/TPU reactive blends - SMDI and PPA based.

Figure 4.118. Stress-Strain behavior for the PVC/TPU reactive blends - SMDI and PPG based.

4.1.1.3. Comparison with Analogous Melt Blends

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The main objective of this research is to produce a PVC/TPU reactive blend that could overcome the problems associated with melt and solution blending techniques producing blends with similar or improved properties. For this reason, melt blends were produced in order to serve as a reference for comparison with the reactive blends. The melt blending process was carried out in an internal mixer at 180 °C, 50 rpm, and 3 minutes of blending. The PVC and the polymerized TPU were added simultaneously. The TPUs were produced from SMDI, PBA, and PHA.

Figures 4.119.-.4.122. show the DSC scan traces for the melt blends. In the aforementioned figures, the DSC scan traces of neat PVC and TPU are also shown. Similarly to the reactive blends, the first run was done on the untreated samples, while the second run was done after quenching the samples from 200 °C to -100 °C rapidly. The blends were characterized within two days of production.

![Figure 4.119. First DSC scan for the PVC/TPU melt blends - SMDI and PBA based.](image-url)
Figure 4.120. Second DSC scan for the PVC/TPU melt blends – SMDI and PBA based.

Figure 4.121. First DSC scan for the PVC/TPU melt blends – SMDI and PHA based.
The DSC scans show one single broad glass transition temperature between those of the neat PVC and TPU. Therefore, the PVC and TPU are partial miscible, as in the case of reactive blends. As was mentioned in Section 4.1.1.2.1., the TPUs based on PBA show a major SS crystalline melting endotherm at approximately 48 °C that disappears in the second scan. Additionally, the TPU based on PHA has a crystalline melting endotherm at approximately 47 °C and an exothermic peak at around 0 °C. These thermal transitions are also present in the melt blends. However, the reactive blends based on PHA did not show the crystalline peak due to the restricted mobility of the SS imposed by the PVC. The appearance of the crystalline peak in the melt blend based on PHA may indicate a less hindering effect of the PVC on SS mobility, in other words, less PVC-TPU interaction.
The second DSC scans show narrower glass transition regions than the first scans for all blends. Additionally, the transitions shifted to slightly higher temperatures. Therefore, there is more phase mixing of the TPU and PVC, after quenching.

Figures 4.123. and 4.124. show the T_g as a function of PVC concentration for the PVC/TPU melt and reactive blends. It is evident that the T_g increased monotonically with an increasing PVC concentration. However, the melt blends have higher glass transition temperatures than the reactive blends by 5 °C, approximately. This behavior indicates that the interaction between the PVC and the TPU in the melt blends is lower than in the reactive ones. These results may be explained by the reduced mobility of the TPU macromolecules, that are not able to destroy the PVC grain structure to the same extent as in the reactive blending.

Figure 4.125. shows the thermogravimetric analysis of the melt blends and the neat polymers. The melt blends have a two-stage degradation process, similarly to the reactive blends. With the exception of the 75/25 PVC/TPU blend, melt blends have better thermal stability than the neat PVC. It is noteworthy that as temperature increases the weight loss rate is lower than the loss rate of the neat PVC. Then, there is a point at around 50% where the blend has lost less material than PVC.

At the end of the thermal degradation process, the 75/25 melt blend has a higher amount of residue than the neat PVC, showing a good flame resistance that is better than that found for the other reactive blends and neat polymers. Comparing the melt blends with the reactive ones, shown in Figure 4.61., indicates that the melt blend has a higher residue than the reactive one. However, the reactive blends left the same amount of residue as the PVC did, but it does not approach the residue left by the melt blend.
Figure 4.123. $T_g$ vs. PVC concentration for the PVC/TPU Reactive and Melt Blends – PBA and SMDI based TPUs.

Figure 4.124. $T_g$ vs. PVC concentration for the PVC/TPU Reactive and Melt Blends – PHA and SMDI based TPUs.
The other two blends have a behavior between the two neat components and their residue. The flammability, then, lies between that of the neat polymers. In conclusion, the thermal stability of the PVC is improved by the inclusion of the TPU but the flammability is reduced.

Figure 4.126. shows the PVC content-temperature curve that corresponds to weight losses of 5 and 50% for the reactive and melt blends. The reactive blends show more stability than the melt blends, with the exception of the 25/75 blend whose decomposition temperature at 5% weight loss is lower than that corresponding to the melt blend. However, at a 50% weight loss the relation is the opposite. The temperature difference at which the blends lose the 5 or 50% of the weight varies between 3 °C to 10 °C, and it is evidence of the advantage of the reactive blending process with respect to the melt blending. The latter have reduced thermal stability. It is important to mention that the melt blends were produced under controlled conditions.
to avoid the thermal degradation of the PVC during the compounding. Thermal
degradation was observed if the melt blend was left 1 or 2 minutes more in the internal
mixer, or if the mixing temperature increased by 5 °C from the set point.

The thermal behavior of the reactive and melt blends differed. Nevertheless, to
confirm that reactive blends have superior performance in technical applications the
mechanical properties were investigated. The stress-strain curves of the melt blends are
shown in Figures 4.127. and 4.128. The data was obtained at room temperature for all
the melt blends, as well for the neat polymers, shown for comparison purposes.

As was mentioned in Section 4.1.1.3., Neat PVC with a T_g well above the room
temperature shows a yielding behavior and failure at smalls strain. While the neat TPU,
with a T_g well below room temperature shows elastomeric behavior and fails at large
elongations and strains. Figures 4.127. and 4.128. show that the stress-strain behavior
of the melt blends lie between those of the neat PVC and TPU. The blends with 75/25
PVC/TPU composition have a similar behavior to the neat PVC, while yielding some
extent of necking, specially in the PBA based blend. The melt blends, however, have
less elastic modulus, yield stress, stress at failure, and a higher elongation at break than
neat PVC. This behavior was originated in the presence of the TPU in the PVC matrix.
The 50/50 and 25/75 PVC/TPU blends show elastomeric behavior similar to the neat
TPU. They exhibit a monotonic stress increase prior to failure without exhibiting yield or
necking. Nevertheless, the elongation at break and tensile strength are lower than
those of the TPU. This behavior is caused by the inclusion of PVC in the blend. The
rigid PVC with high T_g reduces the molecular mobility of the TPU and the hydrogen
bonding strength, giving weaker physical crosslinks.
Figure 4.126. Thermogravimetrical Analysis for the PVC/TPU reactive blends - SPHA.

Figure 4.127. Stress-Strain behavior for the PVC/TPU melt blends - SMDI and PBA based.
Table 4.6. summarizes the mechanical properties obtained from the blends. In Figures 4.129. and 4.130. the mechanical properties are presented for each blend as a function of the PVC concentration. From these figures, it is apparent that the reactive blends have better properties than the melt blends. Reactive blends display higher elongation at break and tensile strength than the melt blends. The low performance of the melt blends is attributable to two factors, namely relatively low molecular weight, and possible thermal degradation of the PVC during compression molding. In conclusion, the reactive blends show better properties than the melt blends. Therefore, the proposed research has been successful in producing reactive blends of PVC and TPU with similar or better properties than those of comparable blends obtained by the melt blending technique.
Table 4.6. Mechanical Properties of the different PVC/TPU melt blends.

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Figure 4.129. Stress-Strain behavior for the PVC/TPU melt blends - SMDI and PBA based.
4.1.2. Reactive Blending of TPU in-situ with PVC in a Twin Screw Extruder

In the previous section, polymerization of TPU in-situ with PVC in internal mixer was studied. The results revealed that the PVC is partially miscible with the TPU and that the reactive blends have better mechanical properties than the analogous melt blends. The purpose of the proposed research, however, is to develop a continuous reactive blending process in a twin screw extruder.

The previous studies\textsuperscript{6} showed that continuous reactive blending processes gave unsatisfactory results not comparable to the results of studies conducted in the internal mixer, because of the lack of control of the stoichiometry balance that resulted in a low molecular weight TPU. Consequently, in order to improve the reactive extrusion processing of PVC/TPU blends, a better control of the feeding rates of the TPU monomers is necessary.
The TPU monomers used in the previous study\textsuperscript{6} were fed using a home-made piston pump to supply a liquid mixture of PBA and BDO and a conventional solid feeder to provide SMDI. The problem encountered was that the required flowrate of MDI was very low to be accurately supplied with the feeder available. Additionally, the SMDI was exposed to a relatively high temperature that could have dimerized it, rendering it useless for TPU polymerization.

The SMDI dimerization may be avoided by keeping it under vacuum or an inert atmosphere and at low temperatures (<8 °C). Therefore, it is not very difficult to understand why the feeding system used in the previous study could have dimerized the MDI disturbing the stoichiometric balance. More precisely, while in the hopper of the solid feeder the SMDI was exposed to heat from the extruder barrel. Then, the SMDI in the hopper was prone to dimerization. To prove this hypothesis, the same equipment from the previous research was used to produce a 90/10 PVC/TPU reactive blend obtaining a molecular weight of $2.4 \times 10^4$ (M\textsubscript{n}), which is even lower than the molecular weight of the neat PVC.

In order to overcome the stoichiometric control problems and the dimerization of the SMDI, several options were considered. Heat up the SMDI above its melting temperature and feed it as a liquid into the extruder or to use one of the modified versions of the MDI which are liquid at room temperature. The first option was discarded right away because of the danger that SMDI vapors poses to health. Additionally, MDI dimerization would be unavoidable at high temperature. The second option was accepted, since feeding problems can be finally overcome.

Three different types of liquid MDI are available. The selected liquid MDI is the so called LMDI. The reason to choose the LMDI is the solubility of the TPUs that are
produced by reaction with diols in THF. This solubility will permit the measurement of the molecular weight. The other liquid MDIs, CDMDI and CDMDIB were not selected because they give crosslink TPU's, as shown in the previous model batch studies.

When the LMDI is used for reactive extrusion, feeding is done using a micropump selected to assure small flow rates that guarantee the fulfillment of the stoichiometry. A schematic representation of the feeding system is presented in Chapter 3.

The continuous reactive blending process is based on the results and procedures of the model batch studies. The most important difference between the two processes is that in the reactive extrusion the monomers are fed at different lengths along the extruder length, while in batch studies they were fed at different blending times.

The extruder screw configuration was specially design to introduce high distributive and dispersive mixing in the first section of the extruder where PVC is compounded and plasticization occurs. In the second section of the extruder, where the MDI is fed, high distributive mixing is provided to guarantee intimate contact between the reactants. The temperature profile was kept low in order to simulate the conditions in the internal mixer. Additionally, the temperature at the MDI feeding port was reduced to prevent allophanate formation and PVC degradation. The temperature was increased along the extruder from the MDI feeding port to the die to permit the high viscous PVC/TPU blends to exit the extruder. The die temperature was 140 °C.

Three different blend compositions were produced by the reactive blending process. They were characterized for thermal and mechanical properties, as well as for molecular weight, morphology, and IR spectroscopy. The REX blends were compared to the analogous internal mixer reactive blends. The PVC/polyol blends obtained in the
first stage of the reactive blending process were not characterized since in the previous study it was shown that the blends obtained in batch model studies are similar to the blends obtained in the first stage of reactive extrusion. The only difference was that mixing in the extruder requires much less time than mixing in an internal mixer as expected. The reason is the increased mixing capability of the extruder, as compared to the internal mixer.

The molecular weight of the PVC/TPU REX blends is presented in Table 4.7. The number average molecular weight, weigh average molecular weight, and polydispersity index are reported. For comparison purposes, the results for the blends obtained in internal mixer are also presented. The first observation is that the neat REX TPU has a higher molecular weight than the TPU obtained using the internal mixer. A similar result is observed for the extruded blends, at all blend compositions. This results reveal that there is enhancement of the reaction rate.

