POLYESTER BASED HYBRID ORGANIC COATINGS

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POLYESTER BASED HYBRID ORGANIC COATINGS

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ABSTRACT

Polyesters are a class of polymers widely used in organic coatings applications. In this work, four types of organic coatings based on polyester polyols were prepared: UV-curable polyester/poly(meth)acrylate coatings, thermal curable polyester polyurethane-urea coatings, thermal curable non-isocyanate polyurethane coatings, and UV-curable non-isocyanate polyurethane coatings.

Polyester/poly(meth)acrylate block copolymers are synthesized using a combination of polycondensation and Atom-Transfer Radical Polymerization (ATRP). All block copolymers are characterized by means of Nuclear Magnetic Resonance (NMR) and Gel Permeation Chromatography (GPC). In the case of unsaturated-polyester-based block copolymers the main chain double bond in the polyester backbone remains almost unaffected during ATRP. The unsaturated block copolymers are crosslinkable and can form networks upon photo-irradiation in the presence of a suitable photoinitiator. These copolymers might be interesting candidates for coatings with better overall properties than those based on neat polyesters.

Thermal curable polyester polyol based Polyurethane-Urea (PUU) coatings were formulated using Partially Blocked HDI isocyanurate (PBH), Isophorone Diamine (IPDA), and polyester polyol. As a comparison, the polyurethane coatings (PU) without adding IPDA were also prepared. The mechanical and viscoelastic properties of the PUU and PU coating were investigated by using tensile test and Dynamic Mechanical Thermal
Analyzer (DMTA). It was found that PUU coating exhibited higher crosslink density, Tg, tensile modulus and strength than the corresponding PU coating.

Thermal curable non-isocyanate polyurethane coatings were prepared by using polyamine and cyclic carbonate terminated polyester. Cyclic carbonate terminated polyester was synthesized from the reaction of the carbon dioxide and epoxidized polyester which was prepared from the polyester polyol. The properties of the epoxidized and cyclic carbonate terminated polyester were characterized by Brookfield viscometer, NMR and Fourier Transform Infrared spectroscopy (FTIR).

UV-curable non-isocyanate polyurethane coatings were formulated by using Acrylated Polyester (APE) oligomer and Non-isocyanate Urethane Dimethacrylates (NUDMA) reactive diluents. The effect of the NUDMA on the viscosity of the APE oligomer was investigated by Brookfield viscometer. The photopolymerization kinetics of NUDMA reactive diluents were investigated by the real time FTIR. It was found that the polymerization conversion and maximum polymerization rate increase with increasing initiator concentration in the range from 0.5 % to 4.0 %. The formulation system containing both the APE oligomer and NUDMA reactive dilues showed higher polymerization overall conversion and maximum polymerization rate than APE oligomer.

After UV curing, the viscoelastic, tensile and thermal properties of the cured films were evaluated as a function of the reactive diluent by using DMTA, tensile test, Differential Scanning Calorimeters (DSC), and Thermal Gravimetric Analysis (TGA). In addition, coating properties such as pencil hardness, chemical resistance, impact resistance, and gloss were also investigated. It was found that crosslink density, storage and tensile modulus, pencil hardness, chemical resistance, gel content, total water
absorption, and Tg were directly proportional to amount of the reactive diluents. Compared to the commercial Ethylene Glycol Dimethacrylate (EGDMA) reactive diluent, the NUDMA reactive diluents show significant improvements in impact resistance and elongation at break properties.
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CHAPTER I

INTRODUCTION

Polyesters are widely used in coating applications, and generally synthesized by polycondensation reaction of various diacids and diols. Most of the polyesters used in the coating industry have low molecular weight (oligomer), and are amorphous, branched. The polyesters are usually crosslinked with isocyanates, melamine or epoxy groups via the thermal curing process and used for coating applications.

Polyesters based organic coatings have appreciable mechanical properties such as high tensile strength together with flexibility. But the presence of ester linkages in the backbone of polyesters makes them vulnerable to hydrolysis. On the other hand, poly(meth)acrylates are better abrasion resistant, hydrolytically stable with superior mechanical properties. Hence, to improve the hydrolytic/oxidative stability and to achieve chemical abrasion resistance properties, it is highly desirable to prepare polyesters and poly(meth)acrylates hybrid organic coating. But there is no report of the synthesis of block copolymers of polyesters with (meth)acrylates in which polyesters are synthesized by reacting small-molecular-weight diacids and diols. Thus, the first focus (Chapter III) of this work was to synthesize different block copolymers of Unsaturated and Saturated Polyesters (UPE and SPE, respectively) with (meth)acrylates. This block copolymer has well-defined molecular weight and narrow polydispersity by combination
of condensation polymerization and ATRP. This work also shows that the unsaturation present in the main chain of the polyesters is almost unaffected during ATRP. The synthesized unsaturated polyester/(meth)acrylate block copolymers can form crosslinked networks upon irradiation. These copolymers might be interesting candidates for coatings with better overall properties than those based on neat polyesters.

Polyester based polyurethane coatings have wide applications in wood, automotive, industrial, and coil coatings due to their high elasticity, toughness, and abrasive properties. Typically, polyurethanes are obtained by the reactions of polyisocyanates with polyols.

Compared with polyurethane coating, polyurea coating has less wide applications due to two major drawbacks. One is the faster curing of the polyurea, the reaction of the isocyanate and amine could be cured within seconds, which makes it good for only two-component spray coating application but limits its wide application for other coatings. Another drawback is that polyamine starting raw material for polyurea is very limited, and usually polyamine is based on the polyether amine. Thus, the second focus (Chapter IV) of this work was to prepare polyester polyol based Polyurethane-Urea (PUU) coatings. These PUU coatings were prepared by formulating polyester polyol, partially blocked isocyanate and isophorone diamine. Such PUU coatings were expected to have a longer pot life than conventional 2K polyurea or polyurethane coating due to the use of partially blocked isocyanate, a better mechanical property than polyurethane coating due to the existence of the extra urea function group, and a better abrasion resistance and chemical resistance property than polyether polyurea coating due to the existence of the ester function group.
One drawback of these polyester polyurethane coatings is their toxic property. The isocyanates starting materials for preparation of polyurethanes are toxic. Exposure to isocyanate can result in health effects such as skin irritation. Also, phosgene is a more toxic material, which is used for preparation of the isocyanate. Alternately, it was known that the carbamate group can be synthesized by the reaction of the primary amine with cyclic carbonate. This provides a useful way to obtain polyurethanes via a non-isocyanate method. Thus, the third focus of this work was to synthesize polyester based non-isocyanate polyurethane (NIPU) coatings by either thermal curing (Chapter V) or UV-curing (Chapter VI and VII).

Thermal curable NIPU are usually prepared from the reaction of polyamine and poly(cyclic carbonate). The poly(cyclic carbonate)s are usually prepared by the reaction of poly(epoxide)s under CO₂ in the presence of catalyst. Most of poly(epoxide)s for nonisocyanate polyurethane synthesis reported are low molecule monomers or polyether based oligomers. It is well known that polyester is a widely used polyol reagent to prepare polyurethanes. But, there is no report of the synthesis of nonisocyanate polyurethanes by using epoxidized polyester oligomer as starting material. Thus, chapter V was focused on synthesis of cyclic carbonate terminated polyester and thus preparation of NIPU.

UV-curable coatings offer many advantages, such as rapid curing, high-energy efficiency and low Volatile Organic Compound (VOC). Photopolymerization can occur at relatively low temperature with a nature of ultrafast curing, which makes UV-curable coating suitable for a widely application in the market sectors where temperature sensitive substrates are coated, like wood, paper and plastics. Most UV-curable coating
systems are free radical based on acrylated oligomers formulated with (meth) acrylate reactive diluents.

UV-curable polyester polyurethane coatings are usually prepared by formulating of the urethane acrylate oligomer with (meth)acrylate reactive diluents. Urethane acrylate is usually prepared by the reaction of a polyester polyl with a diisocyanate to yield an isocyanate terminated oligomer. These oligomers are then reacted with a hydroxyethyl acrylate monomer. UV-curable NIPU coating has never been reported, even though Non-isocyanate Urethane Dimethacrylate (NUDMA) monomers have been prepared, and their photopolymerization properties have been studied by photoinitiated differential scanning calorimetry. Thus, in this work, UV-curable NIPU polyurethane coatings were prepared by formulating of Acrylated Polyester (APE) oligomer with NUDMA. Chapter VI was focused on the investigation of photopolymerization kinetics of NUDMA and their formulations with APE by using real time Fourier transform infrared spectroscopy (FTIR). Chapter VII was focused on the investigation of the viscoelastic, tensile, thermal, and general coating properties.
2.1 Polyesters

Polyesters are polymers which contain the ester repeat units. Polyesters can be obtained by a wide range of reactions, and one of the important reactions is the polyesterification between dibasic acids and diols.

2.1.1 Polyesters history

The first polyesters were synthesized through the reaction of tartaric acid and glycerol by Berzelius in 1847 \(^1\). In 1901, glyptal polyesters were first produced by heating glycerol and phthalic anhydride. At first heating, linear polyester was formed through reaction of the two primary hydroxyl groups in glycerol, and by further heating; cross-linked polyesters were formed through reaction of the third alcohol. The first commercially available polyesters Glyptals™ were made by GE in the 1920s. Glyptals were initially developed for coating application and are now commonly known as alkyd resins. Glyptals were produced by the reactions of glycerol, phthalic anhydride, and the fatty acids of various oils. The double bonds in the fatty acids of the oils can be further
oxidized, giving a cross-linked product. Later on, other polyols such as Monoethylene Glycol (MEG), propylene glycol, pentaerythritol and acids such as maleic anhydride, Isophthalic Acid (IPA), Terephthalic Acid (TPA) were used to vary the properties of the alkyd resin.

In the late 1920s, W. H. Carothers and his collaborators began to make polyesters with the molecular weight between 2500 and 5000 from the reaction of aliphatic diacids with diols. The modern history of polyesters began in 1930s when he established the relationship between polymerization, conversion, functionality and gel point.

However, Carothers's polyesters had a low melting point and poor hydrolytic stability. In the early 1940s, Whinfield and Dickson synthesized polyesters by using aliphatic diols and aromatic acids, instead of aliphatic acids. Among these high-melting-point polyesters, Poly (Ethylene Terephthalate) (PET) and Poly (Butylenes Terephthalate) (PBT) are the most economically important types.

In the late 1930s, a new type of thermosetting resin based on unsaturated polyester was prepared by the polycondensation reactions involving mixtures of saturated and unsaturated dibasic acids or anhydrides with aliphatic diols. By dissolving this kind of unsaturated polyester in styrene, the thermosetting resin was formed. Now, the unsaturated polyesters have been widely used as important matrix resins for glass fiber reinforced composites.

In the late of 1950s and 1960s, with the development of the polyurethane chemistry and technology, the aliphatic polyesters were first found their commercial applications. Much attention was focused on block copolymer in 1970s, and high-performance wholly aromatic polyesters in 1980s. In the 1990s, much intensive research
was carried on the recyclable and/or biodegradable polyesters such as poly (lactic acid) (PLA), poly (ε-caprolactone) (PCL), poly (hydroxyalkanoates) (PHAs) because of the increasing environmental concerns. During this time, a new type of polyester hyperbranched polyaryl esters appeared. Hyperbranched polymers belong to the class of dendritic polymers which provide lower viscosity, better solubility, lower crystallinity, and a larger number of end function groups. Up to now, various polyesters including aliphatic polyesters, aromatic-aliphatic polyesters, wholly aromatic polyester have been prepared. And these polyester materials have been widely used as fibers, engineering plastics, high-performance polymers, thermosetting resins, elastomers as well as coatings. This dissertation deals with the polyester in coating fields only.

2.1.2 Synthetic methods

Generally speaking, there are three ways to prepare polyesters: equilibrium polyesterifications, nonequilibrium polyesterifications, and nonpolyesterifications. Equilibrium polyesterifications are equilibrium process because the equilibrium constant is generally low ($K \approx 4$ for carboxylic acid-alcohol reactions); these polyesterifications are usually carried out at high temperature through bulk polymerization via hydroxyl-carboxyl reactions, hydroxyl-ester, and carboxyl-ester interchange reactions. Nonequilibrium polyesterifications usually have high equilibrium constant ($K = 4700$ for acid chloride-phenol polyarylate synthesis); these polyesterifications are usually carried out at low temperature through solution polymerization by using highly reactive monomers such as acid chlorides. Nonpolyesterifications usually include epoxy-carboxyl reactions, ring-opening polymerization of cyclic esters, and some miscellaneous reactions.
2.1.2.1 Equilibrium polyesterifications

These reactions are usually carried out at high temperature (>180°C) via bulk polymerization in the presence of external catalysts which can be strong protic acids, metal oxides, metal salts, and organometallic compounds of titanium, tin, zirconium \(^{14}\). Among these catalysts, metal catalysts especially titanium alkoxides and tin compounds are preferred industrially because strong protic acids tend to catalyze side-reactions\(^{15,16}\). The small molecule formed during the reaction is usually removed to drive the reaction to completion by adding the toluene or xylene (5-15% mass) into the reaction medium by formation of the azeotropic mixture, and eliminated by applying the vacuum in the last step of the reaction\(^{17}\).

*Direct polymerizations:* These are the most widely used method for the synthesis of polyesters, which can be got by the reactions of diacids and diols, acid anhydrides and diols, or hydroxyl acids, as shown on Figure 2-1.
Transesterification polymerizations: These include hydroxyl-ester, carboxyl-ester, and ester-ester reactions. Among of these, the hydroxyl-ester reaction is the most important one; it is usually used for synthesis of aromatic-aliphatic and wholly aromatic polyesters, such as the PET and PBT polyester synthesis. Carboxyl-ester reaction is limited to synthesis of wholly aromatic polyesters, while ester-ester reaction is rarely used because the reaction is very slow.

2.1.2.2 Nonequilibrium polyesterifications

The nonequilibrium polyesterifications are irreversible reactions having the high equilibrium constant. These reactions usually involve acid chlorides or activated...
carboxylic acids with diols in solution. The nonequilibrium polyesterifications can yield high molecular weight polymers in the mild conditions in a short time without side reactions. So they are suited for synthesis aromatic polyesters having high melting point \(^{20}\), polyesters bearing function groups which are unstable at high temperature \(^{21}\). They are also useful for synthesis cyclic oligomers \(^{22}\).

*Acid Chloride-Alcohol Reactions.* Figure 2-2 shows a typical acid chloride-alcohol reaction which was carried out in THF or CH\(_2\)Cl\(_2\) in the presence of the tertiary amines at -10 to 30 °C \(^{23}\).

![Reaction Equation](image)

*Figure 2-2 Ester synthesis via acid chloride and alcohol reactions*

*Activation Polyesterification:* These reactions were carried out by using dicarboxylic acids and diols as reactants in mild conditions in the presence of the activating agents which can transform the dicarboxylic acid into a more reactive intermediate. Trifluoroacetic anhydride, 1,1'-carbonyldiimidazole \(^{24}\), carbodiimides \(^{25}\), tosyl \(^{26}\) and picryl \(^{27}\) chlorides, and phosphorus derivatives \(^{28}\) have been used as the activating agents. As shown in Figure 2-3, when N, N'-dicyclohexylcarbodiimide (DCC) was used as activating agent, condensation occurs between equimolar acids and alcohols, and produced water will react with carbodiimide groups to form the stable urea byproduct \(^{25}\). By using DCC as activating agent, low-molar-mass (Mn=5000-9000) aliphatic polyesters \(^{29}\), aromatic polyesters starting from hydroxyacids \(^{30}\), and poly(benzyl ester) dendrimers \(^{31}\) were synthesized.
Ester synthesis via acid and alcohol reaction by using N, N'-dicyclohexylcarbodiimide (DCC) as activating agent.

2.1.2.3 Nonpolyesterifications

**Epoxy-Carboxyl Reaction:** At lower temperature (100-120°C), this reaction takes places between the epoxides and carboxylic acids forming polyesters bearing pendant secondary hydroxyl groups \(^{32, 33}\) as shown in Figure 2-4. At higher temperature, side reactions happen, such as esterification of secondary hydroxyl groups or the ring-opening polymerization of epoxy groups. By using this kind of reaction, polyester powder coatings can be prepared \(^{34}\).

![Ester synthesis via acid and alcohol reaction](image)

**Cyclic Esters Ring-Opening Polymerization (ROP):** ROP of cyclic esters and related compounds is an alternative method for the synthesis of aliphatic polyesters, especially degradable aliphatic polyesters such as poly (lactic acid) (PLA), poly (glycolic acid) (PGA), and poly (ε-caprolactone) (PCL). Figure 2-5 shows PCL synthesis via the ROP of ε-caprolactone cyclic ester. Review is available on the cyclic esters ring-opening polymerization to prepare biodegradable aliphatic polyester\(^{35}\).

![Ester synthesis via epoxy-carboxyl reaction](image)
2.1.3 Raw materials

Most of polyesters in coatings fields have relatively low MWs and are amorphous and branched, and they must be cross-linked in order to form useful coating films. Figure 2-6 shows the most important polyols (diols and triols) and Figure 2-7 shows the most important polyacids used as raw materials for synthesis of polyesters. 

Figure 2-6 The important polyols used for polyesters synthesis

Neopentyl glycol (NPG)    Cyclohexanediolmethanol (CHDM)

Hexane diol (HD)

Trimethylolethane (TMP)    Pentaerythritol (PE)
All of the polyols used for polyester synthesis are aliphatic ones. NPG is the most widely used hindered diol, HD is the most widely used linear diol, and TMP is the most widely used triol.

NPG has excellent exterior durability because there is no labile β hydrogen with respect to the hydroxyl functionality. The two methyl groups increase the steric hindrance that imparts chemical resistance, stability towards hydrolysis and corrosion resistance. Its two primary hydroxyl functions ensure good reactivity not only during condensation but also during subsequent crosslinking.

CHDM esterifies more rapidly than NPG, and CHDM based polyesters give cured films with MF resins rapidly than NPG based polyesters, since the two primary hydroxyl groups are less hindered than NPG. The cycloaliphatic structure represents an excellent compromise between hardness and flexibility, which leads to thermal stability and low coloration during curing.
TMP and PE are used to make branched polyesters and increase the functionality of the polyester polyols. PE is little used in polyester resins since this gives resins with too much functionality and very high viscosities.

The polyacids used for polyester synthesis can be aliphatic or aromatic, linear or hindered. Isophthalic acid (IPA) is the most widely used aromatic acid and adipic acid (AA) the most widely used aliphatic acid. Aromatic polyacids are mostly used to increase the hardness of the polyesters. Phthalic anhydride (PA), isophthalic acid (IPA) and terephthalic acid (TPA) are three important aromatic diacids.

Phthalic anhydride (PA) in polyesters has a rather limitation in coatings applications due to its rather poor exterior resistance. PA based polyester coatings are considered to be used for base coating and not recommended for exterior or high performance coatings. Phthalic anhydride is frequently used for preparation of alkyd resins, where cost and not performance is the overriding factor.\(^3\)

Isophthalic acid (IPA) enables the mechanical properties, chemical resistance and hardness to be significantly improved compared to those obtained by using PA. IPA is less reactive than PA and it gives resins that are slightly less soluble. However, IPA remains one of the key products for polyester resins for surface coatings. With its higher melting point, it leads to longer reaction times and is slightly more difficult to use.

Terephthalic acid (TPA) further increases the heat resistance and mechanical properties of polyesters compared to either PA or IPA, but it also reduces the solubility of resins containing it and has a strong tendency towards crystallisation. TPA is less reactive than IPA and requires higher reaction temperatures and the use of catalysts.
Cyclohexane dicarboxylic acid (CHDA) represents an excellent compromise between hardness and flexibility. Corrosion resistance is better than with linear polyacids. Exterior resistance is also better than that from aromatic compounds or aliphatic/aromatic mixtures used for establishing the best compromise between hardness and flexibility. It has good solubility in most of the liquid diols used and its reactivity is quite good. It has poor dilution characteristics in solvents. Its thermal resistance is good and the ranges of colors of the resins obtained are good due mainly to its symmetrical structure.

Trimellitic anhydride (TMA) can be used to increase the functionality of the polyesters without significantly increase the viscosity and the molecular weight. It also can be used to prepare water dispersible polyester.

Hexahydrophthalic anhydride (HHPA) is used when a very high resistance at hydrolysis and excellent yellowing and external resistance are required. However it’s expensive and only used where its benefits justify the extra cost, such as water dilutable products, which require excellent hydrolytic stability, or for automobile coatings which need good color and light stability, such as white topcoats.

Adipic acid (AA) is one of the most frequently used linear diacids since it gives an excellent compromise in terms of technical performance and price. Diacids with much longer chains are significantly more expensive, thus they are limited to specific applications

2.1.4 Hydrolytic stability

The polyesters properties such as thermal properties, solubility, density, hydrolytic stability, and crystallinity are related with the polyester structure parameters such as the nature-aliphatic or aromatic in the polyester chains, ester group content, the
presence, nature and position of substitution on the monomer units, and the number and nature of comonomers. Among of polyester properties for coatings, the hydrolytic stability is the most important ones.

The ester linkage is susceptible to hydrolytic cleavage giving back carboxyl and hydroxy end groups. Most polyester undergoes degradation when heated in the presence of water. The degradation reaction is accelerated in the presence of acid or base catalysts (Figure 2-8). The structural parameters that govern the hydrolytic degradation of aliphatic polyesters have been examined by several authors for the design of biodegradable materials 39, 40. The hydrolysis susceptibility of polyester depends on the concentration of ester bonds, on the polyester polyol acidity, on the hydrophobicity of the glycol or dicarboxylic acid used for polyester synthesis, and on the steric hindrance around the ester groups. As a rule, polyesters from sterically hindered diols, diacids, or hydroxy acids and polyesters with aromatic units offer superior hydrolytic resistance. 2,2-Dimethyl-1,3-propanediol, hydrogenated bisphenol-A, α, α’-disubstituted hydroxyacids, and aromatic monomers are often used for this purpose. On the other hand, hydrolyzable/biodegradable polyesters are unhindered polymers: aliphatic–aromatic copolyesters or polyesters from α- or β-hydroxyacids, or from nonsubstituted aliphatic lactones.

![Ester group hydrolysis](image)

**Figure 2-8 Ester group hydrolysis**

The intensive research done in the last few years proved that the hydrophobicity of the glycol or of the dicarboxylic acid used for polyester polyol synthesis is one of the
most important parameters to improve the hydrolysis resistance of polyester. Thus, the
relative order of hydrolysis resistance of some usual polyester is exactly the order of
hydrophobicity \(^{41}\):

\[ \text{AA-HD} > \text{polycaprolactone} > \text{AA-BD} > \text{AA-DEG} \]

Some new developed glycols, which had hydrophobic groups and relatively high
steric hindrances, were used to improve the hydrolysis resistance of polyeste (BEPG;
Kyowa Hakko Kogyo Co. Ltd.), (see Figure 2-9).

![Figure 2-9 Diols with hydrophobic groups used in hydrolysis resistant polyester polyol synthesis \(^{41}\)]

2.1.5 Polyesters crosslinking mechanism

The formation of a paint film based on a polyester resin implies that it must be
crosslinked or hardened with an external crosslinking agent. Indeed, polyester resins do
not have sufficient film-forming properties except for thermoplastic polyesters. The
polyester can be crosslinked either through acid functionality or hydroxyl functionality.

2.1.5.1 Crosslinking through carboxylic groups

(a) With Melamine Formaldehyde (MF) resins. A melamine formaldehyde resin is
a member of the aminoplast family, which encompasses urea formaldehyde and
benzoguanamine formaldehyde resins that act as crosslinking agent. At a temperature
above 120°C, the following reaction is observed (Figure 2-10) \(^{38}\).
This reaction continues until a hard, completely crosslinked film is obtained. The ratios of polyesters and aminoplast resin vary within the range 60/40 to 80/20 depending upon temperature, nature of melamine resin and the final characteristics of the paint required. Resins of the hexamethoxymelamine type are used for temperatures starting from 150°C, and methylated, butylated or isobutylated formaldehyde resins can also be used. It should be noted that normally this reaction is not designed into polyesters, with the more traditional hydroxyl aminoplast reactions predominating.

(b) With an epoxide resins. This reaction is extensively used in powder coatings, more particularly in hybrid systems that are carboxyl functional polyester systems with epoxy resins, in ratios varying between 50/50 to 70/30. The following reaction takes place (Figure 2-11)

2.1.5.2 Crosslinking through the hydroxyl functions

(a) With an MF resins. The hydroxyl functionality in a polyester resin can react with the ether linkages of the melamine resins through transetherification reactions that
lead to the formation of volatile alcohols. This reaction is principally used in thermosetting liquid paints and is catalysed by acids such as para-toluene-sulphonic acid. In water-dilutable polyesters there is a potential problem of interaction between neutralising amines and the acid used for catalysis. The neutralising agent may generate significant surface defects. For this reason special blocked catalysts have been developed. The curing temperatures range from 120°C to 160°C for polyester/melamine ratios varying between 60/40 to 90/10. These can be found in the majority of thermosetting liquid systems, particularly when their very good compromise between performance and cost price is considered.

(b) With a blocked polyisocyanate. This system is particularly used in coil coating and automobile applications. It enables the hydroxyl functionality of polyester to be crosslinked with polyisocyanate using a single pack system. Crosslinking will only occur with a blocked polyisocyanate or with a mixed crosslinking system, such as melamine with a blocked polyisocyanate. The presence of urethane links enables the mechanical properties and exterior resistance to be improved when required. In liquid coatings, the polyesters used have hydroxyl values of about 110 to 180 mg KOH/g, whereas in powder coatings, polyesters have much lower hydroxyl content (ca. 40 to 110 mg KOH/g). The ratio of powder polyester / polyisocyanate varies from 60/40 to 80/20 for temperatures of 20 minutes at 170°C to 10 minutes at 200°C. The blocked polyisocyanate are either blocked polyisocyanate, for example with caprolactam, which leads to the release during curing of this blocking agent; or uretidiones, which are in fact diisocyanate dimers (such as the dimer of IPDI), which in these cases does not lead to the release of volatile compounds.
2.2 Hybrid polyesters

Hybrid materials usually contain at least two components. They can be organic-inorganic hybrids or organic hybrids. Hybrid polyesters are usually prepared to improve the hydrolytic stability and mechanical properties of the neat polyesters.

2.2.1 Organic-Inorganic hybrid materials

Also named ceramers, represent the natural interface between organic chemistry and inorganic chemistry. This fairly new class of materials, whose first examples date back to the eighties, may take advantage from characteristic properties of both organics and inorganics, such as high ductility and low temperature processing conditions typical of polymers and high modulus, thermal stability and low coefficient of thermal expansion distinctive of inorganic materials. Moreover, organic–inorganic hybrids may display synergistic properties with respect to the bare sum of the plain components’ features, such as remarkable improvements in mechanical, thermal, electrical, and magnetic properties. In particular, the nano-structured morphology of the inorganic domains strongly affects the physical behavior of the hybrids leading to interesting properties such as optical transparency. Due to the wide range of applicability fields of this class of materials, a number of hybrids are already commercially available. A wide spectrum of polymers are employed as the organic phase constituent of ceramers: Polydimethylsiloxane (PDMS), poly(tetramethylene oxide) (PTMO), polycaprolactone (PCL), polyoxazoline, poly(ether ketone), polyethylene oxide, etc. The hybrid inorganic phase is usually a metal oxide. Although many oxides are reported in the literature, such as those of titanium, zirconium, aluminium or cerium,
silicon oxide (silica) is the most widely applied in ceramers, owing to the easiness of its preparation.

2.2.2 Organic hybrid materials

Another class of hybrid polymers is composed of at least two kinds of organic polymers, normally incompatible, and again covalently bonded to each other. The main interest of these materials is to intimately combine the properties of the different kinds of polymers.

*Siliconised Polyester Hybrids.* Modification with organosilicone is one of the ideal methods available for improving the hydrophobicity and heat resistance of polyester. Poly(dimethylsiloxane)s (PDMS) is the most widely used organosilicone. Siliconised polyesters can be used in cookware applications. Coil coated architectural claddings is another major application of siliconised polyesters. In this application, the siliconisation imparts good external durability while choosing suitable polyesters with super exterior durability. The polyesters are usually prepared from the reaction of isophthalic or terephthalic diacids with polyols. The silicone/polyester hybrid was successfully prepared by substituting part of diol with low molecular weight hydroxyl-terminated poly(dimethylsiloxane) (PDMS) during the esterification reaction.

*Poly(acrylate-ester) Hybrids.* Tsavalas et al. carried out with a three component acrylic system of MMA, BA, and acrylic acid (AA) in the presence of a Bayerr Roskydal TPLS2190 unsaturated polyester resin. Latexes were obtained in which the polyester resin was grafted to the acrylic polymer, forming a water-based crosslinkable coating. Both emulsions and latexes were shelf stable for over 6 months, shear stable, and resistant to at least one freeze/thaw cycle. Resin to monomer ratios were
studied as high as 1:1 (wt:wt) and total emulsion solids as high as 45%. Monomer droplet and latex particle sizes were similar, suggesting predominant droplet nucleation. A high level of crosslinking during polymerization was observed in this particular hybrid system. Films, both homogeneous and hard, were achieved with exceptional adhesion. Electron microscopy showed the hybrid particle morphology has internal domains of polyester resin in an acrylic matrix. Kinetic studies showed that as resin content increased in comparison with monomer content, the polymerization rate decreased, suggesting retardive chain transfer as found with the alkyds.

_Epoxy-Polyester Hybrids._ Bisphenol A (BPA) epoxy is a typical epoxy which is used for preparation of epoxy-polyester hybrids. Epoxy-polyester hybrid is usually prepared from reaction of BPA epoxy and carboxylic acid–terminated polyester resins with Mn of a few thousand. Such formulations can be used to prepare hybrid powder coatings. Compared with epoxy powder coatings, epoxy-polyester hybrid coatings have better color retention and UV, but still do not have good exterior durability. The epoxy-polyester hybrid coating has wide applications including water heaters, fire extinguishers, radiators, and transformer covers\(^{34}\).

A variety of polyesters have been used to prepare epoxy-polyester hybrid coatings. Most are derived from neopentyl glycol (NPG) and terephthalic acid (TPA) with smaller amounts of other monomers to adjust the Tg to the desired level and give branching to increase the functionality above 2. An example is a polyester from NPG (364 parts by weight, 3.5 mol), TPA (423 parts, 2.55 mol), adipic acid (AA) (41 parts, 0.24 mol), and trimellitic anhydride (TMA) (141 parts, 0.74 mol)\(^{61}\). The acid number of the resin is 80
mg KOH per gram of resin. The relatively high trimellitic anhydride content increases functionality, compensating for the low (about 1.9) functionality of the BPA epoxy.

2.3 Atom Transfer Radical Polymerization (ATRP)

Atom Transfer Radical Polymerization (ATRP) is one kind of controlled living polymerization. It has been used to prepare polymers with well defined composition and functionalities. Convensional living polymerizations include cationic, anionic, and ring-opening polymerization. Compared to the conventional living polymerization, controlled/living radical polymerizations (CRP) is more tolerant of functional groups and impurities. The three most well-known CRP techniques are nitroxide-mediated radical polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT). Figure 2-12 shows the general mechanism for ATRP. A successful ATRP has very few termination reactions, and has constant radical concentration. The polymer chains grow uniformly.

![ATRP Mechanism Diagram](image)

Various monomers have been successfully polymerized using ATRP: styrenes, (meth)acrylates, (meth)acrylamides, dienes, acrylonitrile, etc. Ring-opening polymerization is also possible. ATRP can be used to polymerize a wide range of acrylates with various side chains (Figure 2-13).
ATRP of 2-hydroxyethyl acrylate (HEA) \(^{70}\) and glycidyl acrylate \(^{71}\) afforded well-defined functional polymers. ATRP of poly(t-Butyl acrylate) afforded polymer with a well-controlled fashion \(^{72}\). ATRP of monomers with long alkyd \(^{73}\) and fluorocarbon \(^{74}\) side chains afforded well-defined homopolymer and block copolymers. ATRP of allyl acrylate afforded polymers with cross-linking networks even at 0 °C \(^{75}\). The synthesis of various polymeric materials with novel functionalities, compositions, and architectures are schematically represented in Figure 2- 14 \(^{69}\).

![Structural formulas of monomers](image-url)
Figure 2-14 Schematic representation of controlled topologies, compositions, and functionalities and molecular composites prepared by ATRP

2.4 Polyurethane (PU) coatings

Polyurethanes (PUs) are a class of polymers containing urethane (-NH-CO-O-) linkage. The PUs were first discovered in 1937 [76]. They are usually prepared from the reaction of polyol and polyisocyanate. Polyurethane coatings have been widely used for wood, plastic, automotive, industrial, and coil coatings, especially for topcoats. Polyurethane coating have overall good mechanical properties including weathering, flexibility, chemical resistance, abrasion resistance [77]. Two-package (2-k) coatings are the largest volume of urethane coatings.
Isocyanates are highly reactive material. They can react with any active hydrogen containing compound. Urethanes are formed when isocyanates react with polyols (Figure 2-15).

\[
\text{R-NCO} + \text{R'-OH} \rightarrow \text{R-NH-CO-OR'}
\]

Figure 2-15 Urethane formation via the reaction of isocyanate with polyol

Polysocyanates used for preparation PU coatings can be aromatic, aliphatic in structure. The commonly used aromatic isocyanates are methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) (Figure 2-16). Compared to TDI, MDI has a lower volatility and thus lower toxicity.

Methylene Diphenyl Diisocyanate (MDI)  
Toluene Diisocyanate (TDI)

Figure 2-16 Aromatic isocyanate chemical structure

The commonly used aliphatic isocyanates include 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), bis(4-isocyanatocyclohexyl)methane (H12MDI), and HDI isocyanurate (Figure 2-17). In general, aromatic isocyanates react faster than aliphatic isocyanates and are less expensive. Aliphatic isocyanates have better color retention and exterior durability.
The polyols for PU coating are usually liquid with at least two hydroxyl groups. Such polyols include polyester polyol, polyether polyol, and acrylic polyol. Polyester urethane coatings are known for their chemical and solvent resistance, flexibility, superior adhesion, and abrasion and corrosion resistance. This broad range of properties is the result of the combination of soft (polyester) segments, which are responsible of the elasticity of the coating, and the hard (polyurethane) segments, which supply the strength of the films.\textsuperscript{78}

The reaction rates of urethane formation decrease in the following order: primary alcohols $>$ secondary alcohols $>$ 2-alkoxyethanols $>$ 1-alkoxy-2-propanols $>$ tertiary alcohols. Aromatic isocyanates react faster than aliphatic isocyanates. In general, it is normal to have high -NCO to -OH ratio (1.1:1.0), which produces harder and more solvent resistant coatings.\textsuperscript{34}
2.5 Non-isocyanate polyurethanes (NIPU)

Polyurethane coatings have wide applications in wood, automotive, industrial, and coil coatings due to their high elasticity, toughness, and abrasive properties. Typically, polyurethanes are obtained by the reactions of polyisocyanates with polyols. Usually polyester, polyether, or polycarbonate is used as polyol reagent. The isocyanate is either aliphatic or aromatic. Isocyanates are toxic material. Exposure to isocyanate can result in health effects such as skin irritation. Also phosgene is a more toxic material, which is used for preparation of the isocyanate.

Alternately, it was known that the carbamate group can be synthesized by the reaction of the primary amine with cyclic carbonate. This provides a useful way to obtain non-isocyanate polyurethanes (NIPU). Such non-isocyanate polyurethane was prepared from the reaction of five-member ring cyclic carbonates oligomers with diamines. Reaction products contain hydroxyl group in the β-position. This leads to the intermolecular hydrogen bonds formation in the NIPU. Intramolecular hydrogen bonds are formed within the structure of poly (hydroxy-urethane)s via the hydroxy group at the β-carbon atom and carbonyl group of the polyurethane chain (Figure 2-18):

![Figure 2-18 Intramolecular hydrogen bonds formation in the NIPU](image)

The hindrance of the carbonyl oxygen atom considerably lowers the susceptibility of the urethane group to hydrolysis. Moreover, polyurethanes exhibiting intramolecular
hydrogen bonds display chemical resistance up to twice greater in comparison with polyurethanes of similar chemical structure without such bonds. The tensile strength of non-isocyanate polyurethanes are similar to those of conventional isocyanate polyurethanes, but display chemical resistance of 30–50% higher and have significantly reduced permeability.

These polyhydroxyurethanes show some useful characteristics, such as high water absorption and thermal stability, because of the existence of the hydroxyl groups as well as no contamination of thermally unstable biuret and allophanate units.

2.5.1 Mechanism for NIPU preparation

The kinetic features of the interaction of cyclic carbonate groups with amino groups were studied by Garipov et al. The proposed 3-stage reaction mechanism is shown in Figure 2-19. The first stage is the nucleophilic attack of amine on cyclic carbonate. Amine attacks the carboxyl group in cyclic carbonates resulting in the formation of a tetrahedral intermediate. The second stage is the deprotonation of tetrahedral intermediate. The tetrahedral intermediate is attacked by another amine resulting in the removal of hydrogen ions. The last stage is the formation of final product. The carbon-oxygen bond is broken, which is favored by the strong electron-withdrawing effect of nitrogen atoms. The new generated alkyl-oxygen ion combines with hydrogen ions, resulting in a rapid formation of the product.
The reactivity of the amine towards cyclic carbonate could be accelerated by using protogenic solvents. When protogenic solvents is used for the reaction, the first stage occurs relatively rapidly due to the increase in the positively. The presence of the electron withdrawing substituent in the alkylene carbonates, which increases the electrophilicity of the carbonyl carbon, could also increase the reactivity of the reaction. The reaction can also be effectively catalyzed by use of triethylamine, piperazine, tetrabutylammonium bromide, glacial acetic acid, methanesulfonic acid. In most cases, five-member cyclic carbonates were used to react with aliphatic amines to form the product with a β-hydroxy-urethane (β-hydroxy-carbamate) group and no CO₂ is eliminated. The reaction of mono-substituted 1, 3-dioxolan-2-one with primary aliphatic amines leads to β-hydroxy- urethanes with two isomeric structures in the position of the hydroxyl group (Figure 2- 19). Studies on the distribution of isomers showed that the product consists of 70–75% of isomer bearing secondary hydroxyl group.
and 25–30% of isomer bearing primary hydroxyl group \(^{87, 89, 90}\). At temperature higher than 100°C the β-hydroxy-urethanes react with another molecule of the amine to form disubstituted urea. The investigations of the model reaction of 4-phenoxyethyl-1,3-dioxolan-2-one show that in the formation of β-hydroxy-urethane linkages mainly primary aliphatic amines take part \(^{91}\). In contrast, aromatic amines react with five-membered cyclic carbonates yielding aliphatic-aromatic amines accompanied by CO\(_2\) elimination \(^{87}\).

2.5.2 Reactants for NIPU preparation

Amines, as one of the key reactants for preparation of NIPU, are usually commercial available products. Amines could be either small molecules such as ethylenediamine and isophorone diamine, or oligomers such as polyoxypropylene diamine and JEFFAMINE® amines. Cyclic carbonates are another key reactants for preparation of NIPU. The Figure 2-20 list the commonly used cyclic monomers structure, which include mono-, bi-, tri-, and functional cyclic carbonate\(^{92, 93}\).
Five-member cyclic carbonates can be synthesized via several methods. The most common involves the reaction of an oxirane with carbon dioxide \(^{94}\). This reaction is highly facile and can be conducted at both atmospheric and elevated pressures with high yields \(^{95}\). Rokicki et al. \(^{96}\) conducted the reaction of an oxirane bearing an ammonium substituent with CO\(_2\) under atmospheric pressure. This reaction is frequently used to convert epoxy resins to cyclic carbonate resins \(^{92}\). Such reaction could be accelerated by using different catalysts such as LiBr, tetrabutylammonium bromide (TBAB) \(^{97}\). The catalysts for the reaction of epoxides and carbon dioxide had been reviewed \(^{98}\). Several proposed reaction mechanisms were reviewed, and quaternary onium salt was found to be the effective catalyst at atmospheric pressure of CO\(_2\). The proposed mechanism is shown in Figure 2- 21.
Figure 2- 21 Mechanism for quaternary onium salt catalyzed reaction between oxirane and CO$_2$ $^{98}$

Cyclo-carbonated soybean oil (CSBO) obtained from the reaction of epoxidized soybean oil (ESBO) and CO$_2$ has aroused research interest for preparing NIPU, because the ESBO is a renewable resource with low price. Rokicki et al $^{99}$ had reported that the epoxy group conversion can be 98% after 120 hours reaction. The reactants ratio is 100g ESBO + 0.4g 18-crown-6 + 0.6g KI, and no solvent was used. The reaction progress was monitored by means of FTIR and 1H NMR as well as by epoxy number determination. The disadvantage of the method is the use of the 6 MPa pressure. Wilkes et al $^{97}$ had reported that the epoxy group conversion was assumed to be 100% in 70 hours which was monitored by the FTIR. The reaction was using ESBO (200 g) and dried tetrabutylammonium bromide (13.52 g; 5 mol% with respect to epoxy groups) and carried out at 110°C. No solvent was used. Other catalysts such as NaI, LiBr, and benzyltrimethylammonium bromide showed very low to medium conversions under the same condition because of the bad solubility in ESBO. The advantage is that the reaction was carried out under atmospheric pressure. And the disadvantage of the method is the
use of large amount of the catalyst, and the conversion rate was determined by FTIR which can be used for a rough assessment, but not as a precise parameter for calculating degree of conversion of epoxy to carbonate groups. In Javni’s study, less amount of tetrabutylammonium bromide (TBAB) catalyst was used. The catalyst concentration is 0.025 mol or 3.4 g catalyst /100 g ESBO. The reaction of ESBO with CO₂ was carried out in different conditions by varying the reaction parameters including temperature and pressure. The progress of conversion of epoxy to carbonate groups was monitored by FTIR, GPC, viscosity, and epoxy oxygen content (EOC).

2.5.3 Preparation of NIPU

Various non-isocyanate polyurethane (NIPU) can be prepared by selecting different kinds of amines and cyclic carbonates starting materials. Linear NIPU can be obtained if bifunctional starting materials are selected, and crosslinked NIPU can be obtained if multi-functional starting materials are selected.

2.5.3.1 Linear NIPU

Linear polyurethanes can be obtained by the reaction of bifunctional five-membered aliphatic cyclic carbonates with diamines (Figure 2-22). In this method, in contrast to the production of typical commodity polyurethanes, no toxic isocyanates are used. The poly (hydroxyurethane)s with $M_n$ around 20,000 were prepared by the polyaddition of bis (cyclic carbonate) and diamine in the DMSO solvent at 70°C or 100 °C for 24h. The bis (cyclic carbonate)s were prepared in the lab by the reaction of bis(epoxide)s and atmospheric pressure of CO₂ in the presence of catalyst at 100 °C for 3days. The polyaddition of bis (cyclic carbonate) and diamine shows high
chemoselectivity, and can be performed in the presence of water, alcohol, and esters. Also, bis (cyclic carbonate) bearing ester group were used as a monomer to react with amine to form poly (hydroxyurethane)s without aminolysis of the ester group. The poly (hydroxyurethane) bearing the more secondary hydroxyl group is the major product. In another article, the model reaction was carried out by the reaction of bifunctional cyclic carbonate with diamine to investigate the ratio of secondary alcohol to primary alcohol moiety in the polyhydroxyurethane. In this model reaction, the equiv of 2,2-bis[p-(1,3-dioxolan-2-one-4-yl-methoxy) phenyl]propane (B5CC) reacts with dioxa-1,12-dodecanediamine (DODDA) in dimethyl sulfoxide (DMSO) at 70 °C for 30 days. The product polyhydroxyurethane contains the secondary alcohol moiety dominantly.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{R} \quad \text{NH}_2 + \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{R} & \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{N} & \quad \text{R} \quad \text{N} \\
\text{R} & \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{OH} & \quad \text{R'} \\
\text{O} & \quad \text{O} \\
\text{OH} & \\
\end{align*}
\]

Figure 2- 22 Reaction of bis-cyclic carbonate with diamine

Amino acid/alcohol such as L-lysine and L-lysinol were chosen as highly functionalized diamine to react with bifunctional five-membered cyclic carbonate to afford optically active poly(hydroxyurethane)s with \(M_n\) of 11,000-24,000. When the L-Lysine was chosen as diamine, the reaction was carried out in N,N-dimethylacetamide (DMAc) solvent in the presence of 1 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 2 equiv of sodium hydride at 70°C for 24 h to afford polyurethane bearing both
hydroxyl and carboxyl group. When the L-lysino1 was chosen as diamine, the reaction was carried out in N-methylpyrrolidone (NMP) at 70°C for 24 h to afford polyurethane bearing only hydroxyl group. These polyurethanes can be crosslinked to form corresponding gels by cupric acetate, sodium tetrahydroborate, and titanium tetraisopropoxide 102.

A series of linear non isocyanate polyurethanes with $M_n$ of 6,000-9,000 and relatively low PDI around of 1.5 were obtained by the polyaddition of phenoxy carbonyloxymethyl ethylene carbonate with diamines 103. These reactions were carried out in N,N-dimethylacetamide (DMAc) at room temperature for 20h. The monomer phenoxy carbonyloxymethyl ethylene carbonate was synthesized from the phenyl chloroformate with glycerol carbonate which was prepared from the glycerol with ethylene carbonate.

The linear non-isocyanate polyurethanes could be synthesized from the reaction of the bis(cyclic carbonates) with diamines in aqueous media 104. The results showed that the bis(cyclic carbonates) with higher hydrophobicity gave the polyhydroxyurethane in higher yields, and the diamine with stronger nucleophilicity gave the polyhydroxyurethane in higher yields. These suggest that the hydrophobicity to protect the carbonate from hydrolysis and sufficient nucleophilicity of the diamine are the important factors to get polyhydroxyurethane in aqueous media. This method is potentially applicable to prepare polyurethane emulsion by an environmentally benign procedure.

The linear non isocyanate polyurethanes can also be synthesized from the one-pot reaction of the bisepoxide, carbon dioxide and diamines 105. The bis(cyclic carbonates)
was prepared from the reaction of bisphenoal A diglycidyl ether with carbon dioxide in 1-Methyl-2-pyrrolidinone (NMP) at 100°C for 24h in the presence of LiCl or LiBr with quantitative yield. After this, 1,12-diaminododecane(DAD) was added into this system, and the mixture was stirred at 70°C for 6h to obtain polyhydroxyurethane with Mn of around 11,000 and Tg of 31.18 °C. When a bifunctional cyclic carbonate containing a quaternary ammonium group was used in the reaction with diamines, a polyurethane-ionomer exhibiting potential bacteriostatic properties was obtained\textsuperscript{106,107}.

2.5.3.2 Crosslinked NIPU

A network of non-isocyanate polyurethanes can be obtained when multifunctional cyclic carbonate oligomers (Figure 2-23) are used in the reaction with multifunctional primary amines\textsuperscript{108}.

![Multifunctional cyclic carbonate oligomers structure](image_url)

**Figure 2-23 Multifunctional cyclic carbonate oligomers structure**

A network of non-isocyanate polyurethane can also be obtained from reaction of linear polyurethanes bearing side hydroxyl groups with diisocyanate or aluminum alkoxide\textsuperscript{101}. When a highly functionalized diamine such as l-lysine is used for the
polyurethane synthesis, the resulting polymer contains additionally carboxyl groups besides primary and secondary hydroxyl groups (Figure 2-24)\textsuperscript{102}.

![Reaction of l-lysine with biscyclic carbonate](image)

**Figure 2-24 Reaction of l-lysine with biscyclic carbonate**\textsuperscript{102}

The polyurethanes containing carboxyl and hydroxyl groups reacted with cupric acetate, sodium tetrahydroborate, and titanium tetra-iso-propoxide to afford the corresponding crosslinked gels immediately. These metallic gels are expected to be novel optically active catalysts.

A network of polyurethane could also be formed from reaction of the amine terminated nonisocyanate polyurethane and epoxy. The amine terminated non-isocyanate polyurethane was prepared from the reaction of excess diamine and biscyclic carbonate. It has been reported that several mono- and bis(cyclic carbonates) were used to modify the polyamine triethylenetetramine (TETA)\textsuperscript{109}. The modified amine curing agents containing β-hydroxyurethane linkage were viscous liquids of a colouring from intense yellow to orange. The presence of β-hydroxyurethane groups in the modified amine curing agent has main two effects on the curing system. The first one is to increase the curing reactivity because of the formation of the hydrogen bond, weakening the C-O
bond in the oxirane ring. The second one is to decrease the density of the crosslinking because some protons are consumed in the reaction with cyclic carbonates and the protons in the urethane linkage are inactive.
CHAPTER III

POLYESTER/POLY(METH)ACRYLATE BLOCK COPOLYMERS BY COMBINED POLYCONDENSATION/ATRP: CHARACTERIZATION AND PROPERTIES

3.1 Abstract

Polyester/poly(meth)acrylate block copolymers are synthesized using a combination of polycondensation and ATRP. All block copolymers are characterized by means of NMR and GPC. Agreement between theoretical molecular weights of the polymers with observed GPC values suggests controlled polymerization. In the case of unsaturated-polyester-based block copolymers the main chain double bond in the polyester backbone remains almost unaffected during ATRP. The unsaturated block copolymers are crosslinkable and can form networks upon photoirradiation in the presence of a suitable photoinitiator. These copolymers might be interesting candidates for coatings with better overall properties than those based on neat polyesters.

3.2 Introduction

Polyesters are a class of polymers widely used in coating applications and are generally synthesized by (i) polycondensation reaction of various diacid and diols and, (ii) ring-opening polymerization (ROP) of the parent cyclic esters. The main
drawback of these polyesters is their poor hydrolytic/oxidative stability. In order to improve the properties modification of polyester by preparing block copolymer is desirable.

Significant progress has been made in the field of living free-radical polymerization including nitroxide-mediated stable free-radical polymerization, \(^{110, 111}\) atom-transfer radical polymerization (ATRP) \(^{112, 113, 114, 115}\) and reversible addition/fragmentation chain transfer (RAFT) polymerization. \(^{116, 117}\) All these controlled polymerizations can be used to synthesize polymers and copolymers. ATRP has already been proven a powerful tool to synthesize polymers that are not accessible through conventional radical polymerization of vinyl monomers. A combination of ring-opening methatesis polymerization (ROMP) with ATRP was prepared for the synthesis of various block copolymers of caprolactone. \(^{118}\) For example, Mecerreyes et al. reported random and block copolymers of caprolactone and methyl methacrylate by ATRP. \(^{119}\) Detrembleur et al. reported homopolymerization and random and block copolymerization of \(\gamma\)-bromo-\(\varepsilon\)-caprolactone. \(^{120}\) Yuan et al. reported controlled polymerization of 5,6-benzo-2- methylene-1,3-dioxepane (BMDO) by ATRP. \(^{121}\) Schappacher et al. synthesized diblock and triblock copolymers of caprolactone and methyl methacrylate (MMA). \(^{122}\)

Polyesters synthesized by polycondensation reactions are widely used in coating applications and for protection of surfaces. Most of the polyesters used in coatings have relatively low molecular weights and are amorphous and branched. These types of polyesters are cost-effective and easily synthesized by polycondensation reaction between various commercially available diols and diacids in bulk conditions and are widely demanded by industry. In general, these type of polyesters are crosslinked by the
reaction with triisocynates or with melamine/formaldehyde (MF) resins and used for coating applications.\textsuperscript{123,124}

High-molecular-weight polyesters or polyester/polyurethanes have appreciable mechanical properties such as high tensile strength together with flexibility. But the presence of ester linkages in the backbone of polyesters makes them vulnerable to acids/bases. On the other hand, poly(meth)acrylates have better abrasion resistant, and hydrolytically stable with superior mechanical properties. Hence, to improve the hydrolytic/oxidative stability and to achieve chemical abrasion resistance properties it is highly desirable to prepare copolymers of polyesters and poly(meth)acrylates. Previously, crosslinked polyester networks were synthesized by a two-step synthesis. First, synthesis of polyester with acrylic or methacrylic chain-ends and then crosslinking by the reaction with reactive diluents upon photo-irradiation.\textsuperscript{125} However, this process may also produce undesirable homopolymers and sometimes phase-separated polymers with inferior properties.