Table 4.7. Molecular weights of the PVC/TPU reactive blends produced in an internal mixer and twin screw extruder.*

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</table>

* Molecular weights based on Polystyrene standards.
Figures 4.131. and 4.132. show the DSC scan traces of the different PVC/TPU reactive blends produced via REX. For the sake of comparison, the DSC scan traces of neat PVC and TPU are also shown. As mentioned before, the samples in the first scan were not pretreated; they were characterized right away after REX. The samples of the second scan were quenched in liquid nitrogen from a temperature of 200 °C immediately before characterization.

DSC results show that the extruded blends, on both scans, have one single broad glass transition temperature between those of the neat polymers, PVC and TPU. This behavior is attributed to the morphology of the blend characterized by a broad distribution of finely dispersed phases with varying compositions\textsuperscript{279}. Additionally, the existence of a single T\textsubscript{g} reveals the partial miscibility of PVC and TPU where these two polymers spontaneously mix, yet they do not form a single, thermodynamically stable phase.

Figure 4.131. First DSC scan for the PVC/TPU reactive blends - LMDI and PBA based.
A detailed observation of the first DSC scans did not provide evidence of either, the endothermic peaks observed in batch reactive blends based on SMDI, or the crystalline melting peak observed in blends based on SMDI and PBA. This result is a consequence of the lack of HS and SS ordering caused by the 2,4’-MID isomer of the LMDI.

A comparison between the first and second scan reveals that the second scans show narrower transitions shifted to higher temperatures. As was mentioned in the previous section, this behavior is attributed to the smaller scale of phase separation, less HS ordering, and more phase mixing of the TPU and PVC.

Figures 4.133. show the glass transition temperature ($T_g$) as a function of PVC concentration for the reactive blends produced by both continuous and batch processes. It was observed that for all the blends, the $T_g$ increases monotonically with an increasing PVC concentration. When comparing the $T_g$s of REX blends and batch
reactive blends, it became apparent that the $T_g$s of REX blends were somewhat lower than those of the batch reactive blends. This result can be attributed to better PVC plasticization with the TPU polyols in REX and increased phase separation of the TPUs segments.

![Graph showing Tg vs. PVC composition for Reactive Extrusion and Internal Mixer processes.](chart.png)

**Figure 4.133.** $T_g$ vs. PVC concentration for the PVC/TPU Reactive Blends.

The FTIR spectra of the different PVC/TPU reactive blends and neat polymers acquired at room temperature are shown in Figure 4.134 and 4.135. The REX blends were dissolved in THF and the solution cast on KBr disks. The aforementioned figure shows that increasing the PVC concentration increases the intensities of the C-Cl stretching vibrations, while carbonyl stretching vibration intensity varies with the blend composition.

**Figure 4.135.** Shows the carbonyl stretching region in the urethane and SS ester linkages of the TPU. As was mentioned before, the carbonyl vibration is subdivided in
to two bands: one at 1700 cm\(^{-1}\) that represents hydrogen bonded carbonyls while the other at 1730 cm\(^{-1}\) related to the non bonded carbonyls. Any variation of the intensity of the bands means changes in the hydrogen bonding of the TPU by the inclusion of the PVC in the blends. In other words, PVC - TPU interaction.

The effect of PVC on the H-bonding of the TPU in REX blends is comparable to the PVC effect on TPU H-bonding in batch produced blends, as evidenced in figure 4.135. Increasing PVC concentration decreases the intensity of the 1700 cm\(^{-1}\) band with respect to the 1730cm\(^{-1}\) band. Therefore, PVC decreases the intra H-bonding of the TPU, meaning that the PVC interacts with the TPU.

The ratio of the bonded to non-bonded carbonyl band for the neat TPU and the 25/75 PVC/TPU REX blend is higher than the ratio for blends with higher PVC concentrations. Therefore, the PVC reduces the intra hydrogen bonding of the TPU. This result can be attributed to the increased interaction between the PVC and the TPU attributable to higher dispersive mixing in the twin screw extruder.

A comparison of the ratio of bonded to non-bonded carbonyl bands between the PVC/TPU REX blend and the corresponding internal mixer blends (Figure 4.82) reveals that REX blends have a higher degree of interaction between PVC and TPU than internal mixer reactive blends. In conclusion, the REX processing improved the interaction between PVC and TPU.

Scanning electron micrographs of the REX blends are shown in Figure 4.136. The three blends show homogeneous morphology regardless of the magnification. Additionally, Figure 4.136. shows that increasing PVC concentration increases the roughness of the surface of the fracture. The same effect was observed in internal mixer blends. Comparison of the micrographs shown in Figure 4.136. with the
micrographs obtained from the internal mixer studies (Figure 4.87) shows that the internal mixer based blends have less roughness on the fracture.

![FTIR Spectra](image)

Figure 4.134. FTIR Spectra acquired at room temperature from the different PVC/TPU extruded reactive blends LMDIB and PBA based.
Figure 4.135. Carbonyl Stretching Region of FTIR Spectra acquired at room temperature from the different PVC/TPU extruded reactive blends LMDI and PBA based.
Figure 4.136. SEM Micrographs of the different PVC/TPU reactive blends PBA-LMDI based, produced by reactive extrusion. a) 25/75 b) 50/50 c) 75/25
Figure 4.137. show the TEM of the PVC/TPU reactive blends produced from the twin screw extruder. The two phase morphology of extruded blends is very similar to those of blends prepared in an internal mixer., in which the PVC/TPU 25/75 blend shows the large domains of PVC rich phase with diffuse interface dispersed in the TPU-SS rich matrix. However, the dispersed phases of the extrudated blend are more intermingled and the boundaries more diffused than that of the internal mixer. In the micrograph for the PVC/TPU 50/50 blend, two domains are observed, but with a different distribution, where the PVC-SS rich phase is the matrix and the white HS rich domains are the dispersed phase. However the dispersed domains as shown in a white color are smaller and more homogeneous dispersed with an average size of 0.2 microns. For the PVC/TPU 75/25 blend once again a continuous phase with very small domains of acicular shape are observed. As seen in the morphology of Figure 4-91, the presence of a PVC rich phase is observed. Nevertheless the amount of dark (acicular shape) domains, related to a higher concentration of PVC on the sample decreased indicating better homogenization than the blends prepared by the internal mixer. The comparison of the different micrographs for both processes leads us to the conclusion that similar morphologies were attained by both the blending methods. However the reactive extrusion blends showed more uniform distribution with smaller dispersed phase. This may be associated with the intensive shearing in the extrusion process as compared to the internal mixer.

The transitions of the blends were studied with DMA technique, as shown in Figures 4.138. to 4.140. Figure 4.138. shows one single peak for all the three blends corresponding to the partial miscibility of PVC with TPU. The peak shifts to higher values as the PVC concentration increases. The comparison between the curves
obtained for internal mixer blends (Figures 4.99 to 4.100) and those for REX blends reveals that the peaks are narrower for the REX blends. Therefore, there is better phase mixing of the polymers in REX blending.

Figure 4.137. TEM Micrographs of the different PVC/TPU reactive blends produced in the extruder, PBA-LMDI based. a) 25/75 b) 50/50 c) 75/25

Figure 4.137. TEM Micrographs of the different PVC/TPU reactive blends produced in the extruder, PBA-LMDI based. a) 25/75 b) 50/50 c) 75/25
Figure 4.138. Tan δ for the PVC/TPU reactive blends – CDMDIB and PBA based.

Figure 4.139. G″ for the PVC/TPU reactive blends – CDMDIB and PBA based.
Figures 4.139. and 4.140. show the loss and storage modulus of the extruded blends. The transition represented by a peak in Figure 4.139. and by a step in Figure 4.140 shift to higher temperatures as the PVC concentration increases.

Both 25/75 and 50/50 PVC/TPU REX blends display a rubbery plateau after the Tg transition. This contrast with the 75/25 PVC/TPU blend which shows a decreasing modulae after the glass temperature. This behavior may be associated with the elastomeric nature of the first two blends and the plastic nature of the latter.

The stress-strain behavior of the REX blends is depicted in Figure 4.141. The REX blends show stress-strain behavior between those of the neat PVC and TPU, while the 75/25 PVC/TPU REX blend behaves similar to neat PVC. This blend displayed yielding and necking and is rather brittle. However when compared to neat PVC it has lower yield stress, lesser stress at failure, and higher elongation at break. The 50/50
and 25/75 PVC/TPU REX blends show elastomeric behavior similar to the neat TPU. The stress increases monotonically prior to the failure without yielding or necking. The last two blends have lower elongation at break than the neat TPU, showing the filler effect of the PVC on the TPU. PVC reduces the mobility of the TPU because of its rigidity uncovered by a high $T_g$. Additionally, the 50/50 and 25/75 PVC/TPU REX blends show at least similar tensile strength similar to the neat TPU showing the reinforcing effect of the PVC on the TPU.

The mechanical properties of the PVC/TPU REX blends are summarized in Table 4.8. and Figures 4.142. and 4.1143. The 75/25 REX blend shows a higher modulus, higher yield strength, the same tensile strength, and lower elongation at break than the equivalent internal mixer blend. Therefore, the reactive extruded blend has a higher degree of ordering and phase distribution enhancing the yield strength and the elastic modulus but reduces the elongation at break. The similitude of tensile strength shows that both blends have the same kind of interactions.

The elongation at break and tensile strength of the REX 50/50 PVC/TPU blend are higher than those of the 50/50 PVC/TPU internal mixer blends. Therefore, there was enhancement of the properties due to the enhanced reaction rate and the degree of mixing caused by higher shear and temperatures during blending. The morphological reason is that higher reaction rates created more HS or improved HS ordering yielding more physical crosslinks that increased the tensile strength. Additionally the blends have higher molecular weights, consequently a more coherent TPU structure.

The 25/75 PVC/TPU REX blend has higher tensile strength but lower elongation at break than the corresponding internal mixer blend. These results indicate that the extrusion process enhanced the degree of mixing and the reaction rate. Nevertheless,
the 25/75 PVC/TPU blend from the internal mixer showed mechanical properties lower than the neat TPU, requiring 15 minutes to complete the second stage. The reason was explained before as the effect of the 2,4'-MDI isomer on the TPU formation. The 25/75 PVC/TPU REX blend has properties that are between those of the neat polymers. Since this blend was processed at the same conditions as the other two, the conclusion is that the extrusion process, with its high dispersive and distributive configuration and higher level of shear, enhanced the polymerization reaction. Consequently, the formation of HS was less, reducing at the same time the extent of 2,4'-MDI SS incorporation.

![Figure 4.141. Stress-Strain behavior for the PVC/TPU reactive blends –SMDI and PBA based.](image)

Table 4.8. Mechanical Properties of the different PVC/TPU reactive blends.
<table>
<thead>
<tr>
<th>Mixing</th>
<th>PVC</th>
<th>TPU</th>
<th>Elastic Modulus (Mpa)</th>
<th>Yield Stress (Mpa)</th>
<th>100% Strain Modulus (Mpa)</th>
<th>Stress at Failure (Mpa)</th>
<th>Strain at Failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch - Internal Mixer</td>
<td>100</td>
<td>0</td>
<td>2023</td>
<td>53</td>
<td>-</td>
<td>33</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>25</td>
<td>1619</td>
<td>35</td>
<td>-</td>
<td>22</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>10.5</td>
<td>20</td>
<td>287</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>75</td>
<td>-</td>
<td>-</td>
<td>2.3</td>
<td>13</td>
<td>706</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>100</td>
<td>-</td>
<td>3</td>
<td>2.6</td>
<td>27</td>
<td>856</td>
</tr>
<tr>
<td>Continuous - Reactive Extrusion</td>
<td>100</td>
<td>0</td>
<td>2023</td>
<td>53</td>
<td>-</td>
<td>33</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>25</td>
<td>1838</td>
<td>41</td>
<td>-</td>
<td>22</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>9.4</td>
<td>38</td>
<td>435</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>75</td>
<td>-</td>
<td>-</td>
<td>4.2</td>
<td>25</td>
<td>659</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>100</td>
<td>-</td>
<td>3</td>
<td>2.6</td>
<td>27</td>
<td>856</td>
</tr>
</tbody>
</table>

Figure 4.142. Tensile Strength vs. PVC concentration for the PVC/TPU reactive blends - PBA and SMDI based - different processing methods.
Figure 4.143. Elongation at break vs. PVC concentration for the PVC/TPU reactive blends – PBA and SMDI based - different processing methods.
CHAPTER V

RESULTS AND DISCUSSION – KINETICS OF TPU POLYMERIZATION

The mechanical properties of the PVC/TPU reactive blends showed that in order to obtain good performance high molecular weight of the blends is required. To achieve this, a better understanding of the kinetics of the TPU polymerization is required.