To the best of our knowledge, there is no report of the synthesis of block copolymers of polyesters with (meth)acrylates in which polyesters are synthesized by reacting small-molecular-weight diacids and diols. In this work, we demonstrate the synthesis of different block copolymers of unsaturated and saturated polyesters (UPE and SPE, respectively) with (meth)acrylates with well-defined molecular weight and narrow polydispersity by combination of condensation polymerization and ATRP. This work also shows that the unsaturation present in the main chain of the polyesters is almost unaffected during ATRP and the synthesized unsaturated polyester/(meth)acrylate block copolymers can form crosslinked networks upon irradiation.
3.3 Materials

MMA, ethyl methacrylate (EMA), ethyl acrylate (EA), butyl acrylate (BA), 2-ethyl hexyl acrylate (EHA), basic aluminium oxide (Aldrich) were passed through a basic alumina column and then distilled under reduced pressure and stored under nitrogen atmosphere. Acetone (GR, Fisher Scientific) was distilled before use. 2-Butanone, 1-propanol, p-xylene, isophthalic acid (IPA), maleic anhydride (MA), 1,6 hexanediol (HD), neopentyl glycol (NPG), dibutyltin oxide (DBTO), 2,2′-bipyridyl (bpy, 98%), CuBr (98%) and CuCl (98%), methylene chloride, triethylamine (Et₃N), bromoisobutyryl bromide (EbiB), bromopropionyl bromide (MBrP), magnesium sulfate (MgSO₄), tetrahydrofuran (THF), pentamethyldiethylenetriamine (PMDETA) were used as received (all from Aldrich). Me₆TREN tris(2-aminoethyl)amine(TREN) was synthesized according to the literature.¹²⁶

3.4 Instrumentation and characterization

The FT-IR spectra of the polyesters and macroinitiators were measured on a Nicolet 380 FTIR spectrophotometer. The results were analyzed using OMNIC software.

The NMR spectrum of all the polyesters, macroinitiators and block copolymers were recorded on a Varian Mercury 300 MHz spectrophotometer. All the NMR spectra were measured by dissolving the samples in CDCl₃.

Molecular weight and molecular weight distribution of all the polyesters, polyester-based macroinitiators and polyester-based (meth)acrylate block copolymers were determined in a Waters 1515/2414 gel permeation chromatography (GPC)
instrument equipped with a refractive index detector using THF as eluent at a flow rate 0.5 mL · min⁻¹ and polystyrene as a calibration standard at room temperature.

The glass transition temperature of all the polyesters and polyester-based block copolymers was measured in a TA instrument DSCQ 1000 model. All the samples were heated from −90 to 130 °C at a heating rate 10 °C · min⁻¹ under nitrogen atmosphere.

TA Instrument DSC-Q1000 (Photo DSC), equipped with a Novacure N2001-A1 as UV-light source, was used to investigate the heat flow of curing the product. The wavelength ranged from 250 to 600 nm and the initiation light source was a 100 W high-pressure mercury short-arc lamp of intensity 250 mW · cm⁻².

Acid number (Aac) was determined according to ASTM standard D 1639-90. Two gram of resin was measured and dissolved in 50 g of an equal mixture of acetone. A phenolphthalein indicator solution was prepared at 0.5 wt-% in methanol. One milliliter of the phenolphthalein indicator was added to the acetone/ethanol solution. The sample was titrated with 0.1 N solution of potassium hydroxide in methanol until the solution obtained a slight pink coloration. The potassium hydroxide solution was prepared by measuring approximately 2.81 g of KOH and dissolved in ethanol in a 500 mL graduated flask. At a given moment during the hydrolysis the acid number was calculated with the following equation

\[ Aac = \frac{56.1 \times N \times V}{m} \]  (3-1)

where \( N \) and \( V \) represented the normality (mol/L) of the basic solution made from potassium hydroxide (KOH), and the volume (mL) of KOH solution required to neutralize the desired amount of oligoester, \( m \), measured in grams.
3.5 Synthesis

In this synthesis part, hydroxyl terminated saturated and unsaturated polyesters were synthesized. These polyesters were used to prepare corresponding macroinitiators. These macroinitiators were used to polymerize different kinds of (meth) acrylates by ATRP.

3.5.1 Synthesis of IPAMA-HDNPG UPE

To synthesize hydroxy-terminated polyester, excess diol was used. The molar ratio of diol to diacid was 10:9. A representative example of the synthesis of hydroxyl-terminated polyester is as follows. IPA (135.5 g, 0.82 mol), MA (80 g, 0.82 mol), HD (132.4 g, 0.9 mol) and NPG (94.4 g, 0.9 mol) were taken in a 500 mL four-necked round-bottom flask which was equipped with a mechanical stirrer, a gas inlet, a temperature controller, a Dean-Stark trap and a condenser. The reaction proceeded under argon to minimize oxidative degradation. To accelerate the reaction, 0.4% (by weight) of DBTO, a trans-esterification catalyst, was used. 0.1% Hydroquinone was added as a radical scavenger to prevent the polymerization of MA. Then 3 wt% xylene was also added into the reaction mixture to remove water from the resin as azeotropic mixture. The reaction temperature was carefully controlled using a temperature controller and a thermocouple in order to minimize evaporation of diol. The temperature of the mixture was increased from 20 to 150 °C at a rate of 4.3 °C · min⁻¹, and then from 150 to 210 °C at a rate of 0.25 °C · min⁻¹. The final temperature was held until the resin had an acid number measured by titration less than or equal to 10 mg KOH per g resin. Other polyesters were also synthesized using similar procedure. The hydroxyl number of polyesters was
determined according to ASTM (ASTM D 1957-86). NMR chemical shifts were $\delta = 8$ (H from IPA), 6 and 7 (CH=CH in the polyester backbone) 4.10 (-OCH$_2$ from polyester backbone), 3.6 (HOCH$_2$ of end group) and 2.25 (-CH$_2$ attached to C=O), 1.7 (O=CCH$_2$CH$_2$, OCH$_2$CH$_2$) 1.4 (-OCH$_2$CH$_2$CH$_3$), respectively. Mn and PDI of the block copolymer were 1 500 and 1.74, respectively.

3.5.2 Synthesis of adipic acid/1,6-hexanediol (AA-HD) SPE

Similar procedure was used for the synthesis of various SPEs. A representative example of synthesis of hydroxyl-terminated polyester is as follows.

The molar ratio of diol to diacid was 5:4. AA (150 g, 1.026 mol) and 57 g HD (151.5 g, 1.28 mol) were added to a 500 mL four-necked round-bottom flask which was equipped with a mechanical stirrer, a gas inlet, a temperature controller, a Dean-Stark trap and a condenser. The reaction proceeded under argon to minimize oxidative degradation. To accelerate the reaction, 0.4 wt% of DBTO, a trans esterification catalyst, was used. Then, 3 wt% of xylene was also added into the reaction mixture to remove water from the resin as azeotropic mixture. The reaction temperature was carefully controlled using a temperature controller and a thermocouple in order to minimize evaporation of diol. The temperature of the mixture was increased from 20 to 150 °C at a rate of 4.3 °C · min$^{-1}$, and then from 150–210 °C at a rate of 0.25 °C · min$^{-1}$. The final temperature was held until the resin had an acid number measured by titration less than or equal to 10 mg KOH per g resin. Other polyesters were also synthesized using similar procedure. The hydroxyl number of polyesters was determined according to ASTM (ASTM D 1957-86). NMR chemical shifts were $\delta = 4.10$ (-OCH$_2$ from polyester
backbone), 3.6 (HOCH$_2$ of end group) and 2.25 (-CH$_2$ attached to C=O), 1.7 (O=CCH$_2$CH$_2$, OCH$_2$CH$_2$) and 1.4 (-OCH$_2$CH$_2$CH$_2$), respectively.

3.5.3 Synthesis of UPE-based difunctional macroinitiator (UPE1) for methacrylate polymerization

A representative example of the synthesis of the polyester-based difunctional macroinitiator is as follows. UPE (88.5 g, 0.052 mol) was taken in a 1 L three-necked round-bottom flask and dry methylene chloride (500 mL) was added into it. The whole mixture was kept on in an ice bath and stirred over a magnetic stirrer under nitrogen atmosphere. The temperature of the mixture was maintained at less than 5 °C. Then Et$_3$N (22 mL, 0.17 mol) was added. EBiB (22 mL, 0.17 mol) was added dropwise into the mixture. The whole reaction was stirred overnight. Then the mixture was filtered to remove the salt produced by the esterification reaction. Then the solution was washed with saturated solution of NaHCO$_3$ in water followed by distilled water (three times) to remove unreacted EBiB and Et$_3$N. Then, MgSO$_4$ was added to remove trapped water and filtered. Dichloromethane was removed by rotary evaporator at room temperature. The product was characterized by IR and NMR spectroscopy.

3.5.4 Synthesis of UPE-based difunctional macroinitiator (UPE2) for acrylate polymerization

UPE (52.5 g, 0.03 mol) was taken in a 500 mL three-necked round-bottom flask and dry methylene chloride (300 mL) was added. The whole mixture was kept in an ice bath and stirred over a magnetic stirrer under nitrogen atmosphere. The temperature of the mixture was maintained at less than 5 °C. Next, Et$_3$N (14 mL, 0.10 mol) was added.
MBrP (11.5 mL, 0.17 mol) was added dropwise into the mixture. The whole reaction was stirred for overnight. Then the mixture was filtered to remove the salt produced by esterification reaction. Then, the solution was washed with saturated solution of NaHCO₃ in water followed by distilled water (three times) to remove unreacted EBiB and Et₃N. Then, MgSO₄ was added to remove trapped water and filtered. Dichloromethane was removed by rotary evaporator at room temperature. The product was characterized by IR and NMR spectroscopy. In IR spectroscopy the broad peak around 3 400 cm⁻¹ for -OH group disappeared which confirmed the synthesis of the macroinitiator. The NMR peak at δ = 3.6 (for end -CH₂OH) disappeared and mergeed with the one at δ = 4.1 (for -OCH₂), thus confirming the completion of the esterification reaction.

Along similar routes, SPE1- and SPE2-based macroinitiators were synthesized by esterification reactions of hydroxyl-terminated SPEs with EBiB and MBrP, respectively.

3.5.5 Synthesis of poly(MMA)-block-UPE1-block-poly(MMA) (PMMA-b-UPE1-b-PMMA)

A representative example of synthesis of triblock copolymers via ATRP is as follows. In a nitrogen-purged 25 mL single-necked round-bottom flask, provided with a B-19 standard joint and a stir bar were added CuBr (0.28 g, 2 mmol) and Me₆TREN (0.48 g, 2 mmol), respectively. Nitrogen purging was continued for 10 min, after which the tube was closed with a rubber septum that was secured by a Cu wire. MMA (5 mL, 50 mmol), acetone (2.5 mL), all purged separately with nitrogen were next injected into the tube with a nitrogen purged gas-tight syringe. The admixture was sonicated for 2 min. A deep brown color resulted. UPE1 (1.7 g, 1 mmol) was then injected. The tube was then put in an oil bath maintained at 50 °C. The polymerization mixture was stirred
magnetically. At suitable time intervals aliquots (1 mL) of the reaction mixture were withdrawn, diluted with 1 mL THF and poured into hexane. The polymers were isolated by centrifugation, dried, redissolved in THF and reprecipitated into hexane. They were finally dried in a vacuum oven at 50 °C for 48 h. After 1.5 h conversion was 90%. The Mn and PDI values were 6400 and 1.90, respectively. A similar polymerization procedure was used for the polymerization of EMA. $^1$H NMR chemical shifts were $\delta = 3.6$ [-OCH$_3$ from PMMA], 0.8 and 1.0 [-CH$_3$ of PMMA]. A similar polymerization procedure was followed to polymerize EMA.

3.5.6 Synthesis of poly(BA)-block-UPE2-block-poly(BA) (PBA-b-UPE2-b-PBA)

CuBr (0.28 g, 2 mmol), Me$_6$TREN (0.48 mL, 2 mmol) and UPE2 (1.7 g, 1 mmol) were taken in a reaction vessel, already purged with nitrogen and the vessel was sealed with a rubber septum. Into the vessel, previously purged BA (5.6 mL, 39 mmol) and acetone (2.8 mL) was added by using a syringe. The reaction mixture was stirred for 3 min at room temperature and then was placed in an oil bath at 50 °C. After 1 h, the conversion was 70% and Mn and PDI were 5000 and 2.07, respectively. A similar polymerization procedure was used for EA and EHA. Chemical shifts of $\delta = 3.9$ [-OCH$_2$ from PBA], 0.8 and 1.0 [-CH$_3$ of PBA] were observed.

3.5.7 Synthesis of poly(MMA)-block-poly(BA)-block-UPE2-block-poly(BA)-block-poly(MMA) (PMMA-b-PBA-b-UPE2-b-PBA-b-PMMA)

The difunctional PBA-b-UPE2-b-PBA macro-initiator (1.8 g, 0.4 mmol) (Mn= 5000, PDI = 2.07) was taken in a round-bottom single-necked flask, dissolved in acetone (1 g) and purged with nitrogen. MMA (2 g, 20 mmol) was nitrogen-purged and injected into
the vessel. Me₆TREN (0.19 mL, 0.8 mmol) and CuCl (0.079 g, 0.8 mmol) were next added under nitrogen. The mixture was sonicated for about 2 min and the vessel was placed in an oil bath at 50 °C and the solution was stirred. A conversion of 40% was reached in 1 h. Mn and PDI of the block copolymer were 8 100 and 2.4, respectively.

3.5.8 Synthesis of poly(BA)-block-poly(MMA)-block-UPE1-block-poly(MMA)-block-poly(BA) (PBA-b-PMMA-b-UPE1-b-PMMA-b-PBA)

The difunctional PMMA-b-UPE1-b-PMMA macro-initiator (2.36 g, 0.4 mmol) (Mn = 6 400, PDI = 1.9) was taken in a round-bottom single-necked flask, dissolved in acetone (1 g) and purged with nitrogen. BA (2 g, 15.6 mmol) was nitrogen-purged and injected into the vessel. Me₆TREN (0.19 mL, 0.8 mmol) and CuBr (0.114 g, 0.8 mmol) were next added under nitrogen. The mixture was sonicated for about 2 min and the vessel was placed in an oil bath at 50 °C and the solution was stirred. A conversion of 90% was reached in 1.5 h. Mn and PDI of the block copolymer were 12 900 and 2.2, respectively.

3.5.9 Bulk ATRP of MMA using UPE-based macroinitiator

A representative example of synthesis of triblock copolymers in bulk condition via ATRP is as follows. In a nitrogen-purged 25 mL single-necked round-bottom flask, provided with a B-19 standard joint and a stir bar were added UPE1 (1.7 g, 1 mmol), CuBr (0.28 g, 2 mmol) and Me₆TREN (0.48 g, 2 mmol), respectively. Nitrogen purging was continued for 10 min, after which the tube was closed with a rubber septum which was secured by a Cu wire. MMA (5 mL, 50 mmol), purged separately with nitrogen were next injected into the tube with a nitrogen-purged gas-tight syringe. The admixture was
sonicated for 2 min. A deep brown color resulted with complete dissolution of polyester. The tube was then put in an oil bath maintained at 50 °C. The polymerization mixture was stirred magnetically. Gelation occurred within 30 min and the polymer was insoluble in organic solvents.

3.5.10 Synthesis of poly(MMA)-block-SPE1-block-poly(MMA) (PMMA-b-SPE1-b-PMMA)

In a nitrogen purged 25 mL single neck round bottom flask, provided with a B-19 standard joint and a stir bar were added CuCl (0.4 g, 4 mmol), CuCl₂ (0.025 g, 0.2 mmol) and bpy (0.13 g, 8.8 mmol), respectively. Nitrogen purging was continued for 10 min, after which the tube was closed with a rubber septum that was secured by a Cu wire. MMA (10 mL, 169 mmol), acetone (10 mL), all purged separately with nitrogen were next injected into the tube with a nitrogen-purged gas-tight syringe. The admixture was sonicated for 2 min. A deep brown color resulted. SPE1 (3.8 g, 2 mmol) was then injected. The tube was then put in an oil bath maintained at 50 °C. The polymerization mixture was stirred magnetically. At suitable time intervals aliquots (1 mL) of the reaction mixture were withdrawn, diluted with 1 mL THF and poured into hexane. The polymers were isolated by centrifugation, dried, redissolved in THF and reprecipitated into hexane. They were finally dried in a vacuum oven at 50 °C for 48 h. After 5 h conversion was 90%. Mn and PDI were 7800 and 1.46, respectively. A similar polymerization procedure was used for the polymerization of EMA. Chemical shifts of δ = 3.6 [–OCH₃ from PMMA], 0.8 and 1.0 [–CH₃ of PMMA] were observed.
3.6 Results and discussion

The main objective of this work is the synthesis of varieties of block copolymers containing poly(meth)acrylate and UPE and/or SPE with improved overall properties.

3.6.1 Synthesis of polyester-based block copolymers

UPE was synthesized via condensation polymerization using equimolar mixture of diacid IPA and MA and mixture of excess diols, e.g., HD and NPG. Similarly saturated hydroxyl telechelic polyesters were synthesized by simple condensation polymerization between diacid and excess diol. (Meth)acrylate block copolymers of UPE and SPE were synthesized via ATRP. Table 3-1 summarizes the abbreviations, composition, molecular weights and molecular weight distributions of hydroxyl-telechelic polyesters synthesized by condensation polymerization.

Table 3-1 Properties of hydroxyl-telechelic polyesters

<table>
<thead>
<tr>
<th>Polyester</th>
<th>Diol : Diacid</th>
<th>Acid # (mg KOH/g resin)</th>
<th>Hydroxyl # (mg KOH/g resin)</th>
<th>$M_n$ (g/mol)</th>
<th>PDI</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPAMA-HDNPG</td>
<td>10 : 9</td>
<td>8.2</td>
<td>125</td>
<td>1500</td>
<td>1700</td>
<td>1.74</td>
</tr>
<tr>
<td>AA-HD-A</td>
<td>5 : 4</td>
<td>8.0</td>
<td>101</td>
<td>1700</td>
<td>1600</td>
<td>1.60</td>
</tr>
<tr>
<td>AA-HD-B</td>
<td>8 : 7</td>
<td>6.0</td>
<td>110</td>
<td>2100</td>
<td>2100</td>
<td>1.60</td>
</tr>
<tr>
<td>AA-HD-C</td>
<td>10 : 9</td>
<td>9.5</td>
<td>130</td>
<td>2300</td>
<td>2400</td>
<td>1.70</td>
</tr>
<tr>
<td>IPA-HD</td>
<td>5 : 4</td>
<td>6.2</td>
<td>120</td>
<td>1500</td>
<td>1600</td>
<td>1.65</td>
</tr>
<tr>
<td>PA-HD</td>
<td>5 : 4</td>
<td>5.3</td>
<td>165</td>
<td>1100</td>
<td>1200</td>
<td>1.60</td>
</tr>
<tr>
<td>AA-NPG</td>
<td>5 : 4</td>
<td>4.0</td>
<td>180</td>
<td>1400</td>
<td>1500</td>
<td>1.60</td>
</tr>
</tbody>
</table>

a) CL = Clear Liquid; b) WS = White Solid

Figure 3-1 shows the chemical structures of different diacids, diols and hydroxyl functional representative UPE and SPE synthesized by simple condensation reactions.
The hydroxyl functional polyesters were converted to macroinitiators for the ATRP of varieties of acrylates and methacrylates. For example, for acrylates polymerizations, the polyesters were modified to macroinitiators the ends of which resemble the structure of acrylate and for methacrylates polymerization the polyester were modified to macroinitiators the ends of which resemble the structure of methacrylate.\textsuperscript{127, 69, 128}

Figure 3- 1 Chemical structure of diacids, diols and representative SPE and UPE
Figure 3-2 shows the general synthesis procedure of polyesters-based block copolymers of poly(meth)acrylates \([\text{poly(meth)acrylate}\text{-}\text{block-}\text{UPE}\text{ and/or SPE}\text{-}\text{block-}\text{poly(meth)acrylate}]\) starting from polyesters synthesis. The ATRP of various (meth)acrylates monomers using polyesters-based macro-initiators was studied in terms of molecular weights variations with monomer conversion and molecular weights distributions.

![Diagram of synthesis process]

Either \(R_1'\) or \(R_2'\) is unsaturated

Figure 3-2 Synthesis of polyester-poly(meth)acrylates block copolymers.
3.6.2 Synthesis of UPE-based block copolymers

ATRP of acrylates and methacrylates were conducted in acetone using CuX/Me₆TREN (X = Cl, Br) catalysts at 50 °C. Both CuBr/Me₆TREN and CuCl/Me₆TREN catalyst systems produced block copolymers with controlled molecular weight with active chain-end. The rate of ATRP with CuCl/Me₆TREN catalyst is slower than CuBr/Me₆TREN. It was reported that the mixed-halide initiating system (EBiB/CuCl) leads to much better control in ATRP of MMA using 4,4’-di(5-nonyl)-2,2’-bipyridine (dNbpy) as the ligand.⁶⁹,¹²⁸ This was attributed to faster initiation by cleavage of the weaker C-Br bonds in EBiB and slower propagation due to the polymer chain, which predominantly contains stronger C-Cl bonds. In contrast to the reported work, the present work shows that in case of acrylates polymerization where the macroinitiator contains MBrP moiety gives better control with the CuBr/Me₆TREN catalyst system than that of CuCl/Me₆TREN catalyst. This result might be attributed to a lesser tendency for cleavage of the C-Br bonds in MBrP containing polyester chain ends and thereby forming a secondary radical that is less stable than the tertiary radical generated from a methacrylate-type initiator which contains EBiB chain ends. In the MBrP/CuCl system, the difference in rate of initiation and rate of propagation is not so much prominent as in EBiB/CuCl system, thereby rendering it a system of less importance for halogen exchange.

Table 3-2 summarizes the results of the ATRP of methacrylates (MMA and EMA) and acrylates (BA, EA and EHA) using UPE-based macro-initiators. From the molecular-weight data it can be observed that the theoretically calculated molecular weights are close to those determined by GPC, suggesting controlled polymerizations.
Table 3-2: Results of ATRP of different (meth)acrylates using UPE-based macroinitiators

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst system</th>
<th>Block Copolymer</th>
<th>Conversion a) (%)</th>
<th>Mn (g / mol) Theor.</th>
<th>PDI</th>
<th>I eff</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuBr/Me6TREN</td>
<td>PEA-b-UPE2-PEA</td>
<td>75</td>
<td>16750</td>
<td>18000</td>
<td>2.2</td>
</tr>
<tr>
<td>2</td>
<td>CuCl/Me6TREN</td>
<td>PEA-b-UPE2-PEA</td>
<td>75</td>
<td>13000</td>
<td>15300</td>
<td>2.15</td>
</tr>
<tr>
<td>3</td>
<td>CuBr/Me6TREN</td>
<td>PBA-b-UPE2-PBA</td>
<td>70</td>
<td>12250</td>
<td>13500</td>
<td>2.25</td>
</tr>
<tr>
<td>4</td>
<td>CuCl/Me6TREN</td>
<td>PBA-b-UPE2-PBA</td>
<td>80</td>
<td>13750</td>
<td>15500</td>
<td>2.22</td>
</tr>
<tr>
<td>5</td>
<td>CuBr/Me6TREN</td>
<td>PEHA-b-UPE2-PEHA</td>
<td>80</td>
<td>13750</td>
<td>15000</td>
<td>2.3</td>
</tr>
<tr>
<td>6</td>
<td>CuCl/Me6TREN</td>
<td>PEHA-b-UPE2-PEHA</td>
<td>70</td>
<td>12250</td>
<td>14300</td>
<td>2.3</td>
</tr>
<tr>
<td>7</td>
<td>CuBr/Me6TREN</td>
<td>PMMA-b-UPE1-b-PMMA</td>
<td>75</td>
<td>16750</td>
<td>18000</td>
<td>2.25</td>
</tr>
<tr>
<td>8</td>
<td>CuCl/Me6TREN</td>
<td>PMMA-b-UPE1-b-PMMA</td>
<td>80</td>
<td>13750</td>
<td>14550</td>
<td>2.08</td>
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<tr>
<td>9</td>
<td>CuBr/Me6TREN</td>
<td>PEMA-b-UPE1-b-PEMA</td>
<td>80</td>
<td>17750</td>
<td>19300</td>
<td>2.18</td>
</tr>
<tr>
<td>10</td>
<td>CuCl/Me6TREN</td>
<td>PEMA-b-UPE1-b-PEMA</td>
<td>76</td>
<td>13150</td>
<td>14000</td>
<td>2.12</td>
</tr>
<tr>
<td>11</td>
<td>CuCl/Me6TREN</td>
<td>PMMA-b-UPE1-b-PMMA</td>
<td>50</td>
<td>3200</td>
<td>4700</td>
<td>2.25</td>
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<tr>
<td>12</td>
<td>CuCl/Me6TREN</td>
<td>PEA-b-UPE2-PEA</td>
<td>51</td>
<td>4500</td>
<td>5550</td>
<td>2.13</td>
</tr>
<tr>
<td>13</td>
<td>CuCl/Me6TREN</td>
<td>PBA-b-UPE2-PBA</td>
<td>52</td>
<td>4600</td>
<td>5350</td>
<td>2.18</td>
</tr>
<tr>
<td>14</td>
<td>CuCl/Me6TREN</td>
<td>PEHA-b-UPE2-PEHA</td>
<td>52</td>
<td>4600</td>
<td>5550</td>
<td>2.12</td>
</tr>
<tr>
<td>15</td>
<td>CuCl/Me6TREN</td>
<td>PEHA-b-PEHA-b-UPE2</td>
<td>30</td>
<td>6000</td>
<td>7600</td>
<td>2.4</td>
</tr>
</tbody>
</table>

a) Determined by means of gravimetry, I eff = Mn (theo)/Mn (GPC), UPE1 and UPE2 are unsaturated polyester (IPA-MA-ND-NPG)-based macroinitiators, the chain-ends of which resemble the structures of methacrylate and acrylate, respectively.