This section contains the following four subjects of results and discussion: i) the effects of chemical structure, NCO content, isomerism and functionality on the rate of reaction. ii) the effects of processing conditions such as shear and pressure independently on the reaction rate. iii) the effect of combined processing conditions during continuous processing in an extruder and iv) the effect of the addition of PVC on the kinetics of TPU.

5.1. Kinetics of TPU Polymerization

As mentioned in the literature survey chapter, there are several methods to measure the kinetics of TPU polymerization that may be classified as direct and indirect methods. In the direct methods the evolution of the concentration of selected chemical reacting specie(s) is recorded using a proper analytical technique while in the indirect techniques a thermal or mechanical property (i.e. heat of reaction or elastic modulae) is followed with respect to time. In this study two indirect methods were used to follow the kinetics of TPU polymerization.
It is worth mentioning that the TPU polymerization is a fast exothermic reaction that starts as soon as the monomers come into contact with each other. Therefore, a single indirect method could not determine the entire course of reaction. The methods selected to determine the coefficients of the rate equation in this study included the Adiabatic temperature Rise and the isothermal Differential Scanning Calorimetry.

5.1.1. Adiabatic Temperature Rise Measurements (ATR)

In this experimental technique, the temperature rise of a catalyzed TPU polymerization reaction under quasi-adiabatic conditions is recorded with respect to time. The concept behind this experimental technique is the relation between the temperature rise and the heat of reaction given by an energy balance. In essence, the energy produced by the reaction is spent in two ways, rising the temperature of the media and in heating the surroundings since perfect adiabatic conditions are impossible to achieve. The balance is given in the following equation,

$$C_p \frac{dT}{dt} = - (\Delta H_{rxn}) \frac{d\alpha}{dt} [\text{NCO}]_0 - U(T - T_{amb}) \quad (5-1)$$

Where $C_p$ is the heat capacity per unit mass. $[\text{NCO}]_0$ is the initial isocyanate molality, $d\alpha/dt$ is the fractional conversion rate, $U$ is the overall heat transfer coefficient per unit mass. $T$ is the experimentally measured quasi-adiabatic temperature, and $T_{amb}$ is the ambient temperature.

Some assumptions implicit in the formulation of equation 5-1 include, reactive medium homogeneity, absence of diffusional limitations during the course of the chemical reaction, that the only source of heat is the chemical reaction, that the density and heat of reaction are constant and that the reaction is irreversible.
Figures 5.1.-5.4. show the quasi-adiabatic temperature rise for different TPU reactant mixtures at different T31 concentrations. It was found that the PVC stabilizer (T31) catalyzed the TPU polymerization as mentioned in a previous study. Therefore, no other material is added as catalysts for the TPU polymerization.

The experimental data obtained from the quasi-adiabatic temperature rise experiments exhibited shorter time to reach a maximum with increasing catalyst concentration, as expected.

If the equation 5-1 is considered under adiabatic conditions the heat losses are zero and hence the equation is given as:

\[ C_p \frac{dT_a}{dt} = - (\Delta H_{rxn}) \frac{d\alpha}{dt} [NCO]_b \]  

(5-2)

where \( T_a \) is the temperature measured under adiabatic conditions. Under this condition, the time can be eliminated from both sides of the equation and integrated between initial and final temperatures and their corresponding conversions. It is assumed that the maximum temperature rise coincides with reaction completion (\( \alpha \to 1 \)). Hence Equation 5-2 becomes:

\[ -(\Delta H_{rxn}) = \frac{1}{[NCO]_b} \int_{T_{ao}}^{T_{af}} C_p(T_a) dT_a \]  

(5-3)

where \( T_{ao} \) and \( T_{af} \) are initial and final adiabatic TPU reactant mixtures temperatures, respectively.

If the heat capacity per unit mass (\( C_p \)) in equation 5-3 is assumed to be a linear function of temperature and almost independent of the conversion, a simple weight average of the heat capacities of the TPU monomers and final product can be used to calculate the heat capacity as a function of temperature for the reacting mass.
Figure 5.1. Experimentally measured quasi-adiabatic temperature rise profiles for TPU-SPBA catalyzed with five different T31 concentrations.

Figure 5.2. Experimentally measured quasi-adiabatic temperature rise profiles for TPU-LPBA catalyzed with five different T31 concentrations.
Figure 5.3. Experimentally measured quasi-adiabatic temperature rise profiles for TPU-CDPBA catalyzed with five different T31 concentrations.

Figure 5.4. Experimentally measured quasi-adiabatic temperature rise profiles for TPU-SPHA catalyzed with five different T31 concentrations.
With the experimental setup used for Adiabatic Temperature Rise some heat is lost to the surroundings even though small. Therefore, the experimental data must be corrected to convert the actual data to adiabatic data. To obtain the correction term equation 5-1 is subtracted from equation 5-2, obtaining:

\[
C_p \left( \frac{dT}{dt} - \frac{dT_a}{dt} \right) = -U(T - T_{amb}) \quad (5-4)
\]

Integrating this equation between time varying from 0 to \(t\) and solving for \(T_a\), equation 5-4 gives:

\[
T_a = T + \frac{U}{C_p} \int_0^t (T - T_{amb}) dt \quad (5-5)
\]

This equation shows that to obtain the adiabatic temperature the integral term must be added to the temperature measured in the course of the experiment at any given instant \(t\). However, to use equation 5-5, the term \(U/C_p\) should be evaluated. This is accomplish considering equation 5-1 at times long enough as to yield negligible variations of temperature with respect to time. At that point, the chemical reaction is complete and its corresponding term in equation 5-1 vanishes, giving:

\[
C_p \frac{dT}{dt} = -U(T - T_{amb}) \quad (5-6)
\]

If the heat capacity is assumed to be constant and integrating the equation at long times \((t>t_o)\), equation 5-6 becomes:

\[
\ln(T - T_{amb}) = \ln(T_o - T_{amb}) - \frac{U}{C_p} (t - t_o) \quad (5-7)
\]

where \(T_o\) and \(t_o\) are initial temperature and arbitrary time, respectively. Thus, the factor \(U/C_p\) may be evaluated from the slope of a linear plot of the natural logarithm of the
difference \( T - T_{amb} \) versus the times difference \( t - t_o \), as shown in Figures 5.5. to 5.8., where \( T_{amb} \) was 28 °C and \( t_o \) 500 s. The values of the slope \( (U/C_p) \) were calculated for each experimental curve by using linear regression, the results are displayed in the respective figures. The corrected adiabatic curves of temperature rise as a function of time with various polyols are shown in Figures 5.9.-5.12.

After the aforementioned corrections, the heat of reaction was calculated from equation 5-3. The heat capacity as function of temperature, \( C_p(T) \), was obtained from Steinle et al.\(^{75}\) They used a linear relation (i.e. \( C_p = mT + b \)) for a TPU polymerization, and suggested \( m \) and \( b \) parameters for the different TPU monomers. The values of \( m \) and \( b \) coefficients in this study are listed in Table 5.1. The average corrected adiabatic temperature rise and corresponding heat of reactions are also reported in the same table.

The results shown in Table 5.1. reveal almost the same heat of reaction \( (\Delta H_{rxn}) \) for all MDI’s except for the system using LMDI. It is important to mention that these values are in excellent agreement with the value obtained by other investigators\(^{155,156}\) for solid MDI (SMDI) systems. The reacting system based on LMDI shows a much smaller value of \( \Delta H_{rxn} \) which maybe associated to the difference in reactivity of the isomers of MDI\(^{85}\), and a possible phase separation of the TPU segments before reaching high conversion. Looking into detail the other systems, the CDMDI based system has a lower heat of reaction than the SMDI one. This could be explained as the effect of less isocyanate in the system (NCO content is lower in the CDMDI one by 4% compared to the SMDI one). However, the difference in the heat of reaction among the different polyols is not significant.
Figure 5.5. Correction Factors for the quasi-adiabatic temperature rise experiments.
TPU-SPBA catalyzed with five different T31 concentrations.

Figure 5.6. Correction Factors for the quasi-adiabatic temperature rise experiments.
TPU-LPBA catalyzed with five different T31 concentrations.
Figure 5.7. Correction Factors for the quasi-adiabatic temperature rise experiments. TPU-CDPBA catalyzed with five different T31 concentrations.

Figure 5.8. Correction Factors for the quasi-adiabatic temperature rise experiments. TPU-SPHA catalyzed with five different T31 concentrations.
Figure 5.9. Corrected adiabatic temperature rise profiles for TPU-SPBA catalyzed with five different T31 concentrations.

Figure 5.10. Corrected adiabatic temperature rise profiles for TPU-LPBA catalyzed with five different T31 concentrations.
Figure 5.11. Corrected adiabatic temperature rise profiles for TPU-CDPBA catalyzed with five different T31 concentrations.

Figure 5.12. Corrected adiabatic temperature rise profiles for TPU-SPHA catalyzed with five different T31 concentrations.
Table 5.1. ATR Experimental Parameters, average temperature rise and heat of reaction.

<table>
<thead>
<tr>
<th>TPU</th>
<th>Cp (b)</th>
<th>Cp (m)</th>
<th>ΔT (°C)</th>
<th>ΔH$_{rxn}$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPBA</td>
<td>9.569 x 10^{-1}</td>
<td>2.785 x 10^{-3}</td>
<td>74</td>
<td>92</td>
</tr>
<tr>
<td>LPBA</td>
<td>9.569 x 10^{-1}</td>
<td>2.785 x 10^{-3}</td>
<td>62</td>
<td>78</td>
</tr>
<tr>
<td>CDPBA</td>
<td>9.450 x 10^{-1}</td>
<td>2.791 x 10^{-3}</td>
<td>68</td>
<td>88</td>
</tr>
<tr>
<td>SPHA</td>
<td>9.594 x 10^{-1}</td>
<td>2.781 x 10^{-3}</td>
<td>70</td>
<td>90</td>
</tr>
</tbody>
</table>

In summary, the results presented demonstrate that the TPU systems with different types of MDI (liquid, solid and isomer) have different heat of reactions. In addition to this result, different catalyzing effect of T31. It is believed that these results are caused by different NCO content and reactivity of MDI isomer. The CDMDI has lower NCO content than the SMDI giving lower heat of reaction. The difference between LMDI and SMDI can be attributed to the reduced reactivity of the isomer 2,4-MDI. The other phenomena could be responsible for the differences in heat of reaction, i.e. diffusional effects. With these results in mind, further kinetic studies using isothermal DSC scanning mode are described in the following section.

5.1.2. Isothermal Scanning Calorimetry

The objective of the isothermal differential scanning calorimetry (DSC) was to determine the heat of reaction in late stages of TPU polymerization i.e. after sample preparation. In contrasts, ATR experiments permit recording the temperature from the moment the reactants are mixed, in other words from early stages of reaction. Additionally, ATR experiments give more accurate results when the reaction progress fast because heat losses are less than if the reaction proceeds slower. In contrasts, DSC experiments do not include the mixing and sample preparation stages. Therefore, in
DSC early stages of reaction are not measured, being this method more suitable for slow reactions.