Figure 3-3a shows representative kinetic plots of disappearance of MMA and EMA in acetone at 50 °C using UPE1 as macroinitiator and CuBr/Me6TREN and CuCl/Me6TREN as catalysts. In acetone the complex becomes soluble and thus good control over polymerization was achieved. Figure 3-3b shows representative kinetic plots of disappearance of EA, BA and EHA in acetone at 50 °C. UPE2 was used as macroinitiator and CuBr/Me6TREN was used as catalyst. Acetone was selected as a
solvent for both methacrylates and acrylates polymerization because: (i) the catalysts are well soluble in acetone and (ii) the Cu(I)Me$_6$TREN complex is stable (no disproportionation) and thereby facilitates the ATRP of (meth)acrylates at 50 °C.$^{129,130}$

Figure 3- 3 (a) Kinetic plots of ATRP of MMA (lines 1 and 2) and EMA (lines 3 and 4) in acetone at 50 °C using UPE1 as macroinitiator. Lines 1 and 3: CuBr/Me$_6$TREN and lines 2 and 4: CuCl/Me$_6$TREN catalysts. (b) Kinetic plots of ATRP of EA (line 1), BA (line 2) and EHA (line 3) using UPE2 macroinitiator in acetone and CuBr/Me$_6$TREN catalyst at 50 °C.
The first order kinetic plots for monomer disappearance were linear for all the polymerization which indicates constant radical concentration throughout the polymerization and hence indicates controlled polymerization. Linear increase of molecular weights and decrease of PDIs suggest control living polymerizations.\textsuperscript{131,132}

Figure 3-4 shows representative GPC chromatograms of (a) UPE1, (b) PMMA-\textit{b}-UPE1-\textit{b}-PMMA tri-block copolymer and (c) PBA-\textit{b}-PMMA-\textit{b}-UPE1-\textit{b}-PMMA-\textit{b}-PBA pentablock copolymer, respectively. Figure 3-5 also shows representative GPC traces of (a) UPE2, (b) PBA-\textit{b}-UPE2-\textit{b}-PBA tri-block copolymer and (c) PMMA-\textit{b}-PBA-\textit{b}-UPE2-\textit{b}-PBA-\textit{b}-PMMA penta-block copolymers, respectively.

![Figure 3-4 GPC traces](image)

Figure 3-4 GPC traces of (a) UPE1, (b) PMMA-\textit{b}-UPE1-\textit{b}-PMMA triblock copolymer and (c) PBA-\textit{b}-PMMA-\textit{b}-UPE1-\textit{b}-PMMA-\textit{b}-PBA pentablock copolymers, respectively.
The symmetrical GPC chromatograms of block copolymers and the shifting to high molecular weight side indicate efficient initiation of unsaturated polyesters-based macroinitiators. There is an increase of PDI (2.4) of the penta-block copolymer of PMMA-b-PBA-b-UPE2-b-PBA-b-PMMA was observed in compare to PDI (2.2) of PBA-b-PMMA-b-UPE2-b-PMMA-b-PBA copolymer. This is attributed to the slow initiation of triblock copolymer PBA-b-UPE2-b-PBA to initiate MMA polymerization. The broadening of GPC trace of pentablock copolymer may be also due to the presence of unreacted triblock macroinitiator with dead chain-ends.

Figure 3- 6 shows a representative NMR spectrum of (a) UPE1 macroinitiator, (b) PMMA-b-UPE1-b-PMMA and (c) poly(EA)-block-UPE1-block-poly(EA) (PEA-b-UPE1-b-PEA) copolymers, respectively. In the spectrum of the unsaturated polyester (not
shown), peaks at $\delta = 7.5$, 8.2 and 8.7 correspond to three different types of aromatic protons coming from IPA, those at $\delta = 6.2$ and 6.8 correspond to double-bond presence in the polyester backbone. Other peaks at $\delta = 4.10$ (-OCH$_2$ from polyester backbone), 3.6 (HOCH$_2$ of end group) and 2.25 (-CH$_2$ attached to C=O) are observed. In spectrum a, a peak at $\delta = 3.6$ (HOCH$_2$ of end group) disappears and merges with the one at $\delta = 4.10$. This shows complete esterification of the hydroxyl group in polyester. In spectrum b, the peak at $\delta = 3.6$ corresponds to (OCH$_3$) of PMMA and the ones at $\delta = 0.8$ and 1.0 correspond to -CH$_3$ from PMMA. In spectrum c, the peak at $\delta = 3.8$ corresponds to (OCH$_2$) of PEA and those at $\delta = 0.8$ and 1.0 correspond to -CH$_3$ from PEA.
In both triblock copolymers (see Figure 3-6b and c) peaks at $\delta = 6.2$ and 6.8 are observed which clearly indicate that main-chain double bonds are present in the final copolymer when the monomer conversion was essentially $< 70\%$. However, NMR spectra of the UPE-based copolymers also suggest that the intensity ratio of protons attached to the unsaturated carbons of maleic ester and aromatic proton signals decreases about $\approx 12\%$ than that of neat UPE suggesting formation of branched structure.

The successful solution-phase ATRP in presence of unsaturation is attributed to the (i) much higher concentration of polymerizable monomer than unsaturation present in the macroinitiator (relatively less reactive), (ii) mild reaction condition ($50^\circ\mathrm{C}$) used in the solution phase ($25\%$ acetone) ATRP and due to (iii) low radical concentration during polymerization (ATRP). On the other hand, bulk ATRP of acrylates and methacrylates using UPE-based macroinitiator resulted very fast polymerization with gelation and disappearance of unsaturation. This is mainly due to high radical concentration and very high conversion with in short reaction time (less than 10 min).
3.6.3 Synthesis of SPE-based block copolymers

Block copolymers of different SPEs were synthesized along the lines described above. Different catalyst systems were employed for the ATRP of meth(acrylates). Methacrylates polymerizations were carried out in acetone using CuCl/bpy catalyst. As regards, the use of the CuCl/bpy instead of CuBr/bpy complex as catalyst, the later did not go completely into solution in acetone. Block copolymer with higher polydispersities were obtained when CuBr/bpy was used. On the other hand, in acetone using either CuBr/PMDETA or CuCl/PMDETA catalyst, mixture was homogeneous initially but with the progress of the reaction the mixture became heterogeneous. The kinetic plots were nonlinear and the molecular weights of the polymer were much higher than the theoretical values and PDIs were broad (PDI ≥ 2).

Acrylate ATRP was conducted in bulk using CuBr/PMDETA catalyst. The polymerization with CuBr/bpy catalyst was also controlled. The theoretical molecular weights were close to experimental molecular weights and PDIs were ≤1.5. The rate of polymerization was slower when CuBr/bpy was used as catalyst.

Table 3-3 summarizes the results of the ATRP of methacrylates (MMA and EMA) and acrylates (BA, EA and EHA) using SPE1 and SPE2 macroinitiators. From the molecular weights and PDIs data it can be observed (Table 3-3) that all the polymerizations were well controlled and the theoretically calculated molecular weights were close to those determined by GPC molecular weights. The lowering the PDIs of the block copolymer in compare to macroinitiator is attributed to the (i) controlled ATRP and (ii) presence of small amount of relatively polydispersed polyester-based macroinitiator in the copolymer. For example, when the block copolymer contain about 14–20 wt% of
polystyrene, a decrease of PDI of macroinitiator from 1.6 to a value of 1.3 for block copolymer (Table 3-3) was observed.

Table 3-3 Results of ATRP of MMA and EMA using SPE-based macroinitiators

<table>
<thead>
<tr>
<th>Polyester (macro-initiator)</th>
<th>Mn (g/mol)</th>
<th>PDI</th>
<th>Block copolymer</th>
<th>Conv. (%)</th>
<th>Mn (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NMR</td>
<td>GPC</td>
<td></td>
<td></td>
<td>Theor.</td>
<td></td>
</tr>
<tr>
<td>AA-HD-1-A</td>
<td>1925</td>
<td>1900</td>
<td>1.60</td>
<td>PMMA-b-AA-HD-1-A-b-PMMA</td>
<td>50</td>
<td>3700</td>
</tr>
<tr>
<td>AA-HD-1-A</td>
<td>1925</td>
<td>1900</td>
<td>1.60</td>
<td>PMMA-b-AA-HD-1-A-b-PMMA</td>
<td>90</td>
<td>12500</td>
</tr>
<tr>
<td>AA-HD-1-C</td>
<td>2580</td>
<td>2600</td>
<td>1.70</td>
<td>PEMA-b-AA-HD-1-C-b-PEMA</td>
<td>85</td>
<td>20000</td>
</tr>
<tr>
<td>IPA-HD-1</td>
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<td>1800</td>
<td>1.65</td>
<td>PMMA-b-IPA-HD-1-b-PMMA</td>
<td>92</td>
<td>6400</td>
</tr>
<tr>
<td>PA-HD-1</td>
<td>1450</td>
<td>1400</td>
<td>1.60</td>
<td>PMMA-b-PA-HD-1-b-PMMA</td>
<td>80</td>
<td>5400</td>
</tr>
<tr>
<td>PA-HD-1</td>
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<td>1400</td>
<td>1.60</td>
<td>PEMA-b-PA-HD-1-b-PEMA</td>
<td>85</td>
<td>5700</td>
</tr>
<tr>
<td>AA-NPG-1</td>
<td>1725</td>
<td>1700</td>
<td>1.60</td>
<td>PMMA-b-AA-NPG-1-b-PMMA</td>
<td>85</td>
<td>7700</td>
</tr>
<tr>
<td>AA-NPG-1</td>
<td>1725</td>
<td>1700</td>
<td>1.60</td>
<td>PEMA-b-AA-NPG-1-b-PEMA</td>
<td>90</td>
<td>8000</td>
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<tr>
<td>AA-HD-2-A</td>
<td>1920</td>
<td>1900</td>
<td>1.60</td>
<td>PBA-b-AA-HD-2-A-b-PBA</td>
<td>70</td>
<td>7500</td>
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<td>AA-HD-2-A</td>
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<td>1900</td>
<td>1.60</td>
<td>PEHA-b-AA-HD-2-A-b-PEHA</td>
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<td>AA-HD-2-A</td>
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<td>1900</td>
<td>1.60</td>
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<td>PEHA-b-AAHD-2-A-b-PEHA</td>
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<td>3000</td>
<td>1.44</td>
<td>A-b-PEHA-b-PMMA</td>
<td></td>
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</tr>
</tbody>
</table>

a) Macroinitiators used to polymerize the methacrylate monomer; b) Calculated from gravimetrical data
In the bulk ATRP of acrylates the CuBr/PMDETA catalyst was stable and no disproportionation occurred. The rate of polymerization was faster than CuBr/bpy catalyst systems. This is because of the lower redox potential of Cu(I)/PMDETA complex than Cu(I)/bpy complex.

Figure 3- 7 shows representative GPC chromatograms of starting macro-initiator SPE1 (Table 3- 1, entry 2) (a), PMMA-\(b\)-SPE1-\(b\)-PMMA (Table 3- 3, entry 2) (b) and PEMA-\(b\)-SPE1-\(b\)-PEMA (Table 3- 3, entry 3) tri-block copolymers, respectively. Figure 3- 8 shows representative GPC traces of starting (a) SPE2 macroinitiator (Table 3- 1, entry 2), (b) PBA-\(b\)-SPE2-\(b\)-PBA (Table 3- 3, entry 9) and (c) poly(EHA)-\(b\)-SPE2-\(b\)-poly(EHA) (PEHA-\(b\)-SPE2-\(b\)-PEHA, Table 3- 3, entry 10) tri-block copolymers, respectively. In all the cases PDI of the tri-block copolymer was lower than that of the macroinitiator. The symmetrical GPC chromatograms of block copolymers and the shifting to high molecular side indicate efficient initiation of SPEs-based macroinitiators. The efficacy of the synthesis of acrylate to methacrylate block copolymer was verified by synthesizing penta-block copolymer of PMMA-\(b\)-PEHA-\(b\)-SPE2-\(b\)-PEHA-\(b\)-PMMA by further initiation of PEHA-\(b\)-SPE2-\(b\)-PEHA. Figure 3- 9 shows the GPC chromatograms of (a) PEHA-\(b\)-SPE2-\(b\)-PEHA (Table 3- 3, entry 11) and (b) PMMA-\(b\)-PEHA-\(b\)-SPE2-\(b\)-PEHA-\(b\)-PMMA (Table 3- 3, entry 12). There is an increase of PDI (1.79) of the penta-block copolymer in compare to PDI (1.44) of tri-block macroinitiator. This is attributed to the slow initiation of triblock copolymer than the propagation of MMA. The GPC trace of pentablock copolymer also shows tail at low elution volume suggesting possibility of unreacted staring macroinitiator with dead chain ends.
Figure 3- 7 GPC traces of (a) SPE1, (b) PMMA-b-SPE1-b-PMMA and (c) PEMA-b-SPE1-b-PEMA tri-block copolymers, respectively.

Figure 3- 8 GPC traces of (a) SPE2 macroinitiator, (b) PBA-b-SPE2-b- PBA and (c) PEHA-b-SPE2-b-PEHA tri-block copolymers, respectively.
3.6.4 Glass transition temperatures of different polyester-based copolymers

The $T_g$s of the UPE and SPEs and their corresponding block copolymers were determined by DSC analyses. Figure 3- 10 shows the DSC of the UPEs and their block copolymers. The UPE (Table 3- 1, entry 2) shows $T_g$ at $-19.3\, ^\circ C$. The tri-block copolymers of UPE, i.e., PMMA-b-UPE1-b-PMMA (Table 3- 2, entry 11), PEHA-b-UPE2-b-PEHA (Table 3- 2, entry 14), PEA-b-UPE2-b-PEA (Table 3- 2, entry 2) and PBA-b-UPE2-b-PBA (Table 3- 2, entry 13) show $T_g$s of $20$, $-65$, $-23.5$ and $-45.7\, ^\circ C$. On the other hand, the pentablock-copolymer PMMA-b-PEHA-b-UPE2-b-PEHA-b-PMMA (Table 3- 2, entry 15) shows a single (broad) $T_g$ at $58.73\, ^\circ C$.

![Figure 3- 9 GPC traces of (a) PEHA-b-SPE2-b-PEHA tri-block and (b) PMMA-b-PEHA-b-SPE2-b-PEHA-b-PMMA penta-block copolymers, respectively](image-url)
Figure 3-10 The DSC thermograms of (a) PMMA-b-PEHA-b-UPE2-b-PEHA-b-PMMA, (b) PMMA-b-UPE1-b-PMMA, (c) UPE, (d) PEA-b-UPE2-b-PEA, (e) PBA-b-UPE2-b-PBA and (f) PEHA-b-UPE2-b-PEHA copolymers, respectively.

Figure 3-11 shows the DSC of the SPEs and their block copolymers. The SPE (Table 3-1, entry 2) shows $T_g$ at $-21 \, ^\circ C$ which is close to the $T_g$ of UPE. The tri-block copolymers PMMA-b-SPE1-b-PMMA (Table 3-3 entry 13), PMMA-b-SPE1-b-PMMA (Table 3-3 entry 14) and PEHA-b-SPE2-b-PEHA (Table 3-3 entry 11) show $T_g$ at 79, 20 and $-38.13 \, ^\circ C$ and the pentablock-copolymer PMMA-b-PEHA-b-SPE2-b-PEHA-b-PMMA shows a (broad) $T_g$ at 52 $^\circ C$. 
In all the block copolymers only one $T_g$ was observed which was in between the glass transition temperature of polyesters and (meth)acrylates. The measured $T_g$ values are close to the $T_g$ determined by Fox equation. The appearance of single $T_g$ of all block copolymers can be readily explained by the miscibility of polyester with respective (meth)acrylate blocks. The miscibility arises due to the (i) formation of block copolymer and (ii) the ester functional group present in (meth)acrylate side chains.

In contrast to UPE the SPE shows melting temperature ($T_m$) at 43 °C ($\Delta H = 48.38 \text{ J} \cdot \text{g}^{-1}$) due to crystalline nature of the polyester. The thermograms of the tri-block copolymers PMMA-$b$-SPE1-$b$-PMMA ($T_m = 70.3$ °C, $\Delta H = 2.73 \text{ J} \cdot \text{g}^{-1}$) (Table 3-3
entry 13), PMMA-\textit{b}-SPE1-\textit{b}-PMMA ($T_m = 42.75 \, ^\circ\text{C}, \Delta H = 31.06 \, \text{J} \cdot \text{g}^{-1}$) (Table 3-3 entry 14), PEHA-\textit{b}-SPE2-\textit{b}-PEHA ($T_m = 36.4 \, ^\circ\text{C}, \Delta H = 23.6 \, \text{J} \cdot \text{g}^{-1}$) (Table 3-3 entry 11) after first heating cycle (Figure 3-11) shows a melting temperature specific to polyester block. After second heating cycle $T_m$s of the polyesters were detected for tri-block copolymers PMMA-\textit{b}-SPE1-\textit{b}-PMMA ($T_m = 43.49 \, ^\circ\text{C}$) (Table 3-3 entry 14) and PEHA-\textit{b}-SPE2-\textit{b}-PEHA ($T_m = 35.13 \, ^\circ\text{C}$) (Table 3-3 entry 11) with a weaker melting enthalpy (Figure 3-10). This may be due to the disruption of the crystalline structure of the polyester during the first heating run and did not grow back to the similar extent during the short heating time of the second run. This suggests that the greater the amount of PMMA the more difficult it is for the polyester to self-organize upon cooling.

The block copolymers containing more than 20 wt% of polyester middle block show $T_m$ some what lower than the $T_m$ of polyester. This result thus suggests that the block copolymers still are flexible and shows crystallinity. Due to combination of flexibility and crystallinity the polyester based acrylic copolymers might be useful as high strength and flexible coating material.

3.6.5 Network formation from unsaturated polyester-based block copolymers

The network formation and the disappearance of double bond in the UPE-based block copolymers were monitored by photo DSC. Figure 3-12 shows the heat flow versus time plots for UPE and three PEHA-\textit{b}-UPE-\textit{b}-PEHA copolymers of different molecular weights. The heat of reaction for the photo polymerization of UPE (Figure 3-12, plot a) was 358.4 J · g$^{-1}$. The heat of reaction decreased from 254.3 to 206 J · g$^{-1}$ with increased molecular weight of the block copolymers from 6 000 to 10 000, respectively. The method of determining photo polymerization of UPE2-\textit{block}-polyacrylate block
copolymers is in accordance to a study by Tryson and Shultz.\textsuperscript{134} The exothermic reaction showed the significant changed at the early stage of exposure time, which indicates the polymerization of UPE2-\textit{block}-polyacrylate, and then it gradually decrease due to termination reaction or by the reduction of double bond in the block copolymers.

![Graph](image_url)

Figure 3-12 Heat flow versus time plot of a series of UV-curable polyesters: (a) neat UPE and (b), (c), (d) are three different PEHA-b-UPE-b-PEHA copolymers of molecular weights 5550, 7400 and 9600, respectively.

3.7 Conclusions

In conclusions, the low cost synthesis of series of novel SPE- and UPEs-based block copolymers of (meth)acrylates were accomplished by the combination of condensation polymerization and ATRP. The polymerizations were well controlled and the main chain double bonds in the unsaturated polyester backbones remained almost
unaffected during polymerization. Because of network formation upon irradiation the UPE-based block copolymer could be suitable candidate for UV curable solvent resistant coating material with superior weather properties.
CHAPTER IV

THERMAL CURABLE POLYURETHANE-UREA COATING BASED ON POLYESTER POLYOLS

4.1 Abstract

Polyurethane-urea (PUU) coatings were formulated using Partially Blocked HDI isocyanurate (PBH), isophorone diamine (IPDA), and polyester polyol. The partially blocked isocyanate (HBP) was prepared from the reaction of the HDI isocyanurate with 2-butanone oxime as a blocking agent. The reaction of the amine/alcohol with the isocyanate was reduced due to the usage of the PBH. As a comparison, the polyurethane coatings (PU) without adding IPDA were also prepared. The thermo-mechanical properties of the PUU and PU coating were investigated by tensile test and DMTA. The glass transition temperature ($T_g$) and crosslink density of the coatings were derived from the tan δ and storage moduli ($E'$), respectively. It was found that the PUU coating exhibited higher crosslink density, $T_g$, tensile modulus and tensile strength value than the corresponding PU coating.
4.2 Introduction

Polyurethane resins are typically prepared from the reaction of the polyisocyanate with polyol, while polyurea resins are typically prepared from the reaction of the polyisocyanate with polyamine. The preparation schemes of urethane and urea are shown in Figure 4-1. Polyurethane resins have wide applications in coatings such as wood, plastic, automotive, industrial coatings, because polyurethane coatings show superior chemical and solvent resistance, flexibility, superior adhesion, and abrasion and corrosion resistance. The properties of the polyurethane coating can be easily tailored by varying the polyols and polyisocyanate. The most common polyols are polyester polyols and followed by polyether polyols. Isocyanate can be aromatic or aliphatic. Aromatic isocyanates react faster than aliphatic isocyanates and are less expensive. Aliphatic isocyanates have better color retention and exterior durability.

\[
\text{a.} \quad \text{R-NCO} + \text{R'-OH} \rightarrow \text{R-NOR'}
\]

\[
\text{b.} \quad \text{R-NCO} + \text{R'-NH}_2 \rightarrow \text{R-NR'N-O}
\]

Figure 4-1 General synthetic scheme for (a) urethane, (b) urea

Compared with polyurethane coating, polyurea coating has less wide applications due to two major drawbacks. One is the faster curing of the polyurea, the reaction of the isocyanate and amine could be cured within seconds, which makes it good for only two-component spray coating application, but limits its wide application for
other coatings\textsuperscript{136,137}. Another drawback is that polyamine starting raw material for polyurea is very limited, and usually polyamine is based on the polyether amine.

Several strategies have been reported to decrease the reaction of the amine and isocyanate. Such as using hindered amine\textsuperscript{138}, blocked amine\textsuperscript{138} and blocked isocyanate\textsuperscript{139,140,141,142,45} reduce the reactivity of the amine towards isocyanate. Hindered amine could be prepared from the reaction of the primary amine with dialkyl maleates via the Michael addition. Blocked amine could be prepared from the reaction of the primary amine with carbonyl compound via the imine formation route\textsuperscript{138}. Blocked isocyanate could be prepared from the reaction of the isocyanate with an active hydrogen compound. Upon heating, the blocked isocyanate decomposes and releases the free isocyanate which reacts with coreactant to form polyurethane or polyurea, respectively\textsuperscript{44}. The overall reaction is illustrated in Figure 4-2. The polyurea coating could also be formed based on moisture curing route. In this case, polyisocyanate reacts with moisture to form free amine. The in-situ generated amine reacts immediately with polyisocyanate forming urea linkage.\textsuperscript{138,143}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure4-2.pdf}
\caption{General synthetic scheme for preparation of polyurea and polyurethane from the blocked isocyanate}
\end{figure}
One of main advantages of polyester over polyether is its more varieties. Industrial polyether is generally limited in monomer composition to propylene oxide, ethylene oxide, butylene oxide and tetrahydrofuran. Industrial polyester is the condensation product of acids and alcohols. The variety of the combination of acids and alcohols adds to the potential versatility of polyester. It has been reported that the amine terminated polyester has been prepared, but the reaction step is complex, which makes it impossible for large-scale production and coating applications. And also, the amine terminated polyester is unstable. The aminolysis of the ester backbone is easy to take place due to the existence of the terminated amine function group. This limits the preparation of the polyurea from the reaction of the polyisocyanate with amine terminated polyester.

In this article, partially blocked isocyanate was prepared to decrease the reaction of the alcohol and isocyanate. The mixture of the polyester polyol, partially blocked isocyanate and isophorone diamine (IPDA) were chosen as the starting materials to prepare polyurethane-urea (PUU) coatings. Such polyurethane-urea (PUU) coatings were expected to have a longer pot life than conventional 2K polyurea or polyurethane coating, a better mechanical property than polyurethane coating due to the existence of the extra urea function group, and a better abrasion resistance and chemical resistance property than polyether polyurea coating due to the existence of the ester function group. As a comparison, the polyurethane coatings (PU) without adding IPDA were also prepared. The mechanical properties of the PUU and PU coating were investigated by using tensile test and DMTA. The glass transition temperature ($T_g$) and crosslink density of the coatings were derived from the tan $\delta$ and storage moduli ($E'$), respectively.
4.3 Materials

Adipic acid (AA), isophthalic acid (IPA), 1,4 butanediol (BD), 1,5-pentanediol (PD), 1,6 hexane diol (HD), p-xylene, dibutyl tin oxide (DBTO), dibutyltin dilaurate, isophorone diamine (IPDA) tetrahydrofuran (THF), 2-butanone oxime (BKO) all Aldrich products were used as received, HDI isocyanurate (3HDI) (Desmodur N-3300, NCO content 21%) was provided by Bayer Corp. The chemical structures of the monomers for preparation of the polyester are shown in Figure 4- 3.

Figure 4- 3 Structures of the monomers for preparation of polyester polyols

4.4 Instrumentation and characterization

Fourier Transform Infrared Spectroscopy was obtained on a Nicolet 380 FTIR instrument (Thermo Electron Corp.). The NMR spectra were taken in a Varian Mercury 300 MHz spectrophotometer. Gel permeation chromatography measurements were performed on a Waters GPC instrument equipped with a series of six Styragel columns (HR 0.5, HR 1, HR 3, HR 4, HR 5 and HR 6) calibrated with narrow-MWD polystyrene
standards. Tetrahydrofuran was used as the mobile phase with a flow rate of 1.0 mL/min. A refractive index (RI) detector (Optilab, Wyatt Technology), and a dual-ultraviolet absorbance detector (Waters 2487), and a laser light scattering detector (Minidawn, Wyatt Technology) were used to obtain number average molecular weight Mn, weight average molecular weight Mw and polydispersity index (PDI). Glass transition and melting temperatures for all samples were measured on a Q1000 differential scanning calorimeter (DSC) from TA Instruments at a heating rate of 10°C/min. The experiments were run under nitrogen atmosphere.