From DSC experimental results, the conversion is expressed as follows:

\[
\alpha = \frac{\Delta H^*_t}{(\Delta H_{rxn})} \quad (5-8)
\]

where \(\Delta H^*_t\) is the measured molar heat of reaction of polymerization as a function of polymerization time, and \(\Delta H_{rxn}\) is the total molar enthalpic heat of reaction measured by the ATR technique. Equation (5-8) includes the fact that the beginning of measurement of the heat flows coincides with the beginning of the polymerization reaction. Nevertheless, in reality the polymerization reaction starts as soon as the monomers come in contact with each other, as explained above. Consequently for kinetic measurements, certain amount of heat of reaction during mixing and sample preparation cannot be measured. Then Equation (5-8) is transformed into:

\[
\alpha = \frac{\Delta H_1 + \Delta H(t)}{(\Delta H_{rxn})} \quad (5-9)
\]

where \(\Delta H_1\) is the measured molar heat of reaction lost during sample preparation and \(\Delta H(t)\) is the molar heat of polymerization as a function of polymerization time measured in the DSC. \(\Delta H(t)\) is obtained by integrating the area under the isothermal traces of the DSC according to:

\[
H(t) = \frac{1000}{[C]_0} \int_0^t \frac{\partial H}{\partial t} dt \quad (5-10)
\]

where \([C]_0\) is the initial isocyanate molality and \(dH/dt\) is the specific heat flow. On the other hand, \(\Delta H_1\) is obtained by subtracting from the total heat of reaction. The heat of
reaction measured from the DSC (\(\Delta H_m\)), and any residual heat of reaction that did not evolve during the experiment (\(\Delta H_r\)), if there is any:

\[
\Delta H_1 = -(\Delta H_{rxn}) - \Delta H_m - \Delta H_r
\]  

(5-10)

To measure the residual heat of reaction (\(\Delta H_r\)) two temperature scans were performed after the isothermal DSC experiment. The first temperature scanning experiment is carried out to determine the presence of any peak, while the second one serves as a baseline for the first temperature scan. To evaluate the residual heat of reaction the second temperature scan (baseline) is subtracted from the first temperature scan. Any difference is the residual heat of reaction.

Figures 5.13.-5.16. show the isothermal specific heat flow with various temperatures without catalyst for 30 minutes. At the beginning of the reaction there is a maximum heat flow. After some time however, the heat flow decreases to zero as shown in the aforementioned Figures. The curves of the heat flow show that TPU polymerization is exothermic as most of step growth polymerizations are. In this kind of polymerization, the rate of reaction is high at the beginning of the reaction due to the high concentration of reactive functional groups. As the reaction progresses, concentration of reactive groups decreases and reduction of reaction rate is observed.

The temperature scans, performed after the isothermal DSC to measure the residual heat of reaction, are shown in Figures 5.17- 5.24. As revealed, an exothermic peak appeared in only lower temperatures (100 and 120 °C) in all the TPU systems. The peaks are marked with arrow symbols. Table 5.2 summarizes the results obtained for the residual heat of reaction, where the full conversion is not achieved in 30 minutes of polymerization time.
Figure 5.13. Isothermal DSC Scan for the TPU Polymerization at different temperatures. SPBA system – No Catalyst.

Figure 5.14. Isothermal DSC Scan for the TPU Polymerization at different temperatures. LPBA system – No Catalyst.
Figure 5.15. Isothermal DSC Scan for the TPU Polymerization at different temperatures. CDPBA system – No Catalyst.

Figure 5.16. Isothermal DSC Scan for the TPU Polymerization at different temperatures. SPHA system – No Catalyst.
Figure 5.17. First DSC Scan of the TPU reactant blend after isothermal scan. SPHA system – No Catalyst.

Figure 5.18. Second DSC Scan of the TPU reactant blend after isothermal scan. SPHA system – No Catalyst.
Figure 5.19. First DSC Scan of the TPU reactant blend after isothermal scan. LPBA system – No Catalyst.

Figure 5.20. Second DSC Scan of the TPU reactant blend after isothermal scan. LPBA system – No Catalyst.
Figure 5.21. First DSC Scan of the TPU reactant blend after isothermal scan. CDPBA system – No Catalyst.

Figure 5.22. Second DSC Scan of the TPU reactant blend after isothermal scan. CDPBA system – No Catalyst.
Figure 5.23. First DSC Scan of the TPU reactant blend after isothermal scan. SPHA system – No Catalyst.

Figure 5.24. Second DSC Scan of the TPU reactant blend after isothermal scan. SPHA system – No Catalyst.
Table 5.2. Heat of reaction ($\Delta H_r$) determined by ATR method for different TPU reactant Mixtures polymerized without catalyst at various Temperatures for 30 minutes.

<table>
<thead>
<tr>
<th>TPU</th>
<th>Temperature (°C)</th>
<th>$\Delta H_r$ (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>2680</td>
</tr>
<tr>
<td>SPBA</td>
<td>120</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3130</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>1450</td>
</tr>
<tr>
<td></td>
<td>140</td>
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<td>0</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>0</td>
</tr>
<tr>
<td>LPBA</td>
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<td>2840</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>1030</td>
</tr>
<tr>
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<td>160</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>0</td>
</tr>
<tr>
<td>CDPBA</td>
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<td>2280</td>
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<tr>
<td></td>
<td>120</td>
<td>730</td>
</tr>
<tr>
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<td>160</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>0</td>
</tr>
<tr>
<td>SPHA</td>
<td>100</td>
<td>3130</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>1450</td>
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<td>0</td>
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<td></td>
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<td>0</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>0</td>
</tr>
</tbody>
</table>

Once all the heat terms of equation 5.9 are evaluated, the conversion may be calculated as a function of time. Then, the kinetic equation 2.8 is fitted to the data and its parameter evaluated. The kinetic equation, expressed as a function of conversion is:

$$\frac{d\alpha}{dt} = \left( A_1 \exp\left(-\frac{E_{a1}}{RT}\right) + A_2 \exp\left(-\frac{E_{a2}}{RT}\right) \right) \left[ \frac{\text{Stab} / \text{Cat}}{C} \right] C_0^{n-1} (1 - \alpha)^n \quad (5-11)$$

Figures 5.25. through 5-28. show the fractional conversions versus the polymerization time profiles (represented symbols). The results demonstrate that higher temperature led to faster polymerization reaching completion earlier than polymerizations conducted at low temperatures. To obtain the kinetic parameters of the
equation (5-11) least squares linear regression technique was used. The kinetic analysis begins with the determination of \( k \) and \( n \). This is done by plotting the conversion rate versus the remaining fractional conversion in a double logarithmic chart. The plots are shown in Figures 5.29.-5.32. Using a linear regression of the data points, \( n \) is the slope and \( k \) is evaluated from the intercept \( \log k[C]_o^{n-1} \). These log-log plots are shown in Figures 5.29.-5.32. The curves seem to be linear within experimental error. However, conversion depends on temperature, monomers and MDIs, after a certain critical conversion is reached. These deviations from the linearity may be originated in different reactivities of the TPU monomers, HS/SS phase separation and side reactions. Additionally, deviations from linearity may be also due to diffusion control caused by increased viscosity and restricted mobility with increasing molecular weight. An important result from the kinetic analysis at this point is that for a given TPU polymerizing system the same overall rate of reaction constant \( (n) \) is obtained regardless the temperature. The values of \( n \) are given in Table 5.3.

The next step in the analysis of the kinetic results is finding the effect of temperature on the kinetic rate constant \( k \) for the uncatalyzed reaction. In this case \( k \) becomes \( k_1 \), since the second term of the equation 5-11 is nil. A semi-ln plot of \( k_1 \) vs. \( 1/T \) yields a straight line where the slope is related to the activation energy and the intercept to the Arrhenius pre-exponential constant. Figures 5.33.-5.36. show the semi-ln plot obtained from the \( k_1 \) values and the line fitted. The results of the Arrhenius parameters for the uncatalyzed reaction are shown in the Table 5.3.

In order to obtain the kinetic parameters related to the catalyst effect, a similar analysis as presented before is conducted at different catalyst concentrations and temperatures. Figures 5.37.-5.40. show the fractional conversions versus the
polymerization time profiles obtained from isothermal DSC scans at 140 °C for the different TPU systems with different catalyst concentrations. Figure 5.41.-5.44. shows the different TPU system polymerized at a single catalyst concentration and different temperatures.

Figures 5.37.-5.40. exhibit that with increasing of catalyst concentration the polymerization proceed faster and completion is achieved in 30 minutes. In these situations, the residual heat of reaction was not measured because was missing. At the same catalyst concentration with varying temperatures, Figures 5.41.-5.44. demonstrate that the polymerization reaction is faster for the higher temperatures. For instance, the polymerization reaction at 180 °C has achieved almost complete conversion in less than 10 minutes while it took more than 30 minutes for the reaction at 100 °C.

Figure 5.25. Experimental and Predicted Isothermal DSC Conversions for TPU reactant mixtures (SPBA) polymerized at different Temperatures – No Catalyst.
Figure 5.26. Experimental and Predicted Isothermal DSC Conversions for TPU reactant mixtures (LPBA) polymerized at different Temperatures – No Catalyst.

Figure 5.27. Experimental and Predicted Isothermal DSC Conversions for TPU reactant mixtures (CDPBA) polymerized at different Temperatures – No Catalyst.
Figure 5.28. Experimental and Predicted Isothermal DSC Conversions for TPU reactant mixtures (SPHA) polymerized at different Temperatures – No Catalyst.

Figure 5.29. Logarithmic Plots of DSC conversion rate vs. remaining conversion for uncatalyzed TPU (SPBA) polymerized at different Temperatures
Figure 5.30. Logarithmic Plots of DSC conversion rate vs. remaining conversion for uncatalyzed TPU (LPBA) polymerized at different Temperatures

Figure 5.31. Logarithmic Plots of DSC conversion rate vs. remaining conversion for uncatalyzed TPU (CDPBA) polymerized at different Temperatures
Figure 5.32. Logarithmic Plots of DSC conversion rate vs. remaining conversion for uncatalyzed TPU (SPHA) polymerized at different Temperatures

\[ \ln[k_1] = \ln[A_1] - \frac{Ea_1}{RT} \]
\[ \ln[k_1] = 0.9604 - \frac{2175.9}{T} \]

\[ r^2 = 0.993 \]

Figure 5.33. Evaluation of Kinetic Parameters for the uncatalyzed TPU (SPBA) polymerized at different Temperatures

\[ \ln[k_1] = \ln[A_1] - \frac{Ea}{RT} \]
\[ \ln[k_1] = 0.9804 - 2175.9/T \]
\[ r^2 = 0.993 \]
Figure 5.34. Evaluation of Kinetic Parameters for uncatalyzed TPU (LPBA) polymerized at different Temperatures

Figure 5.35. Evaluation of Kinetic Parameters for uncatalyzed TPU (CDPBA) polymerized at different Temperatures
In order to obtain the kinetic parameters related to the catalyst effect, a similar analysis as presented before is conducted at different catalyst concentrations and temperatures. Figures 5.37.-5.40. show the fractional conversions versus the polymerization time profiles obtained from isothermal DSC scans at 140 °C for the different TPU systems with different catalyst concentrations. Figure 5.41.-5.44. shows the different TPU system polymerized at a single catalyst concentration and different temperatures.

Figures 5.37.-5.40. exhibit that with increasing of catalyst concentration the polymerization proceed faster and completion is achieved in 30 minutes. In these situations, the residual heat of reaction was not measured because was missing. At the
same catalyst concentration with varying temperatures, Figures 5.41.-5.44. demonstrate that the polymerization reaction is faster for the higher temperatures. For instance, the polymerization reaction at 180 °C has achieved almost complete conversion in less than 10 minutes while it took more than 30 minutes for the reaction at 100 °C.

The values of the overall rate of reaction coefficient (n) and coefficient $k_2$ may be determined for the catalyzed reaction in a similar way as it was done before for uncatalyzed polymerization. Figures 5.45.-5.52. show the conversion rate versus the remaining fractional conversion in a double logarithmic scale for different catalyst concentration. From the data analysis, the value of the overall rate of reaction coefficient (n) for the catalyzed reaction was found to match the same coefficient for the uncatalyzed reaction. The evaluation of the rate constant ($k_2$), is accomplished by subtracting the value of the rate constant of the uncatalyzed reaction ($k_1$) from the overall rate constant ($k$), i.e. $k_2 = k - k_1$.

![Figure 5.37. Experimental and Predicted Isothermal DSC Conversions of the SPBA TPU system polymerized at 140 °C with different Catalyst concentrations.](image)

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Figure 5.38. Experimental and Predicted Isothermal DSC Conversions of the LPBA TPU system polymerized at 140 °C with different Catalyst concentrations.

Figure 5.39. Experimental and Predicted Isothermal DSC Conversions of the CDPBA TPU system polymerized at 140 °C with different Catalyst concentrations.
Figure 5.40. Experimental and Predicted Isothermal DSC Conversions of the SPHA TPU system polymerized at 140 °C with different Catalyst concentrations.

Figure 5.41. Experimental and Predicted Isothermal DSC Conversions of the SPBA TPU system polymerized with 0.002% of Catalyst at different Temperatures.
Figure 5.42. Experimental and Predicted Isothermal DSC Conversions of the LPBA TPU system polymerized with 0.002% of Catalyst at different Temperatures.

Figure 5.43. Experimental and Predicted Isothermal DSC Conversions of the CDPBA TPU system polymerized with 0.002% of Catalyst at different Temperatures.
Figure 5.44. Experimental and Predicted Isothermal DSC Conversions of the SPHA TPU system polymerized with 0.002% of Catalyst at different Temperatures.

Figure 5.45. Logarithmic Plots of DSC conversion rate vs. remaining conversion for the TPU (SPBA) polymerized at 140 °C with different Catalyst concentrations.
Figure 5.46. Logarithmic Plots of DSC conversion rate vs. remaining conversion for the TPU (LPBA) polymerized at 140 °C with different Catalyst concentrations

Figure 5.47. Logarithmic Plots of DSC conversion rate vs. remaining conversion for the TPU (CDPBA) polymerized at 140 °C with different Catalyst concentrations
Figure 5.48. Logarithmic Plots of DSC conversion rate vs. remaining conversion for the TPU (SPHA) polymerized at 140 °C with different Catalyst concentrations.

Figure 5.49. Logarithmic Plots of DSC conversion rate vs. remaining conversion for the TPU (SPBA) polymerized with 0.002% of Catalyst at different Temperatures.

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Figure 5.50. Logarithmic Plots of DSC conversion rate vs. remaining conversion for the TPU (LPBA) polymerized with 0.002% of Catalyst at different Temperatures.

Figure 5.51. Logarithmic Plots of DSC conversion rate vs. remaining conversion for the TPU (CDPBA) polymerized with 0.002% of Catalyst at different Temperatures.
To evaluate the activation energy $E_{a2}$ and pre-exponential term $A_2$ a semi-ln plot of $k_1$ vs. $1/T$ is done. The data must lie on a straight line which slope equals the reduced activation energy term ($-E_{a2}/R$) and the intercept ($A_2\ln\{[\text{Cat}]^c\})$. The Figures 5.53. to 5.56. display the data and the fitted lines. However, To determine the constant $A_2$ requires finding the catalyst coefficient ($c$).

The evaluation of $c$ and consequently of $A_2$, is conducted using the data obtained from the isothermal DSC scans at one temperature and different catalyst concentrations as shown in Figure 5.41.-5.44. Figures 5.57.-5.60. depict logarithmic plots of $k_2$ and the catalyst concentration, which yield a straight line where the slope is the catalyst coefficient ($c$) and the intercept equals $\log[A_2e^{-E_{a2}/RT}]$.

The kinetic parameters obtained from the aforementioned procedure for the different TPU systems are listed in Table 5.3. The overall order of reaction ($n$), $A_1$ and $c$
are almost alike, but $E_{\text{a1}}$ and $A_2$ are quite different. Additionally, it is worth to mention that the values are similar to those found in the previous literature. Replacing the constant values in equation (5-11) the kinetic equation for each polymerization system is obtained. The model can be used to predict the evolution of the fractional conversion. From Figures 5.24.-5.28. and 5.37.-5.44., it is apparent that the model predictions, represented by solid lines, fit well the experimental data.

A first observation from the results in Table 5.3. is that the Arrhenius pre-exponential constant $A_2$ is much larger than $A_1$. On the other hand $E_{\text{a1}}$ is larger than $E_{\text{a2}}$, as expected, since the catalyzed reaction requires less activation energy to start.

![Figure 5.53. Evaluation of Kinetic Parameters for the catalyzed TPU (SPBA) polymerized at different Temperatures](image)

\[ \ln[k_2] = \ln([\text{Cat}] A_2) - \frac{E_{\text{a2}}}{RT} \]

\[ \ln[k_2] = 17.777 - 8928.4/T \]

$r^2 = 0.974$

Figure 5.53. Evaluation of Kinetic Parameters for the catalyzed TPU (SPBA) polymerized at different Temperatures
Figure 5.54. Evaluation of Kinetic Parameters for catalyzed TPU (LPBA) polymerized at different Temperatures

Figure 5.55. Evaluation of Kinetic Parameters for catalyzed TPU (CDPBA) polymerized at different Temperatures
Figure 5.56. Evaluation of Kinetic Parameters for catalyzed TPU (SPHA) polymerized at different Temperatures

\[ \ln[k_2] = \ln([\text{Cat}]cA_2) - \frac{E_{a2}}{RT} \]
\[ \ln[k_2] = 7.0619 - 4352.9/T \]
\[ r^2 = 0.975 \]

Figure 5.57. Evaluation of Kinetic Parameters for the catalyzed TPU (SPBA) polymerized 140 °C and different catalyst concentrations and Temperatures

\[ \log[k_2] = \log[A_2e^{E_{a2}/RT}] + c \log[\text{Cat}] \]
\[ \log[k_2] = 0.910 \log[\text{Cat}] + 0.966 \]
\[ r^2 = 0.999 \]
Figure 5.58. Evaluation of Kinetic Parameters for catalyzed TPU (LPBA) polymerized at 140 °C and different catalyst concentrations and Temperatures

Figure 5.59. Evaluation of Kinetic Parameters for catalyzed TPU (CDPBA) polymerized at 140 °C and different catalyst concentrations and Temperatures
Figure 5.60. Evaluation of Kinetic Parameters for catalyzed TPU (SPHA) polymerized at 140 °C and different catalyst concentrations and Temperatures

Table 5.3. Kinetic Parameters obtained by DSC for the TPU polymerization

<table>
<thead>
<tr>
<th>TPU</th>
<th>n</th>
<th>$A_1$ (mol NCO/Kg sol.s)$^n$</th>
<th>$E_{a1}$ (KJ/Kg mol)</th>
<th>$A_2$ (mol NCO/Kg sol.s)$^n$</th>
<th>$E_{a2}$ (KJ/Kg mol)</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPBA</td>
<td>1.68</td>
<td>1.12E+03</td>
<td>3.89E+04</td>
<td>1.95E+05</td>
<td>3.47E+04</td>
<td>0.91</td>
</tr>
<tr>
<td>LPBA</td>
<td>1.69</td>
<td>1.06E+03</td>
<td>4.00E+04</td>
<td>1.76E+05</td>
<td>3.50E+04</td>
<td>0.88</td>
</tr>
<tr>
<td>CDPBA</td>
<td>1.70</td>
<td>1.03E+03</td>
<td>4.05E+04</td>
<td>1.83E+05</td>
<td>3.48E+04</td>
<td>0.88</td>
</tr>
<tr>
<td>SPHA</td>
<td>1.67</td>
<td>1.12E+03</td>
<td>3.77E+04</td>
<td>1.83E+05</td>
<td>3.33E+04</td>
<td>0.90</td>
</tr>
</tbody>
</table>
The results show that for the different TPU systems investigated in this study, similar overall order of reaction was obtained. Additionally, the value of this term is in agreement with the urethane reaction kinetic data in the preliminary literature, where \( n \) was between 1 to 2\(^{72} \). However, there are differences in the values of the \( \text{Ea}_1 \), \( \text{Ea}_2 \), \( A_1 \) and \( A_2 \) terms which depend on the reacting systems as explained as follows.

A comparison between the activation energies for different polyesters shows that polymerization with PHA had less activation energy than for reaction with PBA. This is translated in faster reaction when using PHA instead of PBA. The resulting lower activation energy in the reaction with PHA is associated with its increased chain mobility as compared to the PBA molecule. The reason is that PHA molecule contains 6 methylene groups between the hydroxyl groups, while PBA only four.

With respect to the different MDIs, it is observed that the reactions with SMDI displays lower activation energy than reactions with the LMDI or CDMDI. The reason is that the SMDI has higher %NCO than CDMDI and higher reactivity than LMDI. The TPU polymerization with LMDI is slower, because of the presence of the 2,4’- isomer that reacts slower than the 4,4’-MDI as mentioned in the Bayer Report\(^{81} \). Finally, the kinetic parameters \( \text{Ea}_1 \), \( \text{Ea}_2 \), \( A_1 \) and \( A_2 \) for the TPU polymerization with CDMDI lies between the values obtained for the other two MDIs. The CDMDI has lower %NCO than other MDIs thus resulting in less probability of reaction between the two reactive functional groups.

### 5.2. Kinetics of TPU Polymerization for Application of Reactive Processing at Different Processing Conditions

The results of the kinetic studies of TPU polymerization investigated in quiescent conditions showed the effect of catalyst concentration and varying temperature. However, in reactive blending operations e.g. in twin screw extruder the materials are
subjected to shearing, and pressure. Therefore, since continuous reactive blending of
the PVC with TPU is desirable, it is of great interest to study the kinetics of TPU
polymerization under shearing and pressure. This is specially valid for applications to
reactive extrusion process.

5.2.1. Effect of Shear on the TPU polymerization under isothermal conditions

The effect of shear on the polymerization was studied using dynamic rheometry,
also known as rheokinetics, using the dynamic mode in a time sweep at a constant
frequency and low strain (2%). Three different isothermal temperatures were used
during the experiments and 5 different levels of frequency were used. As was
mentioned in the Chapter III, the Cox-Merz rule was applied to relate the shear rate
with the frequency.

Figure 5.61. shows the data obtained from the dynamic rheokinetic experiment.
The complex viscosity (\(\eta^*\)), the modulae (\(G', G''\), and \(G^*\)) as well as the torque
increases with increasing reacting time, while \(\tan \delta\) decreases. These results reveal the
formation of a high molecular weight polymer while the reaction mass changes from
liquid to solid (elastomeric) as the reaction proceed. In Figure 5.61 it can be observed
that the modulae, the complex viscosity and the torque increase or decrease rapidly at
the beginning of the reaction then the curves start to level off. After a certain time,
these curves reach a plateau meaning that the chemical controlled polymerization
competed. The different material properties (viscosity, modulae and torque) reach the
plateau at different reaction times, for instance, the complex viscosity curve reaches the
plateau at 540 s, while complex elastic moduli at about 800 s. Therefore, it is necessary
to define the completion point of the polymerization reaction in an unbiased way. The
crossover point of the elastic and dissipative modulae is taken as the criteria to define
the end of the polymerization reaction because the crossover point coincides with the reaching of the plateau for these two variables.

Figures 5.62.-5.66. shows the evolution of $G'$ and $G''$ for TPU polymerization at 120 °C at different frequencies. These figures show that both curves have a sharp increase with respect to time before the crossover point. Additionally, at early stages of the reaction $G''$ is smaller than $G'$. After certain time, the curves start to level off and further in time they reach a plateau. Then, $G''$ becomes larger than $G'$.

The effect of varying frequency on the crossover point becomes apparent when plotting the modulae ($G_c$) and the time ($t_c$) at the cross over point as a function of frequency. Additionally, if frequency is related to shear rate through the Cox-Merz rule, then the effect of shear on the TPU polymerization becomes apparent. Figure 5.67. shows the effect of temperature and shear rate on the crossover point position.