Viscoelastic properties of the cross-linked films were obtained with a Perkin Elmer Pyris Dyamond Dynamic Mechanical Thermal Analyzer (DMTA) with a frequency of 1 Hz and a heating rate of 3 °C/min over a range of -50 to 120 °C. The gap distance was set up at 4 mm for rectangular specimens (length 10 mm, width 8-10 mm and thickness 0.09-0.11 mm). The crosslinking density was determined from the rubbery plateau in the storage modulus vs. temperature plot. Glass transition temperature (T_g) of the crosslinked polyester-urethane-ureas were determined from the tan δ vs temperature plots.

The tensile properties were obtained by an Instron Universal Tester model 1000. The dimensions of the films for tensile testing were 0.09-0.11 mm in thickness, 6.5 mm wide and an initial length of 25 mm. A crosshead speed of 10 mm/min was applied. All the testing was carried out at room temperature. The modulus, tensile stress, and elongation at break were measured. The stress and the strain were calculated using the following equations:

\[ \sigma = \frac{F}{A} = \frac{F}{w \times t} \]  

(4-1)
\[ \varepsilon = \frac{\Delta L}{L_o} \]  

(4-2)

In which, \( \sigma \) is the stress, \( \varepsilon \) means the strain, \( F \) is the load, \( w \) is the width, \( t \) is the thickness, \( \Delta L \) is the change in length of the gauge, and \( L_o \) is the initial gauge length. So, using the given load and elongation data, stress vs. strain plots was constructed.

Pencil hardness (ASTM D 3363-74), cross-hatch adhesion (ASTM D 3359-87), pull-off adhesion (ASTM D 4541-85), impact and reverse impact resistance (ASTM D 2784-94) were performed according to ASTM standards.

4.5 Synthesis

In this synthesis part, four different kinds of polyester polyols were synthesized by the direct polymerization of diacids and diols. The PBH was synthesized by the reaction of HDI isocyanurate with blocking agent.

4.5.1 Synthesis of polyester polyol

To synthesize hydroxyl terminated polyester, excess diol was used. The molar ratio of diol to diacid is 3:2. A representative example of synthesis of polyester polyol is as follows. For synthesis of AA-BD polyester diol, in a 500 ml four-neck round bottom flask which is equipped with a mechanical stirrer, a gas inlet, a temperature controller, a Dean-Stark trap and a condenser, adipic acid (131.53 gm, 0.90 mol), 1,4 butanediol (122 gm, 1.35 mol) was added under argon atmosphere to minimize oxidative degradation. To accelerate the reaction, DBTO (0.4 wt %, 1.01 g), a transesterification catalyst, was used. Then xylene (3 wt %, 7.61 g) was also added to remove water from the resin as a form of azeotropic mixture. In order to minimize the glycol loss by evaporation the reaction
temperature was carefully controlled using a temperature controller and a thermocouple. The mixture was heated to 210 °C. The final temperature was held until the resin had an acid number measured by titration less than or equal to 10 mg KOH/g resin (ASTM D 1639-90). The reaction was completed after 5 hrs and final acid number was 4.9 mg KOH/g resin.

Other polyesters, such as AA-PD and AA-HD were synthesized using the same procedure. For AAIPA-HD polyester synthesis, the molar ratio of diol to diacid is 3:2 while keeping the ratio of AA to IPA is 1:1. The properties of the polyester polyols are shown in Table 4-1.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>Acid #</th>
<th>Hydroxyl #</th>
<th>M_n</th>
<th>PDI</th>
<th>Viscosity (mPa.s)</th>
<th>T_g(°C)</th>
<th>T_m(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA-BD</td>
<td>4.9</td>
<td>155.6</td>
<td>1125</td>
<td>1.34</td>
<td>67.19</td>
<td>-20.4</td>
<td>38.8</td>
</tr>
<tr>
<td>AA-PD</td>
<td>6.5</td>
<td>222.1</td>
<td>1086</td>
<td>1.50</td>
<td>52.79</td>
<td>-5.0</td>
<td>30.0</td>
</tr>
<tr>
<td>AA-HD</td>
<td>6.1</td>
<td>247.2</td>
<td>1101</td>
<td>1.46</td>
<td>33.59</td>
<td>-3.0</td>
<td>41.0</td>
</tr>
<tr>
<td>AAIPA-HD</td>
<td>6.3</td>
<td>176.5</td>
<td>1150</td>
<td>1.27</td>
<td>33.49</td>
<td>-55.8</td>
<td>3.1</td>
</tr>
</tbody>
</table>

*Polyester in methyl ethyl ketone (MEK) solution with polyester concentration of 70 wt %

4.5.2 Synthesis of partially blocked HDI isocyanurate (PBH)

For the synthesis of PBH, in a three neck round bottom flask, HDI isocyanurate (3HDI) (80 g, 0.40 mol NCO) was dissolved in dry THF (80 ml) and cooled to 0 °C. Dibutyltin dilaurate (0.04 g) was added into it. Next, 2-butanone oxime (29.04 g, 0.33 mol) blocking agent was added drop wise with constant stirring under nitrogen atmosphere and kept for 2 h at 0 °C. The mixture was then allowed to stir for overnight at room temperature. THF was removed under vacuum and the product was characterized by IR and NMR. The free NCO content is 2.6 wt% and blocked NCO content was 12.9 wt%.
The product partially blocked isocyanurate (PBH) was characterized by IR and NMR spectroscopy.

4.6 Coating formulation

For preparation of the polyester polyurethane (PU) coatings, polyesters were diluted in methyl ethyl ketone (60 wt% of polyester) and then mixed with the polymer of hexane 1,6 diisocyanate (HDI) isocyanurate. The mole ratio of isocyanate group to hydroxyl group is kept constant at 1.1/1.0). The flow aid agent Tego wet 270 (0.2 wt%, based on the total solid) was added into the mixture. For preparation of the polyester polyurethane-urea coatings (PUU), polyesters were diluted in methyl ethyl ketone (60 wt% of polyester) and then mixed with the isophorone diamine (IPDA) and partially blocked hexane 1,6 diisocyanate (HDI) isocyanurate (PBH). The mole ratio of isocyanate group to hydroxyl and amine group is kept constant at NCO: OH: NH$_2$ = 1.1: 0.7: 0.3. Then the flow aid agent Tego wet 270 (0.2 wt%, based on the total solid) was added into the coating formulations to adjust the surface tension and obtain crater-free films. The films were cast on the aluminum panels with the thickness of 6 mil by a drawbar for the general coating testing. The films were cured at 120 °C for 1h. For mechanical and tensile properties the films were casted on a glass panel with a thickness of 8 mil. The cured films were stored for 3 days under ambient atmospheric conditions before testing. Actual composition for the formulation of polyurethane (PU) and polyurethane-urea coatings (PUU) coatings is given in Table 4-2.
Table 4-2 Formulation of polyurethane-urea (PUU) and polyurethane (PU) coatings

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polyester</th>
<th>IPDA</th>
<th>Crosslinker*</th>
<th>MEK</th>
<th>Tego 270</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt. (g)</td>
<td>Wt. (g)</td>
<td>Wt. (g)</td>
<td>Wt. (g)</td>
<td>(gm)</td>
</tr>
<tr>
<td>AA-BD-PUU</td>
<td>10.00</td>
<td>1.01</td>
<td>11.88</td>
<td>6.67</td>
<td>0.046</td>
</tr>
<tr>
<td>AA-PD-PUU</td>
<td>10.00</td>
<td>1.45</td>
<td>16.96</td>
<td>6.67</td>
<td>0.057</td>
</tr>
<tr>
<td>AA-HD-PUU</td>
<td>10.00</td>
<td>1.60</td>
<td>18.85</td>
<td>6.67</td>
<td>0.061</td>
</tr>
<tr>
<td>AAIPA-HD-PUU</td>
<td>10.00</td>
<td>1.15</td>
<td>13.49</td>
<td>6.67</td>
<td>0.049</td>
</tr>
<tr>
<td>AA-BD-PU</td>
<td>10.00</td>
<td>1.15</td>
<td>13.49</td>
<td>6.67</td>
<td>0.030</td>
</tr>
<tr>
<td>AA-PD-PU</td>
<td>10.00</td>
<td>1.45</td>
<td>16.96</td>
<td>6.67</td>
<td>0.035</td>
</tr>
<tr>
<td>AA-HD-PU</td>
<td>10.00</td>
<td>1.60</td>
<td>18.85</td>
<td>6.67</td>
<td>0.036</td>
</tr>
<tr>
<td>AAIPA-HD-PU</td>
<td>10.00</td>
<td>1.15</td>
<td>13.49</td>
<td>6.67</td>
<td>0.032</td>
</tr>
</tbody>
</table>

*The crosslinker was used modified HDI isocyanurate (PBH) for PUU coating, and HDI isocyanurate for PU coatings
** For PUU coating, total NCO content was used including the blocked NCO

4.7 Results

The objective of this study was to prepare polyester based polyurethane-urea hybrid coatings. Isophorone diamine (IPDA) was selected to work as a chain extender and also provide urea function group. Partially blocked HDI isocyanurate (PBH) was chosen with two functionalities: One function is to slow down the reaction of the isocyanate with polyester polyol and increase the pot life, since the isocyanate function group is blocked. Another function is to reduce the loss of the IPDA at high curing temperature (120°C), since the amine group in the IPDA reacts with the free isocyanate group in the PBH during the mixing at room temperature, making the IPDA less volatile. The diol and diacid starting materials were varied to change the properties of the polyester polyol, thus the properties of the polyurethane-urea coating (PUU). The polyurethane coatings (PU) without adding IPDA were also prepared to compare with the PUU coatings.
4.7.1 Preparation of partially blocked HDI isocyanurate (PBH)

The preparation method of partially blocked HDI isocyanurate (PBH) was illustrated in Figure 4-4a. The reaction of the HDI isocyanurate with blocking agent 2-butanone oxime (BKO) was carried out at 0°C followed by at room temperature. 83.3% of the NCO was reacted with 2-butanone oxime (BKO) to form the blocked NCO, and 16.7% free NCO was left.

![Reaction diagram](image)

Figure 4-4 Reaction strategy for preparation of coatings, (a) polyester-urethane-urea (PUU) coatings, (b) polyester-urethane (PU) coatings
The formation of the blocked NCO and the existence of the free NCO were confirmed by the FTIR and NMR. The FTIR analysis performed in HDI isocyanurate (3HDI) and partially blocked HDI isocyanurate (PBH) were shown in Figure 4- 5. Characteristic band of the free isocyanate group in 3HDI was obtained in the 2247 cm\(^{-1}\) region. In the PBH, the FTIR shows less intense band in the 2247 cm\(^{-1}\) region, which means that there is still free isocyanate left in PBH. The new bands in the range of 3390 cm\(^{-1}\) and 1730 cm\(^{-1}\) regions are attributed to the N-H bond stretching with urethane and C=O non-bonded urethane stretching, which indicates the formation of the urethane in the PBH.

Figure 4- 5 IR spectrum of partially blocked HDI isocyanurate (PBH)

\(^1\)H NMR and \(^{13}\)C NMR analysis performed in partially blocked HDI isocyanurate (PBH) are shown in Figure 4- 6. The \(^1\)H NMR spectra in Figure 4- 6a show one resonance at δ 7.20 ppm indicating the presence of proton from urethane group. The \(^{13}\)C
NMR spectra in Figure 4-6b shows one resonance at δ 122.20 ppm indicating the presence of free isocyanate (-N=C=O) function group.

Figure 4-6 NMR of partially blocked HDI isocyanurate (PBH), (a) $^1$H NMR and (b) $^{13}$C NMR

4.7.2 Tensile properties

The tensile strength, elongation at break, and tensile modulus of PUU and PU coatings synthesized from different polyester polyols are shown in Figure 4-7, and summarized in Table 4-3. For both PUU and PU coatings, the tensile strength and modulus was increased in the order of the systems containing the diol of 1,4-butanediol (AA-BD); 1,5-pentanediol (AA-PD); and 1,6-hexanediol (AA-HD). And the strength and modulus was further increased with the incorporation of the aromatic diacid isophthalic acid (IPA) into the system. The elongation at break is in the range of 100 ~ 150 % for the all the PUU coating systems. The elongation at break is in the range of 20 ~ 50% for AA-BD, AA-PD, and AA-HD based PU coating, and 150% for AA-HD based PU coating. As a comparison of the PUU coating with PU coating, it was found that the tensile modulus of PUU coating is around 2 ~ 3 times higher than those of the PU coatings. The tensile
strength of the PUU coating is around 3 ~ 6 times higher than those of the PU coatings. The elongation at break of the PUU coating is around 3 ~ 5 times higher than those of the PU coatings except the AAIPA-HD based coating. In that case, AAIPA-HD PUU coating showed slightly lower elongation at break than AAIPA-HD PU coating.

Figure 4- 7 Tensile properties of PUU and PU coatings, (a) tensile strength, (b) tensile modulus, (c) elongation at break
Table 4-3 Tensile Properties of polyurethane-urea (PUU) and polyurethane (PU) coatings

<table>
<thead>
<tr>
<th>Samples</th>
<th>Modulus (MPa)</th>
<th>Tensile stress (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA-BD-PUU</td>
<td>9.28 ± 0.43</td>
<td>5.87 ± 1.18</td>
<td>118.73 ± 15.31</td>
</tr>
<tr>
<td>AA-PD-PUU</td>
<td>12.72 ± 2.19</td>
<td>9.38 ± 1.04</td>
<td>150.52 ± 11.85</td>
</tr>
<tr>
<td>AA-HD-PUU</td>
<td>13.64 ± 2.90</td>
<td>11.33 ± 3.51</td>
<td>148.92 ± 26.02</td>
</tr>
<tr>
<td>AAIPA-HD-PUU</td>
<td>55.58 ± 15.41</td>
<td>14.30 ± 0.95</td>
<td>95.48 ± 7.17</td>
</tr>
<tr>
<td>AA-BD-PU</td>
<td>4.46 ± 0.61</td>
<td>0.95 ± 0.48</td>
<td>27.61 ± 14.98</td>
</tr>
<tr>
<td>AA-PD-PU</td>
<td>7.97 ± 0.52</td>
<td>1.98 ± 0.78</td>
<td>28.63 ± 10.30</td>
</tr>
<tr>
<td>AA-HD-PU</td>
<td>8.34 ± 0.74</td>
<td>2.87 ± 1.30</td>
<td>44.00 ± 19.79</td>
</tr>
<tr>
<td>AAIPA-HD-PU</td>
<td>15.18 ± 1.17</td>
<td>6.48 ± 4.71</td>
<td>150.16 ± 59.82</td>
</tr>
</tbody>
</table>

4.7.3 Viscoelastic properties

The viscoelastic properties of the PUU and PU coating films were investigated using DMTA. The storage modulus $E'$ and the $\tan\delta$ transition of PUU and PU coatings synthesized from different polyester polyols are shown in Figure 4-8 and Figure 4-9. The storage modulus ($E'$) remained almost constant as the temperature was increased up to the glass transition and started to decrease during the transition. The decrease reached a minimum value and then slightly increased with temperature forming a rubbery plateau. This changing tendency follows the general rule described as equation below\(^{146}\)

$$E' = 3 \nu_e RT \ (T >> T_g) \ (4-3)$$

where $\nu_e$ is the number of moles of elastically effective network chains per cubic meter of film and $E'$ is tensile storage modulus. This relationship is effective when $T >> T_g$, and for low crosslink density elastomers. For the highly crosslinked system, it can only be used to evaluate the relative density of crosslinking. Crosslink density was calculated by this equation with the $E'$ at corresponding temperature $T$ ($T > T_g + 50^\circ C$). The minimum of storage modulus, $E'(\text{min})$, was recorded as the minimum value in rubbery plateau. The $T_g$ was obtained from the maximum of the $\alpha$-transition.
The storage modulus E’ of PUU and PU coatings synthesized from different polyester polyols are shown in Figure 4-8. The E’ (min) and the crosslink density (νc) of the PUU and PU coatings were independent of the type of the polyester polyols. In comparison with the PU coatings, the PUU coatings exhibited higher E’(min) and the crosslink density (νc) than the corresponding PU coatings. This is due to the incorporation of the IPDA chain extender in PUU coatings. The incorporation of the IPDA could contribute the formation of urea and the increase of crosslink density, leading to the increase of the storage modulus.

Figure 4-8 Modulus (E’) as a function of temperature of polyurethane-urea (PUU) and polyurethane (PU) coatings based on (a) AA-BD, (b) AA-PD, (c) AA-HD, (d) AAIPA-HD
The tan δ of PUU and PU coatings synthesized from different polyester polyols are shown in Figure 4-9. The breadth and maximum of tanδ of the PUU and PU coatings were independent of the type of the polyester polyols for AA-BD, AA-PD, and AA-HD. The breadth of tanδ and maximum of tanδ was decreased with incorporation of the aromatic diacid isophthalic acid (IPA) into the system. As comparison of the PU coatings, PUU coatings showed higher values in the breadth of tanδ and lower values in maximum of tanδ, this indicated that the incorporation of the IPDA increased the heterogeneity of cured coatings.

Figure 4-9 Tan δ as a function of temperature of polyurethane-urea (PUU) and polyurethane (PU) coatings based on (a) AA-BD, (b) AA-PD, (c) AA-HD, (d) AAIPA-HD
The Tg, minimum elastic modulus (E’), crosslink density (νe), breadth of tanδ transition, and maximum of tanδ transition of PUU and PU coatings synthesized from different polyester polyols are summarized in Table 4-4.

Table 4-4 Viscoelastic properties of polyurethane-urea (PUU) and polyurethane (PU) coatings

<table>
<thead>
<tr>
<th>Sample</th>
<th>T for E’min (°C)</th>
<th>E’min (MPa)</th>
<th>νe (mol/m³)</th>
<th>Tg (°C)</th>
<th>Tan δ Breadth (°C)</th>
<th>Max. Tan δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA-BD-PUU</td>
<td>66.95</td>
<td>3.21</td>
<td>378.53</td>
<td>-9.14</td>
<td>46.91</td>
<td>0.62</td>
</tr>
<tr>
<td>AA-PD-PUU</td>
<td>92.94</td>
<td>1.84</td>
<td>201.62</td>
<td>32.60</td>
<td>43.43</td>
<td>0.71</td>
</tr>
<tr>
<td>AA-HD-PUU</td>
<td>79.44</td>
<td>0.92</td>
<td>104.61</td>
<td>42.19</td>
<td>54.62</td>
<td>0.62</td>
</tr>
<tr>
<td>AAIPA-HD-PUU</td>
<td>103.24</td>
<td>1.45</td>
<td>154.13</td>
<td>15.73</td>
<td>36.71</td>
<td>1.03</td>
</tr>
<tr>
<td>AA-BD-PU</td>
<td>26.44</td>
<td>0.06</td>
<td>8.56</td>
<td>-9.54</td>
<td>20.28</td>
<td>1.29</td>
</tr>
<tr>
<td>AA-PD-PU</td>
<td>26.92</td>
<td>0.89</td>
<td>119.18</td>
<td>1.73</td>
<td>23.12</td>
<td>0.98</td>
</tr>
<tr>
<td>AA-HD-PU</td>
<td>30.03</td>
<td>0.78</td>
<td>103.15</td>
<td>2.53</td>
<td>31.26</td>
<td>0.93</td>
</tr>
<tr>
<td>AAIPA-HD-PU</td>
<td>49.55</td>
<td>0.34</td>
<td>42.24</td>
<td>-1.30</td>
<td>22.19</td>
<td>1.56</td>
</tr>
</tbody>
</table>

4.7.4 General coating properties

A summary of the PUU and PU coating properties is found in Table 4-5. After thermal curing, several film properties were evaluated: pencil hardness, cross-hatch adhesion, gloss, and impact resistance. The type of the polyester polyol and the incorporation of the IPDA did not affect pencil hardness, impact resistance, and cross-hatch adhesion of the coatings.
Table 4- 5 Coating properties of polyurethane-urea (PUU) and polyurethane (PU) coatings

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pencil Hardness</th>
<th>Cross-hatch adhesion</th>
<th>Gloss 20°</th>
<th>Gloss 60°</th>
<th>Impact (lb/inch)</th>
<th>Reverse Impact (lb/inch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA-BD-PUU</td>
<td>5H</td>
<td>5B</td>
<td>114.10</td>
<td>127.40</td>
<td>&gt;40</td>
<td>&gt;40</td>
</tr>
<tr>
<td>AA-PD-PUU</td>
<td>5H</td>
<td>5B</td>
<td>118.53</td>
<td>142.58</td>
<td>&gt;40</td>
<td>&gt;40</td>
</tr>
<tr>
<td>AA-HD-PUU</td>
<td>5H</td>
<td>5B</td>
<td>123.62</td>
<td>136.08</td>
<td>&gt;40</td>
<td>&gt;40</td>
</tr>
<tr>
<td>AAIPA-HD-PUU</td>
<td>5H</td>
<td>5B</td>
<td>118.26</td>
<td>140.78</td>
<td>&gt;40</td>
<td>&gt;40</td>
</tr>
<tr>
<td>AA-BD-PU</td>
<td>5H</td>
<td>5B</td>
<td>93.76</td>
<td>123.22</td>
<td>&gt;40</td>
<td>&gt;40</td>
</tr>
<tr>
<td>AA-PD-PU</td>
<td>5H</td>
<td>5B</td>
<td>118.98</td>
<td>130.53</td>
<td>&gt;40</td>
<td>&gt;40</td>
</tr>
<tr>
<td>AA-HD-PU</td>
<td>5H</td>
<td>5B</td>
<td>119.50</td>
<td>132.60</td>
<td>&gt;40</td>
<td>&gt;40</td>
</tr>
<tr>
<td>AAIPA-HD-PU</td>
<td>5H</td>
<td>5B</td>
<td>123.25</td>
<td>137.42</td>
<td>&gt;40</td>
<td>&gt;40</td>
</tr>
</tbody>
</table>

4.8 Discussion

Polyester polyurethane-urea (PUU) coating crosslinking mechanism was illustrated in Figure 4-10. During the mixing step, half of the amine group in isophorone diamine (IPDA) reacted with the free isocyanate function group in the partially blocked isocyanurate (HBP), leading to the formation the urea. This step could not induce the occurrence of the gelation although the viscosity of the mixture was increased since there are no multi-functional groups involved in this reaction. On another hand, this step could hold the isophorone diamine (IPDA) into the system, minimizing its loss in the following heating step. During the heating step, the blocking agent 2-butanone oxime was released and the free isocyanate was formed, such free isocyanate first reacted with the IPDA then reacted with the polyester polyols. Thus crosslinked polyester polyurethane-urea coating was formed. For the preparation of the polyester polyurethane coating as illustrated in Figure 4-4-b, during the mixing step, the free isocyanate function group reacted with the hydroxyl group in the polyester polyol to form the polyurethane. This reaction could induce the occurrence of the gelation since three-functional isocyanate group was
involved during this step. During the heating step, the reaction of the isocyanate with the polyol was accelerated and crosslinked polyurethane (PU) coating was formed. As comparison of the PUU coating with PU coating in terms of the formulation step at room temperature and the following crosslinking step at relative high temperature, it was found that the PUU coatings showed longer pot-life than corresponding PU coatings, which makes PUU coating easier to handle during the formulation step.

Figure 4-10 Reaction mechanism for preparation of the polyester polyurethane-urea coatings

As a comparison of the PUU coating with PU coating, it was found that the tensile modulus and tensile strength of PUU coating showed higher values than those of the corresponding PU coatings. This could be explained that the addition the IPDA leads to formation of the urea unit, increase in physical interaction forces from the hydrogen bonding among urea groups and increase in the hard segments content of the crosslinked films. The elongation at break of the PUU coating also showed higher values than those of the PU coatings except the AAIPA-HD based coating. In that case, AAIPA-HD PUU coating showed slightly lower elongation at break than AAIPA-HD PU coating.
reduction in elongation for PUU coating could be explained that the incorporation of the rigid aromatic unit restrict the polymer movement upon stretching\textsuperscript{147}.

Compared with the PU coating, PUU coating with the incorporation of the IPDA showed two major trends in the dynamic mechanical analysis. One corresponded to broadening of the transition region and the other represented the shift of the maximum tan $\delta$ value toward lower numbers and higher temperatures. The breadth of a transition region is closely related to the degree of heterogeneity\textsuperscript{125,148}. As given in Table 4- 4, tan $\delta$ transition breadths was increased with the incorporation of IPDA, which suggested that the existence of the IPDA has major impact on the heterogeneity, and the incorporation of the IPDA cause the increase of heterogeneity of the systems. The crosslink density has a direct impact on the tan $\delta$ such that it reduces long range segmental motion required for viscous flow behavior\textsuperscript{149}. As a result, the maximum tan $\delta$ can be used to measure the extent of cure. The maximum tan $\delta$ in the tan $\delta$ curve decreases as the incorporation of the IPDA. This indicates that the crosslink density of the PUU coating increases with the incorporation of the IPDA. The maximum tan $\delta$ of PUU coating is lower than that of the corresponding PU coating. This is another evidence to show that the PUU coating has a higher crosslink density, and higher tensile and storage modulus. The Tg was obtained as the maximum of tan $\delta$. It was found the Tg increased with the incorporation of the IPDA, and the Tg of PUU coating is higher than that of corresponding PU coating. An increase in Tg corresponded to a decrease in mobility in the polymer. The extra formation of the urea crosslinking networks in the PUU coating system would hinder the movement of the polymer chains, resulting in the increase of the Tg\textsuperscript{150}. It indicates that with incorporation of the IPDA, the crosslink density of PUU coating enhanced, leading to the increase of
Tg of the coating. The Tg of PUU coating is higher than that of the PU coating. This can be attributed to the additional physical crosslink density formation via the hydrogen bonds between the urea groups in the PUU coating.