The effect of temperature on $G_c$ is observed by comparing the three topmost curves in Figure 5.67. It is apparent, that the three curves are almost coincident with each other sowing negligible effect of temperature on the final structure of the TPU after reaction completion. The modulae changes from about $1.0 \times 10^6$ Pa to about $3.0 \times 10^6$ Pa. The lower value corresponding to the higher temperature of 140 °C while the higher value corresponds to 100 °C following the expected trend. In addition to the effect of temperature on modulae, the effect on crossover time may be analyzed by observing the three lowermost curves in Figure 5.67. It is evident that at constant shear an increment of temperature reduces the crossover time, revealing an increase in reaction rate when temperature increases.

The effect of shear on crossover location may be analyzed from the three lowermost curves in Figure 5.67. At constant temperature, the crossover time ($t_c$)
Figure 5.61. Rheokinetics during the TPU Polymerization, at 100 °C, 25rad/s for the SPBA system.

Figure 5.62. G’ and G” during TPU Polymerization, at 100 °C, 5rad/s for the SPBA system.

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Figure 5.63. $G'$ and $G''$ during TPU Polymerization, at 100 °C, 25rad/s for the SPBA system.

Figure 5.64. $G'$ and $G''$ during TPU Polymerization, at 100 °C, 50rad/s for the SPBA system.
Figure 5.65. $G'$ and $G''$ during TPU Polymerization, at 100 °C, 75rad/s for the SPBA system.

Figure 5.66. $G'$ and $G''$ during the course of TPU Polymerization, at 100 °C, 100rad/s with SPBA.
increases with decreasing shear rate indicating that increasing shearing enhance the rate of reaction. However, the amount of the time change is greater at low shear rate than at high shear rate. For instance, at 25 s\(^{-1}\) the crossover time varies in more than 600 s when temperature changes from 100 °C to 140 °C, while at 75 s\(^{-1}\) the time change is of about 200 s for the same variation in temperature. In addition, the effect of shearing on \(t_c\) is more important at low temperature as compared to the impact of shearing at high temperature. For example, at 100 °C the crossover time decreases 600 seconds, while at 140 °C it does 100 s approximately. In Figure 5.67, an exponential regression curve that fits the experimental data of crossover point is shown. Additionally, in Table 5.4, the complete exponential equation is displayed.

The results obtained from the rheokinetic experiments show that shearing induces a faster polymerization reaction because of the imposed motion on the reacting system. The reason for this phenomenon may be proposed as follows. As the TPU polymerization proceeds, the viscosity increases giving as a result increased viscous dissipation that raises the temperature of the reacting mass specially at points far from the rheometer’s fixtures surfaces. However, such an increase of temperature may reduce the viscosity of the reacting mass improving the diffusivity and hence increasing the reaction rate because of improved molecular mobility. In other words, shearing causes viscous dissipation that increases the temperature and, consequently the molecular mobility, improving the rate of reaction which increases the viscosity and then the viscous dissipation and so on. Even though this explanation is very feasible, it is important to realize that the crossover time variation with respect to shear rate displays a decreasing trend at larger shear rates. In other words, it is impossible to increase the
rate of reaction endlessly by increasing the shear rate. There is a limiting practical value that was not achieved in this rheokinetic study.

![Graph showing shear rate vs. Gc for different temperatures](image)

Figure 5.67. Gc and tc for the TPU Polymerized at different temperatures for the SPBA system.

Table 5.4. Exponential correlation for the rheokinetic experiments of the TPU polymerization

<table>
<thead>
<tr>
<th>Isothermal Temperature</th>
<th>Exponential Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>140 °C</td>
<td>$t_c = 247.13e^{-0.0158\gamma}$</td>
</tr>
<tr>
<td>120 °C</td>
<td>$t_c = 644.40e^{-0.0175\gamma}$</td>
</tr>
<tr>
<td>100 °C</td>
<td>$t_c = 949.36e^{-0.0156\gamma}$</td>
</tr>
</tbody>
</table>
The kinetic equation for TPU polymerization, equation 5.11, is modified to include the effect of shearing with the following assumptions: The procedure consists on comparing the time to reach a selected conversion without shear with the $t_c$ value obtained under shear. The assumptions are; i) all the experiments under shear reach the same value of conversion at $t_c$, and ii) the conversion selected for tests without shear is attained at greater time than $t_c$. Figure 5.68. shows the shift factor as a function of shear rate, together with the exponential regression on the data.

The modification introduced to the kinetic equation will permit the appropriate representation of kinetic data under shear. The kinetic equation has been used to study the polymerization of TPU under quiescent conditions, more specifically, reaction under varying temperature and catalyst concentration. Therefore, modifications are needed to include different effects such as shear, pressure, PVC concentration and miscibility for the PVC/TPU reactive blending. The first two effects are associated to diffusional effects related to the mobility of the chains. The PVC concentration and miscibility effect on the kinetics is associated to chemical changes caused by PVC presence.

The shearing effects are included in the kinetic equation through a modification of the reaction constant $k$. Now the constant is represented as shown in equation 5-12 that is the modified version of equation 5-11.

\[
\frac{d\alpha}{dt} = k^* [C]_0^{n-1} (1 - \alpha)^n
\]

\[
k^* = k' k''
\]

\[
k^* = \left[ A_1 \exp\left( -\frac{E_{a1}}{RT} \right) + A_2 \exp\left( -\frac{E_{a2}}{RT} \right) \right] \frac{[\text{Stab} / \text{Cat}]}{C} \cdot \left[ 1.0 \exp\left( -0.00023 \gamma \right) \right]
\]

(5-12)

where $k^*$ is the modified overall rate constant, $k'$ is the chemical rate constant, $k''$ is the diffusional rate constant and $\gamma$ is the shear rate.
Figure 5.68. shows the exponential regression of shift factor vs shear rate, obtained under the assumptions previously mentioned. The correlation coefficient ($r^2$) is 0.95, which gives a good fitting to the data at 100, 120 and 140 °C. The kinetic equation represents well the data for TPU based on SPBA. It is assumed that the effect of shear for the other TPU systems will be of the same sort as the one obtained for the SPBA system, with different numerical exponent.

![Figure 5.68. Shift Factor as a function of Shear Rate for Rheokinetic studies at different Temperatures](image)

5.2.2. Effect of Pressure on the TPU polymerization under isothermal conditions

The effect of pressure on the kinetics of TPU polymerization was studied under quiescent conditions in two home-made vessels design to withstand high pressure. The vessels consisted of a hollow cylinder with a lid that could move up and down freely, and differed in diameter of the cylindrical cavity and lid. To vary the pressure on the
reacting mixture weights were put on top of the lid. The polymerization was followed by inserting a thermocouple in the reacting blend through a hole drilled on the lid.

Similarly to ATR experiments, the polymerization started once the materials were mixed. However, in pressure effect tests, the starting materials were mixed inside the vessel, and then it was capped with the lid and the weights to get the desired pressure. The reaction was conducted at atmospheric pressure to serve as a baseline for the other tests ran at various pressures. In contrast to ATR experiments, the adiabaticity of the reacting system could not be reached. Therefore, the vessels were kept in an oven at 80 °C to minimize heat losses and maintained at constant thermal condition of the surroundings. Because of the lack of adiabaticity of the reactor, the detailed analysis for determination of kinetic parameters is not obtained. However, it is possible to measure the rate of change of the temperature as the reaction progress as a function of time under different pressures. It is expected that at higher pressures the rate of change of temperature increases, because at the beginning of the reaction there are no diffusional limitations\textsuperscript{154}.

Figure 5.69. shows the experimental temperature profile as a function of polymerization time for TPU polymerized with SPBA and 0.015\% catalyst. In the aforementioned figure, it is observed that there is no data records between after 20 s and before 50 s. This time zone was generated from the experimental setup, initially the TPU components were hand mixed for 30 s with a spoon (as a normal ATR experiment), the temperature rise was measured for 10 s. After this, the thermocouple was disconnected and the vessel was closed, weights were placed on top of it to set the different pressures. This procedure took approximately 30 s. The temperature measurements started once the thermocouple was connected.
In Figure 5.69 it is observed that at the beginning of the reaction with no pressure present no differences in temperature are observed. At intermediate reaction time the greatest difference between the maximum and minimum temperature is of about 8 °C, showing the effect of the pressure on temperature rise. At longer reaction times, the difference between temperatures is reduced, showing that the effect of pressure is reduced. The reason is that viscosity becomes higher and molecular mobility is reduced.

The effect of pressure on the reaction rate is associated with the relationship between pressure and viscosity. If the viscosity is low, an increase on pressure decreases the diffusion rate. Simultaneously, the number density of reacting molecules in the liquid increases along with increasing probability of reaction. Hence, increasing
the pressure increases the rate of reaction and the temperature. If the viscosity reaches a certain critical value, and the polymerization reaction becomes diffusion-controlled, an increase in pressure is expected to decrease the diffusion rate and thus the rate of reaction and temperature.

To get a better picture of the effect of pressure on the rate of reaction it is helpful to plot the rate of temperature change versus time as shown in Figure 5.70. This figure reveals that the results for the different setups followed the same trend represented by the solid line. Additionally, the rate of temperature change was higher at shorter times than at longer ones. This observation reveals that the reaction proceeded faster at initial stages as shown previously in DSC curves. However, the results are not conclusive as to the pressure effect on the TPU polymerization. The reason is based on the fact that the pressure applied by using the vessels was too small to conclude the effect of pressure on the kinetics.

Figure 5.70. Rate of change of Temperature at different Pressure Levels for a SPBA system with 0.0151% of catalyst.
It is important to mention that the pressure generated in the extrusion process is higher than the ones generated in home made vessels used in these studies. Therefore, a pressure effect on the extrusion process should be included. The pressure generated by other means (i.e. compression molding) were limited because of the liquid nature of the reacting mass that flowed out of the vessel through small clearances between the lid and the cylindrical cavity.

The effect of pressure on the kinetic equation can be expressed with an exponential equation. The dependence of rate constant on pressure was found to be exponential in previous research\textsuperscript{154}. Additionally, the pressure influences the viscosity of the system, and variations in viscosity cause variations of diffusivity, that in the end will affect the reaction rate. Therefore, since viscosity depends exponentially on pressure it is expected that the rate constant also depends exponentially on pressure. The modified version of equation 5.12. is as follows:

$$\frac{d\alpha}{dt} = k^* \left[ \frac{1}{b} n \right]^{-1} (1 - \alpha)^n$$

$$k^* = k_i k''''$$

$$k^* = \left[ A_1 \exp \left( -\frac{E_{a1}}{RT} \right) + A_2 \exp \left( -\frac{E_{a2}}{RT} \right) \right] \left[ \text{Stab} \ / \ \text{Cat} \right]^{-n} \left[ S_0 \exp \left( E_{as} \gamma \right) \right] \left[ P_0 \exp \left( E_{ap} P \right) \right]$$

(5-13)

where $k''''$ is the modified diffusional rate constant, that includes the effects of shear and pressure, $S_0$ and $P_0$ are the prexponential factor of the shear and pressure dependence respectively, and $E_{as}$ and $E_{ap}$ are the activation energy of the reaction rate under shear and pressure respectively.

This empirical equation can be only proposed since the numerical coefficients could not be obtained from the experimental data as discussed before.
5.3. Kinetics of TPU in an Extruder – Reactive Extrusion Process

The kinetics of the TPU polymerization in an extruder was investigated for the combined effects of processing conditions including, pressure, shear and Temperature and screw configuration on the extent of TPU polymerization.

The different conditions used in the experiments, as well as the molecular weights determined from GPC characterization are shown in table 5.5. The results reveal that as the screw speed increases, the temperature, die pressure and the corresponding molecular weight also increases as shown in the table 5.5. Moreover, die with 2 holes in comparison to a 3-hole increases the pressure, temperature and resultant molecular weight of the TPU. When the temperature profile of the barrel is 120 °C in all zones, the molecular weight of the TPU is less than one with variable temperature profile. Therefore, the extrusion temperature profile with high temperature produces higher molecular weight of the TPUs because the reaction rate at later stages of the polymerization reaction accelerates.

The effect of the different screw configurations on the TPU polymerization can be investigated by using the screw configuration 1, which has mixing and back flow elements, ad configuration 2 that has mostly a fully intermeshing screw configuration of closed channels with no mixing or backflow. Table 5.5. shows that the molecular weights and polydispersity index (PDI) of the TPUs obtained by using the screw configuration 2 are lower than those obtained with the configuration 1. These results reveal that mixing and back flow contribute to increase the overall rate of reaction because of increased dispersive and distributive mixing as well as longer residence time.
Table 5.5. Molecular Weight Characterization of the Reactive Extrusion of TPU at different processing conditions.*

<table>
<thead>
<tr>
<th>Screw Configuration</th>
<th>Temperature Profile</th>
<th>Screw Speed</th>
<th>Holes in Die</th>
<th>Temperature at Die (°C)</th>
<th>Pressure at Die (MPa)</th>
<th>Sample Name</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>Polydispersity (PDI)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reactive Blending (120-120-120-120-100-120-130-135-140) °C</td>
<td>50</td>
<td>3</td>
<td>148</td>
<td>14.0</td>
<td>TPU 1</td>
<td>53000</td>
<td>98000</td>
<td>1.8</td>
</tr>
<tr>
<td>Screw Configuration 1</td>
<td></td>
<td>100</td>
<td></td>
<td>155</td>
<td>15.0</td>
<td>TPU 2</td>
<td>65000</td>
<td>123000</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td></td>
<td>170</td>
<td>16.0</td>
<td>TPU 3</td>
<td>70000</td>
<td>126000</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>120 °C in all zones</td>
<td>50</td>
<td>2</td>
<td>162</td>
<td>18.0</td>
<td>TPU 4</td>
<td>66000</td>
<td>122000</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>3</td>
<td>135</td>
<td>11.0</td>
<td>TPU 5</td>
<td>49000</td>
<td>89000</td>
<td>1.8</td>
</tr>
<tr>
<td>Screw Configuration 2</td>
<td>Reactive Blending (120-120-120-120-100-120-130-135-140) °C</td>
<td>25</td>
<td>3</td>
<td>136</td>
<td>2.0</td>
<td>TPU 6</td>
<td>54000</td>
<td>98000</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td>138</td>
<td>3.0</td>
<td>TPU 7</td>
<td>13000</td>
<td>20000</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>120 °C in all zones</td>
<td>50</td>
<td>2</td>
<td>132</td>
<td>5.0</td>
<td>TPU 8</td>
<td>17000</td>
<td>25000</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>3</td>
<td>137</td>
<td>5.0</td>
<td>TPU 9</td>
<td>22000</td>
<td>35000</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>120 °C in all zones</td>
<td>50</td>
<td>3</td>
<td>130</td>
<td>1.0</td>
<td>TPU 10</td>
<td>22000</td>
<td>32000</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td></td>
<td>131</td>
<td>1.0</td>
<td>TPU 11</td>
<td>24000</td>
<td>37000</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td></td>
<td>135</td>
<td>1.0</td>
<td>TPU 12</td>
<td>15000</td>
<td>23000</td>
<td>1.5</td>
</tr>
</tbody>
</table>

* Molecular weights based on Polystyrene standards
DSC studies of the different TPUs were performed to determine the effect of the processing conditions on the thermal properties of the TPU. Figures 5.71. and 5.72. show the two DSC scans of the TPUs produced from the twin screw extruder. The first scan of the samples obtained from the extruder are shown in Figure 5.71. and the second scan of the samples quenched in liquid nitrogen are shown in Figure 5.72.

Figure 5.71. First DSC scans for the TPUs Produced via Reactive Extrusion under different Processing Conditions.
Figure 5.72. Second DSC scan for the TPUs Produced via Reactive Extrusion under different Processing Conditions.

Figure 5.72. demonstrate that the glass transition temperature ($T_g$) is located at identical temperature. Therefore, there is no influence of the different processing conditions on the $T_g$. Figure 5.71. shows that some of the samples (TPU1, TPU5, TPU8 and TPU9) have an endothermic peak around 25-50°, which is associated with SS ordering. These TPUs, (except TPU9) were processed at low screw speed (50 rpm) as compared to the others. Reduced speed meant that the aforementioned blends had higher residence time in the extruder than the others. However, some of the TPUs were process at lower screw speed than 50 rpm speed that resulted in increased residence time. These blends do not show the endothermic peak between 25-50 °C. Consequently, it is very difficult to point out the precise cause of the endothermic peak in the DSC scans of some of the blends.
It is observed that the glass transition temperature did not change after quenching and that all other transitions almost disappeared as shown in Figure 5.72. In conclusion, even though the TPUs have different molecular weights their $T_g$ is at the same location. All other thermal transitions observed in Figure 5.71 are attributable to processing history and not to intrinsic structural features of the samples.

5.4. Kinetics of TPU in presence of PVC

The previous studies of our research group\(^6\) revealed the effect of PVC on the kinetics of a SPBA based TPU, polymerized in situ with PVC. The results suggested that the thermal degradation of unstabilized PVC inhibits the TPU polymerization. It was also found that once PVC thermal degradation was controlled by using stabilizer, the PVC acted as a catalyst. In this section, two TPU systems with different polyols were used to investigate the effect of their miscibility with PVC on the kinetics of in situ polymerization. The polyols used in this study are Poly (Butylene Adipate) (PBA) and Poly (Hexamethylene Adipate) (PHA).

The isothermal DSC was conducted to study the TPU polymerization in presence of PVC. The DSC scans of the TPU in situ with PVC are shown in Figure 5.73 and 5.74 for different PVC/TPU compositions for SPBA and SPHA, respectively. Similarly, as shown in Figures 5.73 and 5.74, the plots of 50/50 PVC/TPU composition at different temperatures and stabilizer concentration.

From the calorimetric curves obtained from the DSC, the curves of fractional conversion versus polymerization time can be calculated as shown in Figures 5.75 -5.78 for the PVC/TPU reactive blends at different polymerization conditions. For both PVC/TPU blends based on PBA and PHA, higher temperatures increased the reaction rate and final conversion after 30 minutes. Similarly, the catalysts increased the reaction rate of
the PVC/PBA blend with all the compositions. On the other hand, the effect of addition of PVC was similar to the use of catalyst because of the electrophilic nature of PVC. However, it was observed that the reaction rate decreased with increasing PVC content at low catalyst concentration. For instance, the blend with 75% of PVC exhibited slower reaction rate than that of TPU.

This dual behavior may be originated from two factors. As explained by Parnell\textsuperscript{6}, the first one is a catalytic effect that increases the reaction rate (i.e. 25/75 composition) because of the additives and impurities present in PVC that have a positive catalytic effect on the TPU polymerization. The second one is related to the PVC degradation that yields HCl with had a negative catalytic effect on the TPU polymerization. This process happened even with the addition of T31 that is consumed for the stabilization of PVC, reducing it catalytic effect for TPU polymerization. Consequently, the polymerization rate was reduced or even inhibited.

![Figure 5.73. Isothermal DSC Scan for the TPU Polymerization with different PVC/TPU blend composition. SPBA system – 0.002% Stabilizer](image-url)

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Figure 5.74. Isothermal DSC Scan for the TPU Polymerization with different PVC/TPU blend composition. SPHA system - 0.002% Stabilizer.

Figure 5.75. Experimental and Predicted Isothermal DSC Conversions of the SPBA based PVC/TPU 50/50 blend composition polymerized at 0.002% of Catalyst at different Temperatures.
Figure 5.76. Experimental and Predicted Isothermal DSC Conversions of the SPHA based PVC/TPU 50/50 blend composition polymerized at 0.002% of Catalyst at different Temperatures.

Figure 5.77. Experimental and Predicted Isothermal DSC Conversions of the SPBA based PVC/TPU 50/50 blend composition polymerized at 0.002% of Catalyst at different Temperatures.
Figure 5.78. Experimental and Predicted Isothermal DSC Conversions of the SPHA based PVC/TPU 50/50 blend composition polymerized at 0.002% of Catalyst at different Temperatures.

The reaction rate of the PVC/PBA blend with all the compositions. On the other hand, the effect of addition of PVC was similar to the use of catalyst because of the electrophilic nature of PVC. However, it was observed that the reaction rate decreased with increasing PVC content at low catalyst concentration. For instance, the blend with 75% of PVC exhibited slower reaction rate than that of TPU.

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PVC, reducing its catalytic effect for TPU polymerization. Consequently, the polymerization rate was reduced or even inhibited.

The kinetic data were fitted to the model given in equation 5-11 with least squares linear method. Instead of using \(k_2\) a new constant (\(k_3\)) is added to the equation in order to include the effect of the addition of PVC, as shown in the equation 5-14.

\[
\frac{d\alpha}{dt} = \left( A_1 \exp\left(-\frac{E_{a1}}{RT}\right) + A_3 \exp\left(-\frac{E_{a3}}{RT}\right) [\text{SPVC }]^d \right)C_6^{n-1} (1 - \alpha)^n \quad (5-14)
\]

where, [SPVC] is the concentration of PVC and stabilizer, and \(A_3\) and \(E_{a3}\) are the preexponential factor and the activation energy of the reaction when PVC and stabilizer are combined.

The kinetic parameters were determined by using the same procedure as described for the TPU polymerization in the section 5.1.2., Figures 5.79-5.84. show the curves for the determination of the kinetic parameters.

Figure 5.79. Logarithmic Plots of DSC conversion rate vs. remaining conversion for the SPBA based PVC/TPU 50/50 blend composition polymerized at 0.002% of Catalyst at different Temperatures.

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Figure 5.80. Logarithmic Plots of DSC conversion rate vs. remaining conversion for the SPHA based PVC/TPU 50/50 blend composition polymerized at 0.002% of Catalyst at different Temperatures.

Figure 5.81. Logarithmic Plots of DSC conversion rate vs. remaining conversion for various SPBA based PVC/TPU blend compositions polymerized at 140 °C with 0.002% of catalyst concentration.
Figure 5.82. Logarithmic Plots of DSC conversion rate vs. remaining conversion for various SPBA based PVC/TPU blend compositions polymerized at 140 °C with 0.002% of catalyst concentration.

\[ \ln(k_3) = \ln(A_3) - \frac{E_{a3}}{RT} \]

SPBA
- \( A_3 = 8.23 \times 10^{-2} \)
- \( E_{a3}/R = 9.32 \times 10^2 \)
- \( r^2 = 0.58 \)

SPHA
- \( A_3 = 7.39 \times 10^{-2} \)
- \( E_{a3}/R = 9.07 \times 10^2 \)
- \( r^2 = 0.59 \)

Figure 5.83. Logarithmic Plots of DSC conversion rate vs. remaining conversion for the SPBA based PVC/TPU 50/50 blend composition polymerized at 0.002% of Catalyst at different Temperatures.
Figure 5.84. Logarithmic Plots of DSC conversion rate vs. remaining conversion for the SPHA based PVC/TPU 50/50 blend composition polymerized at 0.002% of Catalyst at different Temperatures.

The experimental data shows that the curves of rate of reaction versus complementary conversion deviated from the linear behavior after a critical conversions ranging from 0.8 to 0.95, depending on the polymerization conditions used. The previous research\(^6\) suggested that the reaction was diffusion control above the critical conversion, only the linear section of the data are used to fit the kinetic model. The orders of reaction (n in Equation 5-14) for SPBA and SPHA in presence of PVC are the same as obtained for the neat TPU polymerization. Any effects of the PVC on the TPU polymerization must be reflected on the value of the overall rate constant k, as shown in the previous research\(^6\). In fact, as it is observed in Figures 5.81. and 5.82 the overall rate constant depends on both temperature and PVC composition. However, it was not possible to separate the effect of temperature from the effect of PVC in the same way.
as the effect of temperature and catalyst in TPU polymerization, due to the non-linear character of the regressions.