4.9 Conclusions

Thermal curable long pot life 2K polyester based polyurethane-urea (PUU) coating was successfully prepared. During the formulation, four different polyester polyols were chosen as the binders, isophorone diamine (IPDA) was chosen as the chain extender and also as the reactant for the formation of urea units, and the partially blocked HDI isocyanurate (PBH) was chosen as crosslinker to increase pot life and reduce the loss the IPDA. As a comparison, the polyurethane coatings (PU) without adding IPDA were also prepared. With the incorporation of the IPDA, the tensile modulus and tensile strength of PUU coating showed higher values than those of the corresponding PU coatings due to the formation of the urea unit and extra physical interaction forces from the hydrogen bonding among urea groups. With the incorporation of the IPDA, PUU coating showed higher value than the corresponding PU coating in terms of crosslink density, Tg, and tan δ transition breadth.
CHAPTER V

PREPARATION OF THE THERMAL CURABLE NON-ISOCYANATE POLYURETHANE COATINGS

5.1 Abstract

Non-isocyanate polyurethane coatings were prepared by the thermo-curing of the polyamine and cyclic carbonate terminated polyester. Cyclic carbonate terminated polyester was synthesized from the reaction of the carbon dioxide and epoxidized polyester which was prepared from the polyester polyol with the epichlorohydrin under the catalyst. The properties of the epoxidized and cyclic carbonate terminated polyester were characterized by Brookfield viscometer, NMR and FT-IR. The cyclic carbonate terminated polyester could react with polyamine to give non-isocyanate polyurethane networks.

5.2 Introduction

Polyurethanes have been an important class of resins for organic coatings because they have toughness, excellent wear and tear properties. And polyurethanes are usually synthesized through the polycondensation reaction between diisocyanate and
This is less desirable because the diisocyanate is highly hazardous, and the phosgene which is the raw material of isocyanate is instable and toxic. It was known that the carbamate group can be synthesized by the reaction of the primary amine with cyclic carbonate. This provides a useful way to obtain non-isocyanate polyurethanes.

Linear non-isocyanate polyurethanes can be obtained by the reaction of bifunctional five-membered aliphatic cyclic carbonates with diamines. Optically active poly(hydroxyurethane)s with \( M_n \) of 11,000-24,000 were prepared by the reaction of L-Lysine with bifunctional five-membered cyclic carbonate. A series of polyurethanes with \( M_n \) of 6,000-9,000 and relatively low PDI around of 1.5 were obtained by the polyaddition of phenoxy carbonyloxymethyl ethylene carbonate with diamines. Polyhydroxyurethane can also be prepared in high yields by the reaction of the bis(cyclic carbonates) with diamines in aqueous media. A network of non-isocyanate polyurethanes can be obtained when multifunctional cyclic carbonate oligomers are used in the reaction with multifunctional primary amines.

The poly(cyclic carbonate)s were usually prepared by the reaction of poly(epoxide)s under \( CO_2 \) in the presence of catalyst. Most of poly(epoxide)s for non-isocyanate polyurethane synthesis reported are low molecule monomers. Recently, epoxidized soybean oil oligomer has been reported as a starting material to prepare non-isocyanate polyurethanes. Polyester is a widely used polyol reagent to prepare polyurethanes by reaction with polyisocyanates. Here, our interest is the preparation of non-isocyanate polyurethanes. In best of our knowledge there is no report of the synthesis of non-isocyanate polyurethanes by using epoxidized polyester oligomer as starting material. In this chapter, hydroxyl terminated polyester was first prepared, then
epoxidized polyester was prepared from the hydroxyl terminated polyester with the epichlorohydrin under the catalysts, and lastly, cyclic carbonate terminated polyester was synthesized from the reaction of epoxidized polyester and the carbon dioxide. The hydroxyl terminated, epoxidized terminated, and cyclic carbonate terminated polyesters were characterized by FTIR and NMR. Non-isocyanate polyurethane coatings were prepared by the thermo-curing of the cyclic carbonate terminated polyester and polyamine.

5.3 Materials

Materials: Adipic Acid (AA), p-xylene, 1,6 hexane diol (HD), trimethylolpropane (TMP), dibutyl tin oxide (DBTO), zinc perchlorate hexahydrate, tetrabutylammonium bromide (TBAB), epichlorohydrin (>99%), isophorone diamine (>98%), sodium hydroxide (>97%), acetone, and dichloromethane, all Aldrich products were used as received.

5.4 Characterization

The FT-IR spectra of the hydroxyl terminated, epoxidized terminated, and cyclic carbonate terminated polyester were measured in a Nicolet 380 FTIR spectrophotometer. The results were analyzed using OMNIC software. The NMR spectrum of the hydroxyl terminated, epoxidized, and cyclic carbonate terminated polyester were taken in a Varian Mercury 300 MHz spectrophotometer.
5.5 Synthesis

In this synthesis part, hydroxyl terminated, epoxy terminated, and cyclic carbonate terminated polyesters were prepared.

5.5.1 Synthesis of hydroxyl terminated polyester (H-PE)

Adpic acid (AA) (146.14 g, 1 mol), 1,6 hexane diol (HD) (118.18 g, 1 mol) and Trimethylolpropane (TMP) (67.09 g, 0.5 mol) were taken in a 500 ml four-neck round bottom flask which was equipped with a mechanical stirrer, a gas inlet, a temperature controller, a Dean-Stark trap and a condenser. The reaction proceeded under argon to minimize oxidative degradation. To accelerate the reaction, 0.4 wt % of DBTO, a transesterification catalyst, was used. Then, 3 wt % of p-xylene was also added into the reaction mixture to remove water from the resin as azeotropic mixture. The reaction temperature was carefully controlled using a temperature controller and a thermocouple in order to minimize evaporation of diol. The temperature of the mixture was increased from 20-150 °C at a rate of 4.3 °C/min, and then from 150-210 °C at a rate of 0.25 °C/min. The final temperature was held until the resin had an acid number measured by titration less than or equal to 10 mg KOH/g resin. The hydroxyl number of polyesters (297 mg KOH/g resin) was determined by ASTM method (ASTM D 1957-86).

5.5.2 Synthesis of epoxidized polyester (E-PE)

Epichlorohydrin (17.135 g) was added carefully while stirring the hydroxyl terminated polyester H-PE (50 g) and zinc perchlorate hexahydrate (1.5 g) mixture at 80 °C. After 20 hours reaction, the temperature was cooled down to 60 °C and 300 mL acetone was added. Then, 23.15 g of NaOH (32% aqueous solution) was added drop wise.
Stirring was continued for 5 hours. Filtered while hot and the solvent were removed under reduced pressure to yield epoxidized polyester (E-PE).

5.5.3 Synthesis of cyclic carbonate polyester (CC-PE)

Epoxidized polyester (E-PE) (20g) and the catalyst tetrabutylammonium bromide (TBAB) (0.654 g) were placed in a 50 mL reactor, stirred, and heated. The reaction was carried out at 110 °C for 12 hours to yield cyclic carbonate polyester (CC-PE). The conversion of epoxy to carbonate was monitored by IR spectroscopy.

5.5.4 Polyurethane preparation

0.25 g of cyclic carbonate polyester (CC-PE) was placed in a 2 mL vial followed by isophorone diamine and acetone and mixed thoroughly. The viscous solution was poured into a mold and heated at 70 °C for 24 h.

5.6 Results and discussion

Epoxidized polyester (E-PE) was obtained in the reaction of the hydroxyl terminated polyester (H-PE) with epichlorohydrin by using zinc perchlorate hexahydrate as catalyst. Figure 5- 1 gives the overall synthetic approach by using hydroxyl terminated polyester as starting materials to prepare non-isocyanate polyurethane. FTIR results in Figure 5- 2b show the new peaks at 909 and 854 cm⁻¹ formation which correspond the epoxy group. 
¹H NMR in Figure 5- 3b and 
¹³C NMR in Figure 5- 4b also show the epoxy group formation.

Cyclic carbonate polyester (CC-PE) was prepared from the epoxidized polyester (E-PE) and carbon dioxide. FTIR results in Figure 5- 2c show the new peak at 1802 cm⁻¹
formation which correspond cyclic carbonate, and the peaks at 909 and 854 cm\(^{-1}\) disappearance which correspond the epoxy group. \(^1\)H NMR in Figure 5- 3c and \(^{13}\)C NMR in Figure 5- 4c also show the cyclic carbonate group formation and epoxy group disappearance. H-PE has a Brookfield viscosity of 5800 mPas, the E-PE has a Brookfield viscosity of 1100 mPas, and the CC-PE has a Brookfield viscosity of 9400 mPas.

Figure 5- 1 Non-isocyanate polyurethane preparation procedure
Figure 5- 2 FTIR spectra of hydroxyl terminated polyester (H-PE), epoxidized polyester (E-PE) and cyclic carbonate polyester (CC-PE)

Figure 5- 3 $^1$H NMR spectra (300 MHz, CDCl$_3$) of hydroxyl terminated polyester (H-PE), epoxidized polyester (E-PE) and cyclic carbonate polyester (CC-PE)
Figure 5- 4 $^{13}$C NMR spectra (300 MHz, CDCl$_3$) of hydroxyl terminated polyester (H-PE), epoxidized polyester (E-PE) and cyclic carbonate polyester (CC-PE)

The CC-PE formation with time was monitored by using IR spectroscopy by focusing on the appearance of a new peak at 1805 cm$^{-1}$ due to the carbonyl of the cyclic carbonate moieties. As shown in Figure 5- 5, the peak intensity in 1805 cm$^{-1}$ keep increase with the reaction time.
The polyurethane was prepared by the reaction of cyclic carbonate polyester (CC-PE) with isophorone diamine at 70 °C. The non-isocyanate polyurethane formation with time was monitored by focusing on the disappearance of cyclic carbonate peak at 1805 cm⁻¹. Figure 5-6 shows the polyurethane formation with time when the mole ratio of isophorone diamine (IPDA) to CC-PE is fixed (the mole ratio of amine to cyclic carbonate is 1.25). It shows that most of the cyclic carbonate was disappeared after 24 hours reaction. Figure 5-7 shows the polyurethane formation with different amine to cyclic carbonate ratio when curing time is fixed. It shows that when the amine to cyclic carbonate mole ratio is 1.25, most of the cyclic carbonate was disappeared after 24 hours reaction.
Figure 5-6 FTIR spectra of non-isocyanate polyurethane formation with time by using CC-PE cured with IPDA under 70°C (NH₂/CC=1.25)

Figure 5-7 FTIR spectra of non-isocyanate polyurethane formation at different amine to cyclic carbonate ratio by using CC-PE cured with IPDA under 70°C × 24h
5.7 Conclusions

In conclusions, the hydroxyl terminated, epoxidized, and cyclic carbonate terminated polyesters were synthesized and characterized by NMR. The cyclic carbonate terminated polyester formation with time was monitored by using IR spectroscopy. Non-isocyanate polyurethane coatings were prepared by the thermo-curing of the cyclic carbonate terminated polyester and polyamine.
6.1 Abstract

The photopolymerization kinetics of non-isocyanate urethane dimethacrylates (NUDMA) were studied. Three NUDMA reactive diluents were synthesized from urethane diols which were prepared from the reaction of cyclic carbonate with amino alcohol. The effect of the NUDMA type and content on the viscosity of the acrylated polyester (APE) oligomer was investigated by Brookfield viscometer. The real time Fourier transform infrared spectroscopy (FTIR) was used to investigate the photopolymerization kinetics of reactive diluents and photoinitiator (PI). PI Darocur 4265 showed highest overall conversion and maximum polymerization rate. The polymerization conversion and maximum polymerization rate increase with increasing initiator concentration in the range from 0.5 % to 4.0 %. The formulation system containing both the APE oligomer and NUDMA reactive dilutes showed higher polymerization overall conversion and maximum polymerization rate than APE oligomer.
6.2 Introduction

UV-curable coatings offer many advantages, such as rapid curing, high-energy efficiency and low volatile organic content (VOC)\textsuperscript{153}. Photopolymerization can occur at relatively low temperature with a nature of ultrafast curing, which makes UV-curable coating suitable for a widely application in the market sectors where temperature sensitive substrates are coated, like wood, paper and plastics.\textsuperscript{154, 155} Most UV-curable coating systems are free radical based on acrylated oligomers formulated with (meth)acrylate reactive diluents.

Reactive diluent is an important component of the UV-curable coating formulation solutions. Reactive diluent has two functions. One is to dilute the viscosity of the oligomer and thus facilitate the coating application process. The second functionality is to copolymerize with oligomer chemically bound into the final crosslinked film and thus adjust the final film properties.\textsuperscript{156, 157}

The reactive diluent affects the film properties, cure rates and degree of polymerization. It is generally considered that mono-functional reactive diluent like 2-ethylhexyl acrylate makes the film softer with reduced mechanical strength, whereas multi-functional reactive diluent induces higher mechanical strength to the film with relatively hard character.\textsuperscript{157}

Recently, a novel reactive diluent named as GPTEMA with long-branched chain was synthesized through the reaction of glycerol propoxylate triglycidyl ether (GPTE) and methacrylic acid. This reactive diluent can reduce the polymerization shrinkage and improve the double bond conversion.\textsuperscript{158} The addition of the tripropane glycol diacrylate (TPGDA) reactive diluent into the UV curable polycarbosilane system could accelerate
the curing reaction rate of the polymer.\textsuperscript{159} The addition of vinyl pyrrolidinone reactive diluent into the polyesterpolyol acrylates system could increase the mechanical property of the polymer.\textsuperscript{160}

Photopolymerization kinetics of methacrylate reactive diluents\textsuperscript{161, 162, 163} and oligomers\textsuperscript{164} have been widely studied. The effects of the reactive diluents on the oligomers photopolymerization kinetics were also investigated.\textsuperscript{165, 166} Generally, the reactivity of the function groups determines the rate of polymerization, whereas the chemical structure and the functionality of both the oligomer and the reactive diluent determine the final degree of polymerization.\textsuperscript{167} It is generally observed that past an optimum point an increase in the functionality will lead to the decrease in final conversion. This is due to the fact that the increase in functionality will lead to increase in the viscosity and crosslink density with the resulting gel effect, which set a limit to the extent of conversion.\textsuperscript{168}

The incorporation of urethane function group into the coating system could make the crosslinked film with excellent physical and mechanical properties such as high impact and tensile strength, abrasion resistance and toughness combined with excellent resistance to chemicals and solvent.\textsuperscript{168, 169, 170, 171, 172, 173} However urethane was usually formed via the reaction of the isocyanate and polyol, which makes urethane environmentally less attractive. Recently, urethane dimethacrylate monomer prepared via the non-isocyanate route from the reaction of a urethane diol with methacrylic anhydride has been reported.\textsuperscript{174, 175, 176} The urethane dimethacrylate monomer photopolymerization has been reported using photoinitiated differential scanning calorimetry.\textsuperscript{174} Up to now, no systematic investigation of the kinetic of the urethane dimethacrylates reactive diluents in
coating system has been studied by real time Fourier transform infrared spectroscopy (FTIR). It is known that UV-curable acrylated polyester shows good properties such as high hardness, toughness, solvent resistant, and an excellent ratio value of properties to cost. It has been widely used as a oligomer for UV-curable coatings.\textsuperscript{177}

In this study, acrylated polyester (APE) oligomer and non-isocyanate urethane dimethacrylate (NUDMA) reactive diluents were synthesized, and characterized by \textsuperscript{1}H nuclear magnetic resonance (NMR), \textsuperscript{13}C NMR. The effects of the NUDMA reactive diluent content and type on the viscosity of the APE oligomer were studied. The effects of the photoinitiator content and type on the NUDMA reactive diluents photopolymerization kinetics were investigated by real time Fourier transform infrared spectroscopy (FTIR).

6.3 Materials

Adipic Acid (AA), isophthalic acid (IPA), 1, 6 hexane diol (HD), trimethylolpropane (TMP), \textit{p}-xylene, dibutyl tin oxide (DBTO), ethylene carbonate (EC), propylene carbonate (PC), 2-aminoethanol (EOA), 3-aminopropanol (POA), methacrylic anhydride (MAA, 94%), dichloromethane, hydroquinone, Triethylene diamine (TEA) all Aldrich products were used as received. 4-(dimethyl-amino)pyridine (DMAP) was obtained from Acros Organics. Photoinitiators Irgacure 184, Irgacure 500, Darocur 1173, Irgacure 819, and Darocur 4265 were obtained from Ciba Specialty Chemical, NY. Ethylene glycol dimethacrylate (EGDMA) was obtained from Sartomer USA, PA.
6.4 Instrumentation and characterization

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Mercury 300 MHz spectrometer (Varian) in CDCl$_3$ as a solvent for APE, DMSO as a solvent for NUDMA. Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet 380 (Thermo Electron Corp). Real time FTIR was recorded with an external Lesco Super Spot MKII UV Source. The samples for the real time FTIR measurement were cast on a KBr plate as a thin film around 25 µm. The UV-light was delivered through a flexible light guide. The KBr plate was positioned at an angle of 45° and at a distance of 2 cm to the end of the light guide to facilitate full KBr plate exposure to UV-light. The UV-light intensity was measured to be 20 mW/cm$^2$ (Digital UV AB Light Meter, General UV513AB). Viscosity measurement was accomplished by Laboratory Brookfield viscometer (DVII+ PRO Digital) at room temperature. A spindle SC4-25 was used at a shear rate of 10 s$^{-1}$.

6.5 Synthesis

In this synthesis part, three different kinds of urethane diols and corresponding urethane dimethacrylates were synthesized as reactive diluents. Acrylated polyester was synthesized as oligomer.

6.5.1 Synthesis of non-isocyanate urethane diols

EOAEC urethane diol preparation: Ethylene carbonate (88.06 g, 1.00 mol) was dissolved in 100 mL dichloromethane, and such solution was drop added into the 2-aminoethanol (61.08 g, 1.00 mol) and dichloromethane (200 mL) mixture at 0°C. After finish adding, the mixture was stirred at room temperature for 24 hour. The slightly yellow liquid (yield: 98%) was got by rot vaporing the dichloromethane. $^1$H NMR (300
1H NMR (300 MHz, DMSO-$d_6$) $\delta$ (ppm) = 3.03 (q, -CH$_2$NH-), 3.35 (m, -OCH$_2$CH$_2$NH-), 3.52 (m, -OCH$_2$CH$_2$OH), 3.94 (t, -OCH$_2$CH$_2$OH), 4.59 - 4.69 (m, -OH), 6.97 (t, -NHCOO-). $^{13}$C NMR (300 MHz, DMSO-$d_6$) $\delta$ (ppm) = 43.06 (-C$_2$H$_4$NH-), 59.60 (-CH$_2$C$_2$H$_2$OH), 60.08 (HOCH$_2$CH$_2$-), 65.64 (-COOCH$_2$-), 156.56 (C=O, carbamate).

POAEC urethane diol preparation: POAEC diol was prepared using the same procedure as for EOAEC diol. From ethylene carbonate (88.06 g, 1.00 mol) and 3-aminopropanol (75.11 g, 1.00 mol), product POAEC (149.04 g) was obtained (91% yield). The final product was a clear liquid. 1H NMR (300 MHz, DMSO-$d_6$) $\delta$ (ppm) = 1.53 (t, -CH$_2$CH$_2$CH$_2$-), 2.98 - 3.09 (q, -CH$_2$NH-), 3.36 - 3.43 (m, -OCH$_2$CH$_2$NH-), 3.52 (m, -OCH$_2$CH$_2$OH), 3.93 (m, -OCH$_2$CH$_2$OH), 4.49 - 4.69 (m, -OH), 7.00(m, -NHCOO-). $^{13}$C NMR (300 MHz, DMSO-$d_6$) $\delta$ (ppm) = 32.81 (-CH$_2$CH$_2$CH$_2$-), 37.69 (-CH$_2$NH-), 58.62-59.68 (-CH$_2$CH$_2$OH), 65.64 (-COOCH$_2$-), 156.57 (C=O, carbamate).

POAPC urethane diol preparation: POAPC diol was prepared using the same procedure as for EOAEC diol. From propylene carbonate (102.09 g, 1.00 mol) and 3-aminopropanol (75.11 g, 1.00 mol), POAPC (131.20 g) product was obtained (74% yield). The final product was a clear liquid. 1H NMR (300 MHz, DMSO-$d_6$) $\delta$ (ppm) = 0.97 - 1.14 (m, -CH$_2$CHCH$_3$), 1.53 (quin, -CH$_2$CH$_2$CH$_2$-), 2.93 - 3.09 (m, -CH$_2$NH-), 3.30 - 3.44 (m, -OCH$_2$CH$_2$-), 4.50 - 4.67 (m, -OCH$_2$CH(CH$_3$)O-, -OCH(CH$_3$)CH$_2$O-), 6.88 - 7.05 (m, NHCOO-). $^{13}$C NMR (300 MHz, DMSO-$d_6$) $\delta$ (ppm) = 16.98 (-OCH$_2$CH(CH$_3$)OH), 17.00 (-OCH(CH$_3$)CH$_2$OH), 32.77 (m, -CH$_2$CH$_2$CH$_2$-), 37.65 (-CH$_2$NH-), 58.54 (HOCH$_2$CH$_2$-), 64.09 (-OCH$_2$CH(CH$_3$)O-), 64.54 (OCH(CH$_3$)CH$_2$O-), 68.97 (-OCH(CH$_3$)CH$_2$O-), 70.86 (-OCH$_2$CH(CH$_3$)O-), 156.18 -156.45 (C=O, carbamate).
6.5.2 Synthesis of non-isocyanate urethane dimethacrylate

EOAED urethane dimethacrylate preparation: Urethane diol EOA-EC (14.9 g, 0.1 mol) was dissolved in dichloromethane (300 mL) at 0 °C, 4-(dimethyl-amino)pyridine (DMAP) catalyst (122 mg, 1 mmol), and 0.05 wt % hydroquinone (inhibitor) (28 mg) were added in, followed by drop addition of triethylene diamine (TEA) (28.3 g, 0.28 mol), and then drop addition of methacrylic anhydride (39.4 g, 0.24 mol) under the N₂ atmosphere. The reaction mixture was stirred at 0 °C for 24 h. Then, saturated sodium bicarbonate solution (294.7 g) was dropped added to get two phase separated mixture. The product (top layer) was collected, washed with brine (300 mL × 3) and water (300 mL × 2), and dried in anhydrous magnesium sulphate. After dichloromethane was evaporated, the final liquid product was pale yellow color (yield: 42%). ¹H NMR (300 MHz, DMSO-d₆) δ (ppm) = 1.86 (m, 6 H, -CH₃), 3.27 (qd, J = 5.67, 1.39 Hz, 2 H, -CH₂NH-), 4.07 (td, J=5.57, 1.63 Hz, 2 H, -OCH₂CH₂O-), 4.12 (m, 2 H, -OCH₂CH₂NH-), 4.14 - 4.30 (m, 2 H, -OCH₂CH₂O-), 5.62 - 5.78 (m, 2 H, trans C=CH₂) 5.98 - 6.12 (m, 2 H, cis C=CH₂), 7.42 (t, 1 H, -NHCOO-). ¹³C NMR (300 MHz, DMSO-d₆) δ (ppm) = 18.11 (-CH₃), 39.79 (-CH₂NH-), 62.11 (-NHCOOCH₂-), 63.32 (-CH₂CH₂O-), 63.49 (-COOCH₂-), 126.18 (C=CH₂), 136.10 (C=CH₂), 156.46 (C=O, carbamate), 166.67 (C=O, ester).

POAED urethane dimethacrylate preparation: POAED urethane dimethacrylate was prepared using the same procedure as for EOAED dimethacrylate. From of POAEC (16.3 g, 0.1 mol) and methacrylic anhydride (39.4 g, 0.24 mol), POAED (24.01 g) product was obtained (82% yield). The final product was a pale liquid with lower viscosity than POAEC diol. ¹H NMR (300 MHz, DMSO-d₆) δ (ppm) = 1.75 (m, -CH₂CH₃CH₂-), 1.86 (m, -CH₃), 2.99 - 3.15 (m, -CH₂NH-), 4.07 (td, -OCH₂CH₂O-), 4.12
(m, 2 H, -OCH\textsubscript{2}CH\textsubscript{2}NH-), 4.08 (m, COOCH\textsubscript{2}CH\textsubscript{2}-), 4.14 - 4.29 (m,-OCH\textsubscript{2}CH\textsubscript{3}O-), 5.66(dd, trans C=CH\textsubscript{2}), 6.02 (d, cis C=CH\textsubscript{2}), 7.29 (t, -NHCOO-). \textsuperscript{13}C NMR (300 MHz, DMSO-\textit{d}_6) \delta (ppm) = 17.92 (-CH\textsubscript{3}), 28.49 (m, -CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}O-), 37.18 (-CH\textsubscript{2}NH-), 61.68 (-NHCOC\textsubscript{2}H\textsubscript{5}-), 62.05 (-COOC\textsubscript{2}H\textsubscript{5}-), 62.27 (-CH\textsubscript{2}CH\textsubscript{2}O-), 125.93(C=CH\textsubscript{2}), 136.00 (C=CH\textsubscript{2}), 156.02 (C=O, carbamate), 166.43 (C=O, ester)

**POAPD urethane dimethacrylate preparation:** POAPD urethane dimethacrylate was prepared using the same procedure as for EOAED dimethacrylate. From of POAEC (17.7 g, 0.1 mol) and methacrylic anhydride (39.4 g, 0.24 mol), POAPD (22.05 g) product was obtained (70% yield). The final product was a pale liquid with lower viscosity than POAPC diol. \textsuperscript{1}H NMR (300 MHz, DMSO-\textit{d}_6) \delta (ppm) = 1.18 (dd, -CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.74 (quin, -CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}O-), 1.86 (m, -CH\textsubscript{2}=C(CO)CH\textsubscript{3}), 3.06 (q, -CH\textsubscript{3}NH-), 4.13 (m, -COC\textsubscript{2}H\textsubscript{5}CH\textsubscript{2}CH\textsubscript{2}O-), 4.01 - 4.13 (m, -OCH\textsubscript{2}CH(CH\textsubscript{3})O-,-OCH(CH\textsubscript{3})CH\textsubscript{2}O-), 4.89 - 5.06 (m, -OCH\textsubscript{2}CH(CH\textsubscript{3})O-,-OCH(CH\textsubscript{3})CH\textsubscript{2}O-), 5.65(dt, trans C=CH\textsubscript{2}), 6.01 (s, cis C=CH\textsubscript{2}), 7.29 (m, -NHCOO-). \textsuperscript{13}C NMR (300 MHz, DMSO-\textit{d}_6) \delta (ppm) = 16.51 (-CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 17.86 (-CH\textsubscript{2}=C(CO)CH\textsubscript{3}), 28.57 (-CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}O-), 37.08 (-CH\textsubscript{3}NH-), 62.01(-COOC\textsubscript{2}H\textsubscript{5}-), 64.41 (-OCH(CH\textsubscript{3})CH\textsubscript{2}O-), 66.46 (-OCH\textsubscript{2}CH(CH\textsubscript{3})O-), 67.42 (-OCH\textsubscript{2}CH(CH\textsubscript{3})O-), 68.94 (-OCH(CH\textsubscript{3})CH\textsubscript{2}O-), 125.86 (C=CH\textsubscript{2}), 135.98 (C=CH\textsubscript{2}), 155.69 (C=O, carbamate), 166.50 (C=O, ester).

**6.5.3 Synthesis of the acrylated polyester (APE) oligomer**

The synthesis of acrylated polyester oligomer consists of two steps illustrated in Figure 6-9. In the first step, hydroxyl terminated polyester polyol was prepared by using excess diol. The molar ratio of alcohol to acid is 11:8. Adpic acid (AA) (100 g, 0.6 mol), isophthalic acid (IPA) (113.67 g, 0.68 mol), 1,6 hexane diol (HD) (161.71 g, 1.37 mol)
and trimethylolpropane (TMP) (45.90 g, 0.34 mol) were taken in a 500 mL four-neck round bottom flask which was equipped with a mechanical stirrer, a gas inlet, a temperature controller, a Dean-Stark trap and a condenser. The reaction proceeded under argon to minimize oxidative degradation. To accelerate the reaction, 0.4 wt % of DBTO, a transesterification catalyst, was used. Then, 3 wt % of p-xylene was also added into the reaction mixture to remove water from the resin as azeotropic mixture. The reaction temperature was carefully controlled using a temperature controller and a thermocouple in order to minimize evaporation of diol. The temperature of the mixture was increased from 20-150 °C at a rate of 4.3 °C /min, and then from 150-210 °C at a rate of 0.25 °C/min. The final temperature was held until the resin had an acid number measured by titration less than or equal to 10 mg KOH/g resin. The hydroxyl number of polyesters (160.4 mg KOH/g resin) was determined by ASTM method (ASTM D 1957-86). $^1$H NMR (300 MHz, CHLOROFORM-d) δ (ppm) = 0.92 (m, -CH$_2$CH$_3$), 1.33 - 1.47 (m, -OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$O-, -CCH$_2$CH$_3$), 1.50 - 1.66 (m, OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$O), 1.72 - 1.85 (m, -OCOCH$_2$CH$_2$CH$_2$COO-), 2.29 (m, -OCOCH$_2$CH$_2$CH$_2$COO-), 3.98 - 4.14 (m, RCOOCH$_2$H$_2$-, R is aliphatic group), 4.26 - 4.43 (m, RCOOCH$_2$H$_2$-, R is aromatic group), 7.50- 8.71 (m, Ar-H)

In the second step, the temperature was reduced to 120 °C. Acrylic acid (AA, the mole ratio of the acid in the AA to the hydroxyl in the polyester polyol kept at 1.05), 1 wt % p-toluene sulphonyl acid (p-TSA, catalyst) and 0.05 wt % hydroquinone (inhibitor) (based on the total amount of the polyester polyol and acrylic acid) were added in, the temperature was maintained at 120 °C for 14h. Then, 1.5 wt % of 3- methyl-3-hydroxymethyl-oxetane was added in, and maintained at 120 °C for another 20 min. Then
solvent and residual were removed in vacuo resulting in a light yellow acrylated polyester oligomer. $^1$H NMR (300 MHz, CHLOROFORM-$d$) $\delta$ (ppm) = 0.92 (m, -CH$_2$CH$_3$), 1.33 - 1.47 (m, -O CH$_2$CH$_2$CH$_2$ CH$_2$CH$_2$ CH$_2$O-, -CCH$_2$CH$_3$), 1.50 - 1.66 (m, -OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$O-), 1.72 - 1.85(m, -OCO CH$_2$CH$_2$ CH$_2$CH$_2$COO-), 2.29 (m, -OCO CH$_2$CH$_2$CH$_2$CH$_2$COO-), 3.57 -3.69 (m, -CH$_2$-OH), 3.98 - 4.14 (m, RCOOCH$_2$-, R is aliphatic group), 4.26 - 4.43 (m, RCOOCH$_2$-, R is aromatic group), 5.74 - 5.89 (m, trans C=CH$_2$), 6.03-6.14 (m, OCOCH= CH$_2$), 6.31 - 6.44 (m, cis C=CH$_2$),7.50- 8.71 (m, Ar-H). The average molecular weight was found to be Mn = 3500, with a PDI = 1.8 via GPC.

6.6 Coating formulation

For neat reactive diluent photopolymerization kinetics study, formulation was prepared by mixing selected reactive diluent with different photoinitiator type and content. For study the effect of the reactive diluent on the acrylated polyester (APE) oligomer photopolymerization kinetics, formulation was prepared by mixing selected reactive diluent and APE oligomer with different content including 2 wt% of Darocur 4265 based on the total formulation. The chemical structures of the photoinitiators were depicted in Figure 6- 1.
6.7 Results and discussion

The overall object of this study is to prepare non-isocyanate urethane dimethacrylates (NUDMA) and investigate their potential applications as reactive diluents for UV-curable coatings, by studying the effect of NUDMA type and content on the viscosity of the oligomer and photopolymerization kinetics of the NUDMA. The commonly used reactive diluent ethylene glycol dimethacrylate (EGDMA) was also chosen to compare with the NUDMA reactive diluents.
The NUDMA reactive diluents were prepared from the reaction of urethane diols and methacrylic anhydride. The urethane diols were synthesized from the reaction of amino alcohols with cyclic carbonate via non-isocyanate route shown in Figure 6-2.

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<tr>
<td>2</td>
<td>$\text{CH}_3\text{CH}_2\text{CH}_2$</td>
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<td>3</td>
<td>$\text{CH}_3\text{CH}_2\text{CH}_2$</td>
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Figure 6-2 UDMA reactive diluents synthesis scheme
To investigate the NUDMA type and content on the viscosity of the oligomer, and compare NUDMA with conventional EGDMA reactive diluent, coating formulations containing different reactive diluents and concentration were prepared and corresponding viscosity properties were studied by Brookfield viscometer.

6.7.1 Preparation of reactive diluents and oligomer

In this preparation part, three different kinds of non-isocyanate urethane dimethacrylates were prepared as reactive diluents. The acrylated polyester was prepared as the oligomer.

6.7.1.1 Preparation of non-isocyanate urethane dimethacrylate reactive diluents

The synthesis of non-isocyanate urethane dimethacrylate consists of two steps. In the first step, urethane diol was prepared by modification of the Assumption’s procedure. The reaction time was extended from 16 h to 24 h, and yield was increased from 87% to 91% for POAEC diol synthesis. It has been reported that urethane diols prepared from reaction of linear diamine like 1,6-hexanediame with cyclic carbonate were solid state. While urethane diols prepared from the reaction of the branched diamine or amino alcohol with cyclic carbonate were liquid state. And the urethane diols prepared from the branched diamine shows higher viscosity than the one prepared from the amino alcohol. The aim of this study is to prepare monomers used as reactive diluents, thus requiring the monomer to be liquid with a relatively low viscosity. As consequences, only amino-alcohols were chosen as starting materials. All these three urethane diols EOAEC, POAEC, POAPC prepared were liquid with relatively higher viscosity than water. The characterization of the synthesized urethane diols were carried
out by $^1$H NMR and $^{13}$C NMR. The $^1$H NMR spectra in Figure 6- 3a, 6- 4a and 6- 5a showed two resonances at $\delta$ 6.88 - 7.05 indicating the presence of protons from urethane group, which correspond to the pseudo E and Z urethane conformer.$^{174, 180}$

Figure 6- 3 NMR of EOAEC urethane diol, (a) $^1$H NMR and (b) $^{13}$C NMR

Figure 6- 4 NMR of POAEC urethane diol, (a) $^1$H NMR and (b) $^{13}$C NMR
In the second step, urethane dimethacrylate was prepared by modification of Assumption’s procedure. In this study, the 4-(dimethyl-amino)pyridine (DMAP) catalyst amount was reduced from 10 mol% to 1 mol%, triethylene diamine (TEA) was added to accelerate the reaction of urethane diols with methacrylic anhydride. 0.05 wt % inhibitor hydroquininone based on total reactants weight was also added to prevent the polymerization of the double bonds. The yield was increased from 40% to 82% for POAED urethane dimethacrylate synthesis as compared with Assumption’s procedure.

The characterization of the synthesized urethane dimethacrylates were carried out by $^1$H NMR and $^{13}$C NMR. The $^1$H NMR spectra in Figure 6- 6a, 6- 7a and 6- 8a showed two resonances at $\delta = 5.7$ and 6.0 ppm indicating the presence of protons from the double bond of a methacrylate group. The $^{13}$C NMR spectra in Figure 6- 6b, 6- 7b and 6- 8b showed two resonances at $\delta = 126$ and 136 ppm indicating the presence of carbons from the double bond of a methacrylate group.
Figure 6-6 NMR of EOAED urethane dimethacrylate, (a) $^1$H NMR and (b) $^{13}$C NMR

Figure 6-7 NMR of POAED urethane dimethacrylate, (a) $^1$H NMR and (b) $^{13}$C NMR

Figure 6-8 NMR of POAPD urethane dimethacrylate, (a) $^1$H NMR and (b) $^{13}$C NMR

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6.7.1.2 Preparation of acrylated polyester (APE) oligomer

A typical poly-condensation technique was used to prepare APE oligomer. The synthesis of acrylated polyester oligomer consists of two steps illustrated in Figure 6-9. In the first step, hydroxyl terminated polyester polyol was prepared by using excess diol monomer. In the second step, acrylated polyester (APE) was formed via the reaction of polyester polyol with acrylic acid. The average molecular weight was found to be \( \text{Mn} = 3500 \), with a PDI = 1.8 via GPC. The characterization of the synthesized polyester polyol and acrylated polyester were carried out by \(^1\text{H} \) NMR as shown in Figure 6-10. The \(^1\text{H} \) NMR spectra in Figure 6-10b showed three new resonances at \( \delta = 5.74, 6.03 \) and 6.31 ppm indicating the presence of protons from the double bond of an acrylate group. The peak intensity at \( \delta = 3.57 - 3.69 \) corresponding to the proton in \(-\text{CH}_2\text{-OH}\) group was lower in Figure 6-10a comparing with those in Figure 6-10b, which indicated that acrylation reaction was carried out.
Figure 6-9 The synthesis of oligomer acrylated polyester (APE)
6.7.2 Viscosity

The viscosity of the synthesized urethane diols and corresponding urethane dimethacrylates were investigated by using Brookfield viscometer.

6.7.2.1 Viscosity of urethane diols vs urethane dimethacrylates

Viscosity is an important property for a monomer to be as a reactive diluent. The viscosity of the synthesized urethane diols and corresponding urethane dimethacrylates were shown in Figure 6-11. The viscosity of the urethane dimethacrylates was dropped significantly after methacrylation of the corresponding urethane diols. The viscosity of POAPC urethane diol was dropped from 2487 to 192 mPa·s for that of POAPD urethane.
dimethacrylate. The viscosity of EOAEC urethane diol was dropped from 786 to 57 mPa·s for that of EOAED urethane dimethacrylate. The viscosity of POAEC urethane diol was dropped from 818 to 22 mPa·s for that of POAED urethane dimethacrylate. It has been reported that urethane diols could be used as reactive diluents and cross-linkers for high solid coating. The incorporation of the urethane diol could raise the application solids, increase film hardness, water resistance and exterior durability.\textsuperscript{182, 183, 184} So it is expected that the urethane dimethacrylate with even much lower viscosity could have a potential application for use as reactive diluent. Compared to the POAED, the EOAED shows higher viscosity, which could be explained that the shorter chain makes the molecule stiffer, increasing the viscosity; the POAPD shows higher viscosity, which could be explained that hindrance effect induces the increase in viscosity due to the incorporation of the side methyl group making the molecule more bulky. POAPD shows higher viscosity than the EOAED indicating that the hindrance effect plays a more important role than the chain spacer effect on the viscosity increase.

![Viscosity of the synthesized urethane diols and corresponding urethane dimethacrylates](image.png)

Figure 6-11 The viscosity of the synthesized urethane diols and corresponding urethane dimethacrylates

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6.7.2.2 Viscosity of reactive diluents with acrylated polyester (APE)

First, as to be reactive dilutes, the non-isocyanate urethane dimethacrylates (NUDMA) synthesized are anticipated to reduce the viscosity of the acrylated polyester (APE) oligomer. The viscosities of the formulations were investigated and compared to that of the neat APE oligomer. The viscosity was studied as a function of amount and type of reactive diluent. The commonly used reactive diluent ethylene glycol dimethacrylate (EGDMA) was chosen to compare with the NUDMA reactive diluents. The results for this experiment are presented in Figure 6-12.

![Figure 6-12 Viscosity behavior of neat APE oligomer and APE/reactive diluent mixtures](image)

Figure 6-12 Viscosity behavior of neat APE oligomer and APE/reactive diluent mixtures

The viscosity of the APE oligomer used for all runs was found to be 10840 mPa·s. As expected, EGDMA and all three NUDMA reactive diluents effectively reduce the viscosity of the APE oligomer. At 10 wt % loading of reactive diluents, the viscosity of
the formulation was decreased to 6740 mPa·s (62%) for POAPD, 5586 mPa·s (52%) for EOAED, 4886 mPa·s (45%) for POAED, and 2985 mPa·s (28%) for EGDMA. The viscosity of the formulation systems were further decreased with the addition of the reactive diluents in the loading range of 10 – 40 wt %.

Compared to the formulation containing EGDMA and APE, the formulation containing NUDMA and APE always show higher viscosity. These are due to hydrogen bond formation via the urethane group in the NUDMA system. Among the three NUDMA reactive diluents, the POAED reactive dilute shows the lowest viscosity reduction followed by the EOAED and POAPD reactive diluents. NUDMA systems show higher viscosity than the EGDMA system. The viscosity order of the NUDMA formulation system follows the same viscosity order of the neat NUDMA reactive diluent.

6.7.3 Kinetics studies by real-time FTIR

It has been widely accepted that the real time FTIR is an excellent tool for determining both the rate and conversion of the photopolymerization. This technique offers the opportunity to investigate the kinetics of the photopolymerization by monitoring the decay of the intensity of the peak at specific wavelength. In this study, the alkene twisting vibration at 810 cm\(^{-1}\) was used to monitor the double bond conversion. The conversion of double bond at a given time was calculated from the change in the absorption peak area as function of time:

\[
\text{Conversion (\%)} = \frac{[A_{\text{cm}^{-1}}]_t - [A_{\text{cm}^{-1}}]_0}{[A_{\text{cm}^{-1}}]_0} \times 100
\]

(6-1)

where \([A_{\text{cm}^{-1}}]_t\) and \([A_{\text{cm}^{-1}}]_0\) were the IR absorbance at specified bands at starting time and the given time, respectively. In this study, neat NUDMA reactive diluents
containing different photoinitiator type and content, and formulation containing NUDMA reactive diluents and APE oligomer were prepared. Experiments were performed at ambient temperature at UV-light intensity of 20 mW/cm$^2$ in the range of 280-400 nm (Digital UV AB Light Meter, General UV513AB).

6.7.3.1 Effect of PI type and concentration

It is known that the photoinitiator generates the free-radicals that initiate radical polymerization of the unsaturated oligomer or reactive diluents. The photoinitiators used for free radical polymerization reactions has been thoroughly reviewed.\footnote{156, 190, 191} The typical absorption spectra of the common used photoinitiators are listed in the literature.\footnote{156} The chemical structures of the photoinitiators in this study are shown in Figure 6-1. In order to investigate the effect of photoinitiators on the neat reactive diluent, 2 wt% of each photoinitiator was added. The double bond conversion was monitored as a function of time.

Figure 6-13a shows the effect of PI type on polymerization conversion. All the initiators have similar photopolymerization behavior and maximum conversion is reached after 10 sec of irradiation. The highest overall conversion was observed for PI Darocur 4265 (62%), followed in order by Irgacure 819(60%), Darocur 1173(53%), Irgacure 500(32%), Irgacure 184 (23%). The overall conversion for Darocur 4265 and Irgacure 819 were comparatively higher than the rest of other three PI. This can be attributed to the more proximity of $\lambda_{\text{max}}$ value of Darocur 4265 and Irgacure 819 for n–\(\pi^*\) transition falling nearer to the major emission line at 365 nm.\footnote{156, 166, 192}

Figure 13.b shows the effect of PI type on polymerization rate. And the data were summarized in Table 1. All the initiators have similar photopolymerization behavior and
maximum polymerization rate ($R_{p}^{\text{max}}$) is reached after around 3 sec of irradiation. The highest polymerization rate was observed 0.158 s$^{-1}$ for PI Darocur 4265, followed in order by Irgacure 819 (0.148 s$^{-1}$), Darocur 1173 (0.094 s$^{-1}$), Irgacure 500 (0.047 s$^{-1}$), Irgacure 184 (0.040 s$^{-1}$). This is in the same order as the overall conversion. It indicates that strength of photoinitiator absorption of the UV light dominates the maximum polymerization rate ($R_{p}^{\text{max}}$).

Since PI Darocur 4265 showed highest overall conversion and maximum polymerization rate, it was chosen as the PI for further photopolymerization kinetics of reactive diluents and its formulation with APE oligomer.

Figure 6- 13 Polymerization conversion (a) and polymerization rate (b) of EOAED reactive diluents as a function of exposure time for different type PI with 2 wt % concentration

Figure 6- 14 shows the effect of PI Darocur 4265 content on the polymerization conversion and rate of EOAED reactive diluent. And the data were summarized in Table 1. With increasing initiator concentration in the range from 0.5% to 4.0%, the polymerization overall conversion was increased from 26 % to 65 %, and maximum polymerization rate was increased from 0.083 s$^{-1}$ to 0.207 s$^{-1}$. This is due to the greater amount of molecules available for reaction.
Figure 6-14 Polymerization conversion (a) and polymerization rate (b) of EOAED reactive diluent as a function of exposure time for PI Darocur 4265 with different concentration.

Table 6-1 Photopolymerization kinetics data as a function of photoinitiator type (with 2 wt %) and photoinitiator Darocur 4265 concentration

<table>
<thead>
<tr>
<th>Photoinitiator Type (2 wt %)</th>
<th>Conversion (%)</th>
<th>$R_{\text{max}}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Darocur 4265</td>
<td>55</td>
<td>0.158</td>
</tr>
<tr>
<td>Irgacure 819</td>
<td>54</td>
<td>0.148</td>
</tr>
<tr>
<td>Darocur 1173</td>
<td>44</td>
<td>0.094</td>
</tr>
<tr>
<td>Irgacure 500</td>
<td>27</td>
<td>0.047</td>
</tr>
<tr>
<td>Irgacure 184</td>
<td>18</td>
<td>0.040</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Darocur 4265 Concentration (wt %)</th>
<th>Conversion (%)</th>
<th>$R_{\text{max}}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>26</td>
<td>0.083</td>
</tr>
<tr>
<td>1.0</td>
<td>47</td>
<td>0.131</td>
</tr>
<tr>
<td>2.0</td>
<td>55</td>
<td>0.153</td>
</tr>
<tr>
<td>3.0</td>
<td>59</td>
<td>0.173</td>
</tr>
<tr>
<td>4.0</td>
<td>65</td>
<td>0.207</td>
</tr>
</tbody>
</table>

6.7.3.2 Effect of oligomer and reactive diluents type

The chemical structure of the reactive diluents may affect the polymerization kinetics. Figure 6-15 shows the polymerization conversion and rate of APE oligomer and four different reactive diluents as a function of exposure time at 2.0 wt% PI Darocur 4265 concentration. And the data were summarized in Table 6-2. The overall conversion for APE (71%), EGDMA (70%), and POAPD (68%) are similar, which are higher than the overall conversion for POAED (57%) and EOAED (55%). The maximum polymerization
rate \( (R_p^{\text{max}}) \) for APE (0.237 s\(^{-1}\)), EGDMA (0.236 s\(^{-1}\)) is similar, which is higher than the one for POAPD (0.181 s\(^{-1}\)), POAED (0.153 s\(^{-1}\)) and EOAED (0.153 s\(^{-1}\)).

Figure 6- 15 Polymerization conversion (a) and polymerization rate (b) of APE oligomer and four reactive diluents as a function of exposure time at 2.0 wt % PI Darocur 4265 concentration

Table 6- 2 Photopolymerization kinetics data as a function of reactive diluent type and concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conversion (%)</th>
<th>( R_p^{\text{max}} ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>APE</td>
<td>71</td>
<td>0.237</td>
</tr>
<tr>
<td>EGDMA</td>
<td>70</td>
<td>0.236</td>
</tr>
<tr>
<td>EOAED</td>
<td>55</td>
<td>0.153</td>
</tr>
<tr>
<td>POAED</td>
<td>57</td>
<td>0.153</td>
</tr>
<tr>
<td>POAPD</td>
<td>68</td>
<td>0.181</td>
</tr>
<tr>
<td>EGDMA-10</td>
<td>71</td>
<td>0.236</td>
</tr>
<tr>
<td>EGDMA-20</td>
<td>78</td>
<td>0.236</td>
</tr>
<tr>
<td>EGDMA-30</td>
<td>77</td>
<td>0.208</td>
</tr>
<tr>
<td>EGDMA-40</td>
<td>65</td>
<td>0.152</td>
</tr>
<tr>
<td>EOAED-10</td>
<td>74</td>
<td>0.24</td>
</tr>
<tr>
<td>EOAED-20</td>
<td>74</td>
<td>0.25</td>
</tr>
<tr>
<td>EOAED-30</td>
<td>78</td>
<td>0.233</td>
</tr>
<tr>
<td>EOAED-40</td>
<td>80</td>
<td>0.233</td>
</tr>
<tr>
<td>POAED-10</td>
<td>77</td>
<td>0.235</td>
</tr>
<tr>
<td>POAED-20</td>
<td>77</td>
<td>0.254</td>
</tr>
<tr>
<td>POAED-30</td>
<td>88</td>
<td>0.289</td>
</tr>
<tr>
<td>POAED-40</td>
<td>92</td>
<td>0.246</td>
</tr>
<tr>
<td>POAPD-10</td>
<td>75</td>
<td>0.254</td>
</tr>
<tr>
<td>POAPD-20</td>
<td>81</td>
<td>0.267</td>
</tr>
<tr>
<td>POAPD-30</td>
<td>82</td>
<td>0.263</td>
</tr>
<tr>
<td>POAPD-40</td>
<td>85</td>
<td>0.251</td>
</tr>
</tbody>
</table>
6.7.3.3 Effect of formulation with different reactive diluents type and concentration

Figure 6-16 shows the polymerization conversion as a function of exposure time of the formulation of APE with different reactive diluents. And the data were summarized in Table 6-2. For APE oligomer, the overall polymerization conversion was 71%. For EGDMA system, the overall conversion did not change with the addition of 10 wt% reactive diluents, increased to the maximum with addition of 20 wt% reactive diluents, the decreased slightly with addition of 30 wt % reactive diluents, and decreased apparently with further addition of reactive diluents to 40 wt% reactive diluents. The overall conversion was 71%, 78%, 77%, and 65% with addition of 10 wt%, 20 wt%, 30 wt%, and 40 wt% of reactive diluents separately. For all the three NUDMA systems, the overall conversion increased with content of the reactive diluents in the load range of 10-40 wt%. It indicates that the polymerization conversion of the formulation system was higher than those of the neat system (either neat oligomer or reactive diluents), except the EGDMA system with 40 wt % reactive diluents concentration.
Figure 6-16 Polymerization conversion as a function of exposure time of the formulation of APE with different reactive diluents: (a) EGDMA, (b) EOAED, (c) POAED, and (d) POAPD.

Figure 6-17 shows the polymerization rate as a function of exposure time of the formulation of APE with different reactive diluents. And the data were summarized in Table 6-2. The effect of the reactive diluents type and content on the maximum polymerization rate exhibits the similar trends as overall polymerization conversion. For APE oligomer, the maximum polymerization rate was 0.237 s\(^{-1}\). For EGDMA system, the maximum polymerization rate remained constant with the addition of 10 wt% and 20 wt% reactive diluents (within experimental error), and decreased with further addition of reactive diluents to 40 wt% reactive diluents. For all the three NUDMA systems, the maximum polymerization rate initially increased with addition of reactive diluents, and reached the maximum in the load of 20 wt% or 30 wt%, then decreased with further...
addition of reactive diluents. Compared with the APE oligomer, all the three NUDMA system showed higher maximum polymerization rate in the load range of 10-40 wt% reactive diluents, except for the EOAED system with the reactive diluents concentration of 30-40 wt%. It indicates that the addition of the NUDMA reactive diluents could increase the maximum polymerization rate.