Figures 5.85. and 5.86. show the experimental results of PVC/TPU 50/50 blend with different amounts of catalyst. It is apparent that T31 at 50/50 PVC composition with 0.006% of the stabilizer overcomes the inhibiting effect of PVC degradation product (HCl). Specifically, the hydrogen chloride consumes the stabilizer (T31) and resulting in its action as catalysts for the TPU polymerization until its concentration is enough to act as catalysts. This is the reason why the reaction rate is same below the critical stabilizer concentration.

Figure 5.87. and 5.88. show the conversion curves for three PVC/TPU blends with a higher concentration than the critical concentration of T31. The inhibit effect reduced thus all the different compositions have a higher conversion than that of catalyzed neat TPU. In Figures 5.87. and 5.88. it is clear the catalytic effect of T31-stabilized-PVC on TPU polymerization and their reactive blends. It is observed that the reactive blend with low PVC concentration has higher conversion than the ones with high PVC concentration. This phenomenon is due to the consumption of a constant amount of T31 that is divided into stabilization and catalysis. In other words, the blend with higher concentration of PVC required more T31 for stabilizing the PVC and catalyzing the TPU polymerization than one with lower PVC concentration.

The influence of different polyols on the TPU polymerization kinetics in presence of PVC is very little. As shown in the chemical formula in Table 3.1., the series of polyols used in this study show similar solubility with PVC as a plasticizer because of the number and structure of carbonyl groups. Therefore, there is no significant difference in the kinetics of TPU polymerization with different polyols due to the presence of PVC.
<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0005%</td>
</tr>
<tr>
<td>5</td>
<td>0.002%</td>
</tr>
<tr>
<td>10</td>
<td>0.004%</td>
</tr>
<tr>
<td>15</td>
<td>0.006%</td>
</tr>
<tr>
<td>20</td>
<td>0.009%</td>
</tr>
</tbody>
</table>

Figure 5.85. Experimental and Predicted Isothermal DSC Conversions of the SPBA based PVC/TPU 50/50 blend composition polymerized at 140 °C with different Catalyst concentrations.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0005%</td>
</tr>
<tr>
<td>5</td>
<td>0.002%</td>
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<td>10</td>
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<tr>
<td>15</td>
<td>0.006%</td>
</tr>
<tr>
<td>20</td>
<td>0.009%</td>
</tr>
</tbody>
</table>

Figure 5.86. Experimental and Predicted Isothermal DSC Conversions of the SPHA based PVC/TPU 50/50 blend composition polymerized at 140 °C with different Catalyst concentrations.
Figure 5.87. Experimental Isothermal DSC Conversions for various SPBA based PVC/TPU blend compositions polymerized at 140 °C with 0.009% of catalyst concentration.

Figure 5.88. Experimental Isothermal DSC Conversions for various SPHA based PVC/TPU blend compositions polymerized at 140 °C with 0.009% of catalyst concentration.
6.1. Model studies of Reactive Blending of TPU in-situ with PVC in a Batch Mixer

6.1.1. Stage 1: PVC compounding and plasticization

The melt blending of PVC and polyesters was studied to obtain the “optimal conditions” for producing homogeneous blends without thermal degradation. It was found that processing variables such as temperature and fill factor in an internal mixer play an important role in the incorporation of ingredients and good mixing. However, the mixing time and rotor speed did not have a significant influence on incorporating polyols into PVC. The optimal conditions obtained for the blending of PVC and polyester in a batch mixer was used to establish the conditions for reactive blending in the batch mixer and the counter rotating intermeshing twin screw extruder.

The thermal analysis conducted by DSC studies showed that the use of polyester polyols resulted in partially miscible or immiscible blends depending on the varying composition of PVC. The increase in the number of methylene groups between the carbonyl groups of the polyester polyols (PBA to PHA) did not significantly affect their miscibility with PVC. However, the introduction of a pendant group into the polyol chain, such as PPA, formed the immiscible blends, as compared to the addition of PBA to PVC. In addition, the blend of PVC with a polyether polyol, such as a PVC/PPG blend, created immiscible blends due to the presence of a pendant groups in the PPG chain that hinders the ether
group. The shift of the glass transition temperature of the blends of polyester polyols with small amounts of BDO and PVC was associated with the plasticization effects for the PVC.

Consistent with the findings of the thermal analysis, a SEM micrographs of the PVC/polyester polyol blends based on PBA and PHA demonstrated homogeneous one-phase morphology. However, the PVC micro grains were visible in the SEM micrographs of the PVC/PPA blend at a low PVC concentration and in immiscible blends, such as the PVC/PPG blend.

6.1.2. Stage 2: In Situ Polymerization of the TPU with PVC

The polymerization in situ of TPU based on PBA and PHA with PVC produced partially miscible blends. The PBA, PHA, and PPA polyester polyols tend to form miscible blends, as shown by the presence of one glass transition in DSC studies. However, the broadness of the transition reveals the heterogeneous and multiphase morphology of these blends. Conversely, the presence of two glass transitions in DSC scans revealed that the blends of PVC with the polyether (PPG) are immiscible.

The PVC/TPU reactive blends based on PPA did not produce the TPU with a high molecular weight. The presence of the methyl pendant group seems to hinder the ester groups. In addition, their mechanical properties were inferior to those of the PBA and PHA based blends, showing no elastomeric behavior.

The miscibility of the PVC/TPU blends was also investigated by FTIR. The studies of the FTIR spectra revealed that blending of PVC with the TPU hindered the intra-molecular hydrogen bonding, favoring the interaction between PVC and TPU (see for instance, PVC/TPU (LPBA) REX blend), and thus resulting in a reaction induced phase separation at the late stage of the reactive blending process.
The SEM observations of the PVC polyester blends revealed homogeneous one phase morphology. In contrast, TEM microscopy exposed the multiphase morphology of the PVC/polyester polyol blends, in agreement with DSC findings. The effect of reactive blending on the morphology of the PVC/polyester blends is demonstrated in the case of PPA based blends. The PVC/PPA blends at low PVC content showed PVC micro grains in SEM that are not visible after reactive blending.

The reactive blending of PVC with TPU based on different MDIs resulted in blends with similar thermal properties. However, the insolubility of the blends based on CDMDI in THF demonstrated the presence of chemical crosslinks. Additionally, as a consequence of different NCO functionality and reactivities, the TPU segment distributions were different for the different blends with different mechanical behavior.

The morphology, thermal and mechanical properties of reactive blends of PVC with TPU (PBA and PHA based) were compared to their analogous melt blends to determine the effects of processing conditions on their properties and performance. The comparative studies showed that the properties of the reactive blends were better compared to those of the melt blends.

The thermal analysis showed that both reactive and melt blends displayed a single and broad glass transition region. Nevertheless, the $T_g$ of the PVC/TPU(PBA) reactive blend was lower, demonstrating a better plasticization of the PVC by the low molecular weight polyols, as compared to the plasticization of PVC with TPU with high molecular weight.

The thermal stability of the reactive blends was also better than that of the respective melt blends. This was due to less thermal degradation in the reactive blends.
than the melt blends, because of the low processing temperature for the reactive blending process.

The tensile strength and elongation at break of the reactive blends were better than those of the melt blends. At this point, the reactive blending process of PVC with TPU with optimal processing conditions is an alternative, novel method superior to the melt blending process.

6.2. Reactive Extrusion of TPU in-situ with PVC in a Twin Screw Extruder

The PVC/TPU reactive blends were produced successfully via REX. The counter-rotating twin screw extruder was equipped with a screw configuration intended to intensify dispersive or distributive mixing where required. The auxiliary equipment consisted of feeders that were calibrated before every experiment. The PVC and solid MDI were fed as solids, while the polyols and LMDI were fed using reciprocating pumps for low flow-rate and home-made setups. All feeders were calibrated to give accurate feeding and to comply with the stoichiometry required for the polymerization of a high molecular weight TPU in-situ with PVC.

The REX processing conditions were similar to those used for the internal mixer reactive blending. The principal difference was that the temperature profile along the extruder was gradually increased from 120 °C at the feeding port to 140 °C at the die. This facilitated the exit of the high viscosity blends out of the extruder.

The thermal properties of the reactive blends obtained by REX were similar to those of the blends obtained by batch reactive blending. Nevertheless, the molecular weights and mechanical properties of REX blends were higher than those of the batch reactive blends. Therefore, REX processing enhanced the TPU polymerization as compared to batch process. Additionally, the FTIR spectra showed that the degree of
interaction between the PVC and TPU was higher in the extruded blends than those in the internal mixer.

The two phase morphology of the reactive blends was studied by TEM. The observed phase morphology exhibited the dispersion of a PVC-SS phase in a HS matrix at low PVC concentration. A phase inversion occurred at a 50% TPU composition, where the TPU domains were dispersed in the PVC-SS matrix. Morphology of the extruded reactive blends are similar to the ones obtained from the internal mixer. However, a higher degree of phase mixing was attained in the REX process, compared to the batch mixer, showing the effects of higher shear, temperature, and pressure on the final morphology of the reactive blends.

6.3. Kinetics of TPU Polymerization

The kinetics of TPU polymerization was investigated using thermal and rheological methods. The thermal methods included adiabatic temperature rise and isothermal differential scanning calorimetry. The isothermal frequency sweep was conducted for the rheological method.

The TPU polymerization of TPUs based on different monomers was characterized with an Arrhenius type, phenomenological rate law. The kinetic parameters obtained for the different TPU systems agreed reasonably well with each other, as well as with the previous literature. The data calculated by the empirical kinetic model matched with the experimental data over a wide range of polymerization temperatures and T31 (catalyst) concentrations.

In general, increasing the length of the polyester chain increased the reaction rate of TPU. On the other hand, the presence of MDI isomers (2,4) reduced the reaction
rate due to different reactivity. Additionally, decreasing the NCO content decreased the reaction rate because of a reduced number of reactive groups.

The individual effect of processing conditions, such as shear and pressure on the kinetic model, was studied by using a rheometer and two home-made pressure vessels mounted with ATR. The results of the rheokinetic studies revealed that all TPUs under consideration showed similar behavior. It was found that at the beginning of the reaction, the modulae changed drastically with respect to time. However, by increasing the reaction time, the conversion at the steady state was reached depending on the frequency. To analyze the rheokinetic results, the crossover of the modulae (\(G'\) and \(G''\)) was taken to be the completion of reaction. The module (\(G'\) or \(G''\)) corresponding to the crossover point was independent of the shear rate. But the time to reach the crossover point decreased with an increasing shear rate. As a consequence, the shearing increased the reaction rate of the polymerization of TPU. Because of the limitation of applied pressure on the vessel, the effect of pressure was not found. However, a significant effect of pressure on the reaction in the twin screw extruder might be found in the variation of molecular weight of the TPU due to the high pressure generated during the reactive extrusion process.

The studies of the effect of PVC on the kinetic of TPU polymerization revealed that a sufficient amount of stabilizer/catalysts will give two benefits for less PVC degradation and catalyzing the TPU polymerization simultaneously. The possible reason is that below a critical concentration of catalyst, the product of the degradation of PVC consumes the stabilizer, leaving almost no catalyst available for TPU polymerization acceleration.
Finally, when the TPU polymerization was conducted in a twin screw extruder, the combined effects of temperature, pressure, and (shear) on the molecular weight of TPUs were observed. TPUs with molecular weights higher than those TPUs of the quiescent one-shot method were obtained. Additionally, the introduction of dispersive mixing and back flow elements configuration also increased the molecular weight and mechanical properties due to the intensive dispersive and distributive mixing. This agrees well with the studies of kinetics conducted by ATR and rheokinetic studies.
REFERENCES


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