Figure 6- 17 Polymerization rate as a function of exposure time of the formulation of APE with reactive diluents: (a) EGDMA, (b) EOAED, (c) POAED, and (d) POAPD

6.8 Conclusions

Three urethane dimethacrylate monomers were synthesized via a non-isocyanate route. The addition of the non-isocyanate urethane dimethacrylate could reduce the viscosity of the acrylated polyester (APE) oligomer dropply. Such urethane dimethacrylates could use as reactive diluents for UV-curable coating. photopolymerization kinetics of non-isocyanate urethane dimethacrylates were studied. PI Darocur 4265 shows highest overall conversion and maximum polymerization rate, it
was chosen as the PI for photopolymerization kinetics of reactive diluents and its formulation with APE oligomer. The polymerization conversion and maximum polymerization rate increase with increasing initiator concentration in the range from 0.5 % to 4.0 %. The reactive diluents non-isocyanate urethane dimethacrylate showed lower polymerization overall conversion and maximum polymerization rate than APE oligomer. But formulation system showed higher polymerization overall conversion and maximum polymerization rate than APE oligomer.
CHAPTER VII

MECHANICAL AND FILM PROPERTY OF UV-CURABLE NON-ISOCYANATE POLYURETHANE COATINGS

7.1 Abstract

Three non-isocyanate urethane dimethacrylates (NUDMA) reactive diluents were synthesized by the reaction of the cyclic carbonate with the amino alcohol followed by the reaction with the methacrylic anhydride. These NUDMA reactive diluents were formulated with acrylated polyester (APE) oligomer to prepare UV-curable polyurethane coatings. For comparison, ethylene glycol dimethacrylate (EGDMA) was also used as reactive diluents. After UV curing, the viscoelastic, tensile and thermal properties of the cured films were evaluated as a function of the reactive diluent by using dynamic mechanical thermal analysis (DMTA), tensile test, differential scanning calorimeters (DSC), and thermal gravimetric analysis (TGA). In addition, coating properties such as pencil hardness, chemical resistance, impact resistance, and gloss were also investigated. It was found that crosslink density, storage and tensile modulus, pencil hardness, chemical resistance, gel content, total water absorption, and Tg were directly proportional to amount of the reactive diluents. The NUDMA reactive diluents show significant improvements in impact resistance and elongation at break properties compared to
EGDMA. It was found that the optimum level of the NUDMA reactive diluents concentration is between 10-20 wt %.

7.2 Introduction

In recent years, UV-curable coating has received considerable increasing attention because it is environmentally benign, fast curing, and lower energy consumption.\textsuperscript{168} UV-curable resin usually consists of three major components: photoinitiator, oligomer, and reactive diluent.\textsuperscript{194} The photoinitiator starts the photopolymerization when the resin system is exposed to UV light. The oligomer photopolymerizes to form crosslinked film and the structure of the oligomer governs viscoelastic properties of the final cured film. The reactive diluent lowers the viscosity of the resin, and copolymerizes with oligomer chemically bound into the final crosslinked film.\textsuperscript{156}

The photoinitiator for free radical polymerization usually contains aryl ketone chemical structure shown in Figure 7-1, which has strong UV light absorption in the range of 200-400 nm to produce free radicals. The structure of \( R_1 \) substituent influences the absorption wavelength number; while the structure of \( R_2 \) substituent influences the photoinitiator decomposition mechanism by scission process (unimolecular photoinitiator) or abstraction process (bimolecular photoinitiator). The alkyl \( R_2 \) substituent will lead to the scission process due to the relatively low bond energy of CO-alkyl; while the aryl \( R_2 \) substituent will lead to the abstraction process due to the relatively high bond energy of CO-aryl. After absorbing UV light, the CO-aryl bond cannot be broken but remains the excited state until it abstracts hydrogen from the hydrogen donor usually provided by tertiary amine.\textsuperscript{195}
There are three major types of oligomers widely used in UV-curable coatings: epoxy acrylate, polyester acrylate (acrylated polyester, APE), and urethane acrylate. The most widely used epoxy acrylate is bisphenol A (BPA) acrylate oligomer. The advantages of such epoxy acrylate include low cost, good adhesion, hardness, chemical and solvent resistance. This makes epoxy acrylate suitable for a wide variety of applications, ranging from wood coatings for furniture and parquet flooring to disk coatings and optical fiber coatings. The drawbacks of such epoxy acrylate include high viscosity, low flexibility, and yellowing. This makes epoxy acrylate less suitable for application on flexible substrates, low viscosity application techniques such spray and dip coating, and outdoor applications.

The second type of oligomer is polyester acrylate (or acrylated polyester, APE) oligomer; Polyester acrylates are usually prepared via the reaction of either the hydroxyl terminated polyesters with acrylic acid or the carboxyl terminated polyesters with hydroxyethyl acrylate. Acrylated polyesters have been studied in Soucek’s group. The advantage of acrylated polyesters is their versatile chemistry. Acrylated polyester with varieties of functionality, chemical backbone and molecular weight could be prepared by tailoring the starting monomers. Compared with epoxy acrylate, acrylate polyester usually shows relatively lower hardness property. Its hardness and abrasion resistance could be increased by incorporation of the tetraethylorthosilicate (TEOS) oligomers to prepare inorganic/organic hybrid.
The third type of oligomer is urethane acrylate oligomer. Urethane acrylate is usually prepared by the reaction of a polyol with a diisocyanate to yield an isocyanate terminated oligomer. These oligomers are then reacted with a hydroxyethyl acrylate monomer. Urethane acrylate is widely used as oligomer for UV coatings since it provides excellent physical and mechanical properties such as high impact and tensile strength, abrasion resistance and toughness combined with excellent resistance to chemicals and solvents. \(^{168, 171, 198, 170, 172, 173}\) Drawback of the urethane acrylate is the toxicity of the isocyanate starting material.\(^{199}\)

The reactive diluents are usually acrylic or methacrylic monomers which are added to reduce the viscosity of precured liquid oligomer and modify the property of final cured solid film.\(^{200}\) Generally mono-functional reactive diluents lead to decreased modulus and increased ductility, whereas di- and multi-functional reactive diluents lead to the opposite.\(^{201}\) It was well established that high degree of functionality leads to high reaction rates and high degree of crosslink density,\(^{202}\) but also leads to reduced final degree of conversion, because of early gelation of the irradiated sample and related mobility restrictions of the reactive sites. In addition, the greater crosslink density leads to glassy polymer materials, which are harder but also less flexible than monofunctional type systems.\(^{187, 163}\) The effect of monomer structure on oxygen inhibition of (meth)acrylates photopolymerization were investigated. Compared to acrylates, methacrylates are much less sensitive to oxygen.\(^{203}\) The effect of the chemical structure and functionality of the reactive diluents (ethylhexylacrylate, hexanediol diacrylate, and isobornyl acrylate as reactive diluents) on the thermal and mechanical properties of the UV-curable urethane acrylate oligomer were investigated. The functionality of the
reactive diluent does not affect the onset value of the glass transition temperature, but the increase of the amount of the diacylate monomer reactive diluent leads to an increase in the equilibrium and storage modulus in the rubbery state.\textsuperscript{204}

One of the main goals in UV-curable coatings is to create new reactive diluents that undergo fast and extensive polymerization to give final coatings having the desired properties. Very promising results have been obtained by introducing acrylate monomer (Acticryl CL-960) containing a urethane group into a UV-curable polyphenoxyacrylate formulation. This urethane acrylate reactive diluent has distinct advantage of imparting both hardness and elasticity to the cured films.\textsuperscript{187} Recently, urethane dimethacrylate monomer prepared via the non-isocyanate route from the reaction of a urethane diol with methacrylic anhydride has been reported.\textsuperscript{174, 175, 205} Photopolymerization of the urethane dimethacrylate monomer was investigated with respect to polymerization rates and conversions using photoinitiated differential scanning calorimetry.\textsuperscript{174} The urethane dimethacrylates as reactive diluents formulated with other acrylated oligomer to prepare UV-curabale coatings has never been reported. Previously, it has been reported that the addition of the urethane diol into the high solid coating system can increase the application solids and hardness.\textsuperscript{199} Herein, it is expected that the addition of the urethane dimethacrylate into the UV-curable coating system could also increase mechanical properties.

In this chapter, UV-curable polyurethane (PU) coatings were prepared by using acrylated polyester (APE) as oligomer, and non-isocyanate urethane dimethacrylate (NUDMA) as reactive diluents. The UV-curable PU coating prepared by this method shows more environmental friendly compared with conventional UV-curable PU coatings.
which consists of urethane acrylate oligomer and (meth)acrylate reactive diluents, and increased mechanical property compared with UV-curable acrylated polyester coating which consists of acrylated polyester oligomer and (meth)acrylate reactive diluents. As to our knowledge, it is the first time to make UV-curable PU coating by using acrylated polyester (APE) as oligomer, and non-isocyanate urethane dimethacrylate (NUDMA) as reactive diluents.

7.3 Materials

Adipic Acid (AA), isophthalic acid (IPA), 1, 6 hexane diol (HD), trimethylolpropane (TMP), p-xylene, dibutyl tin oxide (DBTO), ethylene carbonate (EC), propylene carbonate (PC), 2-aminoethanol (EOA), 3-aminopropanol (POA), methacrylic anhydride (MAA, 94%), dichloromethane, hydroquinone, Triethylene diamine (TEA) all Aldrich products were used as received. 4-(dimethyl-amino)pyridine (DMAP) was obtained from Acros Organics. Photoinitiator Darocur 4265 was obtained from Ciba Specialty Chemical, NY. Aluminum panels (type A, alloy) (3×6 in) panels were obtained from Q-panel Lab Products.

7.4 Instrumentation

The NMR spectra were taken in a Varian Mercury 300 MHz spectrophotometer. Molecular weight and its distribution were determined by GPC (Waters Corporation). The coating was cured by a Fusion UV-curing chamber (F300SQ Series) having a mercury arc bulb (150 mW cm⁻², UVB, 257 nm). Tensile and release tests were performed on an Instron 5567 (Instron Corp., Grove City, PA). The viscoelastic properties were measured on a dynamic mechanical thermal analyzer (DMTA, Q800, TA
Instruments). The thermo properties were characterized by differential scanning calorimeters (DSC, Q200, TA Instruments) and thermogravimetric analysis (TGA, Q50, TA Instruments).

7.5 Synthesis

In this synthesis part, acrylated polyester oligomer was synthesized by using two-step reactions. Non-isocyanate urethane dimethacrylate reactive diluents were also prepared by using two-step reactions.

7.5.1 Synthesis of the acrylated polyester (APE) oligomer

A typical poly-condensation technique was used to prepare APE oligomer. The synthesis process consists of two steps. In the first step, hydroxyl terminated polyester polyol was prepared by using excess diol. The molar ratio of alcohol to acid is 11:8. Adpic acid (AA) (100 g, 0.68 mol), isophthalic acid (IPA) (113.67 g, 0.68 mol), 1,6 hexane diol (HD) (161.71 g, 1.37 mol) and trimethylolpropane (TMP) (45.90 g, 0.34 mol) were taken in a 500 ml four-neck round bottom flask which was equipped with a mechanical stirrer, a gas inlet, a temperature controller, a Dean-Stark trap and a condenser. The reaction proceeded under argon to minimize oxidative degradation. To accelerate the reaction, 0.4 wt % of DBTO, a transesterification catalyst, was used. Then, 3 wt % of p-xylene was also added into the reaction mixture to remove water from the resin as azeotropic mixture. The reaction temperature was carefully controlled using a temperature controller and a thermocouple in order to minimize evaporation of diol. The temperature of the mixture was increased from 20-150 °C at a rate of 4.3 °C/min, and then from 150-210 °C at a rate of 0.25 °C/min. The final temperature was held until the
resin had an acid number measured by titration less than or equal to 10 mg KOH/g resin. The hydroxyl number of polyesters (160.4 mg KOH/g resin) was determined by ASTM method (ASTM D 1957-86). In the second step, the temperature was reduced to 120°C. Acrylic acid (AA, the mole ratio of the acid in the AA to the hydroxyl in the polyester polyol kept at 1.05), 1 wt % p-toluene sulphonic acid (p-TSA, catalyst) and 0.05 wt % hydroquinone (inhibitor) (based on the total amount of the polyester polyol and acrylic acid) were added in, the temperature was maintained at 120 °C for 14h. Then, 1.5 wt % of 3- methyl-3-hydroxymethyl-oxetane was added in, and maintained at 120 °C for another 20 min. Then solvent and residual were removed in vacuo resulting in a light yellow acrylated polyester oligomer.\textsuperscript{\textcircled{1}}\textsuperscript{1}H NMR (300 MHz, CHLOROFORM-d) δ (ppm) 0.84 - 0.98 (m, 2 H) 1.33 - 1.47 (m, 8 H) 1.50 - 1.53 (m, 1 H) 1.56 - 1.69 (m, 11 H) 1.73 - 1.83 (m, 4 H) 2.22 -2.39 (m, 6 H) 3.57 - 3.69 (m, 1 H) 3.99 - 4.16 (m, 6 H) 4.27 - 4.44 (m, 5 H) 5.75 - 5.89 (m, 1 H) 6.03 - 6.16 (m, 1 H) 6.32 - 6.44 (m, 1 H) 7.45 - 7.56 (m, 1 H) 8.11 - 8.28 (m, 2 H). The average molecular weight was found to be $M_n = 3500$, with a PDI = 1.8 via GPC.

7.5.2 Synthesis of non-isocyanate urethane dimethacrylate reactive diluents

The synthesis process consists of two steps. In a typical procedure to prepare EOAED, In the first step, urethane diol (EOA-EC) was prepared by modification of the Rokicki’s procedure.\textsuperscript{178} Ethylene carbonate (88.06 g, 1.00 mol) was dissolved in 100 mL dichloromethane, and such solution was drop added into the 2-aminoethanol (61.08 g, 1.00 mol) and dichloromethane (200 mL) mixture at 0°C. After finish adding, the mixture was stirred at room temperature for 24 hour. The slightly yellow liquid (yield: 98%) was got by rot vaporing the dichloromethane. In the second step, urethane dimethacrylate was
prepared by modification of Assumption’s procedure. Urethane diol EOA-EC (14.9 g, 0.1 mol) was dissolved in 300 mL dichloromethane at 0°C, 4-(dimethyl-amino)pyridine (DMAP) catalyst (122 mg, 1 mmol), and 0.05 wt % hydroquinone (inhibitor) (28 mg) were added in, followed by drop addition of triethylene diamine (TEA) (28.3 g, 0.28 mol), and then drop addition of methacrylic anhydride (39.4 g, 0.24 mol) under the N₂ atmosphere. The reaction mixture was stirred at 0°C for 24 hours. Then saturated sodium bicarbonate solution (294.7 g) was dropped added to get two phase separated mixture. The product (top layer) was collected, washed with brine (300 ml × 3) and water (300 ml × 2), and dried in anhydrous magnesium sulphate. After dichloromethane was evaporated, the final liquid product with pale yellow color was got (yield: 42%). \(^1^H\) NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) (ppm) = 1.86 (m, 6 H, -CH₃), 3.27 (qd, \(J = 5.67, 1.39\) Hz, 2 H, -CH₂NH-), 4.07 (td, \(J = 5.57, 1.63\) Hz, 2 H, -OCH₂CH₂O-), 4.12 (m, 2 H, -OCH₂CH₂NH-), 4.14 - 4.30 (m, 2 H, -OCH₂CH₃O-), 5.62 - 5.78 (m, 2 H, trans C=CH₂) 5.98 - 6.12 (m, 2 H, cis C=CH₂), 7.42 (t, 1 H, -NHCOO-). \(^1^C\) NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) (ppm) 18.11 (-CH₃), 39.79 (-CH₂NH-), 62.11 (-NHCOOCH₂-), 63.32 (-CH₂CH₂O-), 63.49 (-COOCH₂-), 126.18 (C=CH₂), 136.10 (C=CH₂), 156.46 (C=O, carbamate), 166.67 (C=O, ester). Figure 7-2 summarizes the urethane dimethacrylate prepared by this method.
Figure 7-2 Reactive diluents chemical structure

7.6 Coating formulation and evaluation

Aluminum and glass panels were used as the substrate for film preparation. The substrates were cleaned with distilled water and acetone and dried. The formulations were made by taking specific amount of synthesized non-isocyanate urethane dimethacrylate reactive diluent EOAED, POAED, POAPD, or dimethacrylate EGDMA.
and mixing them with specific amount of synthesized APE oligomer and 2 wt% (based on the total resin) photoinitiator Darocur 4265 in a glass vial at room temperature thoroughly for 20 min. The formulations are shown in Table 7-1. The films were cast on either aluminum or glass substrates with a thickness of 150 µm (6 mil) by a drawdown bar. The films were UV cured using a Fusion UV System processor (P300) at the belt speed of 5 fpm and stored in a dust free cabinet for testing purposes.

Table 7-1 The formulation of non-isocyanate PU with different reactive diluents at different concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>APE oligomer (wt %)</th>
<th>Reactive Diluent (wt %)</th>
<th>Photoinitiator (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APE</td>
<td>100</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>RD₁₀⁻¹⁰</td>
<td>90</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>RD-20</td>
<td>80</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>RD-30</td>
<td>70</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>RD-40</td>
<td>60</td>
<td>40</td>
<td>2</td>
</tr>
</tbody>
</table>

a. Photoinitiator weight percentage (wt%) is based on the total weight of oligomer and reactive diluents
b. RD means EGDMA, EOAED, POAED, and POAPD in specific case

Coating properties were evaluated according to ASTM methods including pencil hardness (D3363-05), impact resistance (G14), gloss rating (D523-89), and MEK double rubs (D4752-06). The gel content of the cured coating films was determined by Soxhlet extraction using acetone for 48 h. The insoluble gel fraction was dried under vacuum for 24 h at 60°C and weighed to determine the gel content. To measure the water absorption of a crosslinked coating, around 0.2 g coating sample was dried in vacuum for 24 h at 100°C, and then dipped in water at room temperature for 72 h. Afterwards, the wet sample without free water was weighed. The water absorption was then calculated from the difference in the weights of the sample before and after soaking in the water according to equation 7-1.
Water absorption = \[ \frac{w_{t\text{after}} - w_{t\text{before}}}{w_{t\text{before}}} \times 100\% \] (7-1)

where \( w_{t\text{after}} \) is the weight of the sample after dipping in the water, and \( w_{t\text{before}} \) is the weight of the sample before dipping in the water.

7.7 Results

The overall objective of was to prepare a UV-curable non-isocyanate PU coating, The UV-curable non-isocyanate PU coating consists of acrylated polyester as oligomer, non-isocyanate urethane dimethacrylate as reactive diluent and Darocur 4265 as free radical photoinitiator. In this study, we focused on the non-isocyanate urethane dimethacrylate (NUDMA) reactive diluents. The NUDMA was prepared from the reaction of urethane diol and methacrylic anhydride. The liquid urethane diol was synthesized from the reaction of amino alcohol with cyclic carbonate via non-isocyanate route shown in Figure 6-2. It is of interest to study the effect of the NUDMA reactive diluents on the coating properties, and compare NUDMA with conventional EGDMA.

To investigate the effect of the NUDMA reactive diluents on the coating properties, and compare NUDMA with conventional EGDMA reactive diluent, coatings containing different reactive diluents and concentration were prepared; the formulation was shown in Table 7-1. After UV curing, the general coating properties (hardness, gloss, MEK rub resistance and impact resistance) of non-isocyanate polyurethane coating were measured to evaluate effects of the urethane group on the film properties. The thermal and mechanical properties of the cured films were obtained using DSC, TGA and tensile test, respectively. The viscoelastic properties of the coating were investigated using DMTA. The glass transition temperature \( (T_g) \) and crosslink density of the coatings were
derived from the tan δ and storage moduli ($E'$), respectively. In addition, water absorption and gel content properties of the films were also investigated.

7.7.1 Tensile properties

The tensile strength, elongation at break, and tensile modulus as a function of reactive diluents content are shown in Figure 7-3, and summarized in Table 7-2. The tensile strength is increased with the addition of any each of these four reactive diluents. When EGDMA is used as the reactive diluent, the tensile strength shows a large increase from 1.99 MPa at 0 wt % to 6.19 MPa at 10 wt % till 13.36 MPa at 20 wt % EGDMA reactive diluents content, and a minor increase from 13.36 MPa at 20 wt % to maximum of 14.5 MPa at 30 wt % EGDMA reactive diluents content. The tensile strength is decreased to 9.78 MPa at 40 wt % EGDMA reactive diluents content. When EOAED or POAPD is used as the reactive diluent, the tensile strength shows a continuous increase with the amount of reactive diluent, and reaches the maximum at 40 wt % reactive diluents content. The maximum tensile strength of EOAED system is 29.51 MPa, which is 2.1 times higher than the EGDMA system; and the maximum tensile strength of POAPD system is 26.30 MPa, which is 1.8 times higher than the EGDMA system. When POAED is used as the reactive diluent, the tensile strength shows increase with the amount of reactive diluent initially, and reaches the maximum at 30 wt % reactive diluents content. The maximum tensile strength of POAED system is 21.96 MPa, which is 1.5 times higher than the EGDMA system.

For EGDMA system, the elongation at break is decreased with the addition of reactive diluents. The elongation at break shows a continuous decrease from 20.64 % at 0 wt % to the minimum of 1.26 % at 40 wt % EGDMA reactive diluents content. For all
these three NUDMA systems, the elongation at break increased from 20.64 % to 27.95 % (EOAED system), 27.19 % (POAED system) and 25.56 % (POAPD system) with the addition of 10 wt % reactive diluents, separately. The elongation at break of these three NUDMA systems remained constant as the reactive diluents increased to 20 wt % (within experimental error). After which, the elongation at break decreased as the reactive diluents increased from 20 wt % to 40 wt %. As comparing of the NUDMA system with the EGDMA system, the elongation at break of these three NUDMA systems is always higher than that of the EGDMA system at the same percent loading in the range of 10 – 40 wt %. The elongation at break of these three NUDMA systems is around 1.6-1.7 times higher than that of the EGDMA system at 10 wt % loading, 2.8-2.9 times higher at 20 wt % loading, 3.0-4.8 higher at 30 wt % loading, and 2.2-5.0 times higher at 40 wt % loading.

The tensile modulus shows a continuous increase with the addition of any each of these four reactive diluents in the percent loading range of 10-40 wt %. At 10 wt % loading of reactive diluents, the tensile modules increased from 12.60 MPa to 48.62 MPa for EGDMA system, and to around 23 MPa for the three NUDMA system; as the percent loading is increased from 10 -20 wt %, the tensile modulus increased to 212 MPa for EGDMA system, and to around 87 MPa for the three NUDMA system; as the percent loading is increased from 20 -30 wt %, the tensile modulus increased to 524 MPa for EGDMA system, and to around 345 MPa for the three NUDMA system; as the percent loading is increased from 30 -40 wt %, the tensile modulus increased to 968 MPa for EGDMA system, and to around 974 MPa for the three NUDMA system. The tensile modules of the EGDMA systems is around 2 times higher than that of the NUDMA
system in the percent loading range of 10-20 wt %, 1.5 times higher at 30 wt % loading, and almost equal at 40 wt % loading.

Figure 7-3 Tensile properties of UV cured coating as a function of reactive diluents: (a) tensile strength; (b) elongation at break; (c) tensile modulus
Table 7-2 Tensile properties of UV cured coating as a function of reactive diluents type and content

<table>
<thead>
<tr>
<th>Samples</th>
<th>Modulus (MPa)</th>
<th>Elongation at break (%)</th>
<th>Tensile stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APE</td>
<td>12.60 ± 0.60</td>
<td>20.64 ± 0.93</td>
<td>1.99 ± 0.09</td>
</tr>
<tr>
<td>EGDMA-10</td>
<td>48.62 ± 3.63</td>
<td>15.83 ± 1.40</td>
<td>6.19 ± 0.22</td>
</tr>
<tr>
<td>EGDMA-20</td>
<td>212.10 ± 13.38</td>
<td>9.77 ± 0.44</td>
<td>13.36 ± 0.84</td>
</tr>
<tr>
<td>EGDMA-30</td>
<td>523.79 ± 100.16</td>
<td>3.76 ± 0.98</td>
<td>14.05 ± 2.62</td>
</tr>
<tr>
<td>EGDMA-40</td>
<td>968.31 ± 238.84</td>
<td>1.26 ± 0.30</td>
<td>9.78 ± 3.34</td>
</tr>
<tr>
<td>EOAED-10</td>
<td>21.49 ± 0.82</td>
<td>27.95 ± 1.49</td>
<td>4.98 ± 0.31</td>
</tr>
<tr>
<td>EOAED-20</td>
<td>89.20 ± 3.49</td>
<td>28.37 ± 2.76</td>
<td>15.88 ± 1.68</td>
</tr>
<tr>
<td>EOAED-30</td>
<td>348.70 ± 31.13</td>
<td>13.60 ± 0.43</td>
<td>20.55 ± 2.02</td>
</tr>
<tr>
<td>EOAED-40</td>
<td>1010.93 ± 139.55</td>
<td>4.71 ± 0.43</td>
<td>29.51 ± 3.80</td>
</tr>
<tr>
<td>POAED-10</td>
<td>26.14 ± 1.92</td>
<td>27.19 ± 1.16</td>
<td>5.91 ± 0.28</td>
</tr>
<tr>
<td>POAED-20</td>
<td>97.50 ± 3.68</td>
<td>26.91 ± 1.21</td>
<td>16.11 ± 0.99</td>
</tr>
<tr>
<td>POAED-30</td>
<td>428.42 ± 84.37</td>
<td>11.33 ± 2.34</td>
<td>21.96 ± 1.34</td>
</tr>
<tr>
<td>POAED-40</td>
<td>1114.39 ± 46.87</td>
<td>2.72 ± 1.01</td>
<td>21.53 ± 6.56</td>
</tr>
<tr>
<td>POAPD-10</td>
<td>22.36 ± 2.38</td>
<td>25.56 ± 2.08</td>
<td>4.29 ± 0.35</td>
</tr>
<tr>
<td>POAPD-20</td>
<td>73.65 ± 7.17</td>
<td>22.23 ± 2.03</td>
<td>10.75 ± 0.36</td>
</tr>
<tr>
<td>POAPD-30</td>
<td>258.00 ± 31.20</td>
<td>18.00 ± 2.75</td>
<td>20.46 ± 1.77</td>
</tr>
<tr>
<td>POAPD-40</td>
<td>796.94 ± 54.08</td>
<td>6.30 ± 1.64</td>
<td>26.30 ± 3.42</td>
</tr>
</tbody>
</table>

7.7.2 Viscoelastic properties

The viscoelastic properties of the UV cured coating films were investigated using DMTA. An example of the DMTA data, depicting storage modulus (E’), loss modulus (E’’), and tanδ, is shown in Figure 7-4.
Figure 7-4 Dynamic mechanical properties of APE coating system. $E'$ storage modulus; $E''$, loss modulus; $\tan \delta = E'/E''$

The storage modulus ($E'$) remained almost constant as the temperature was increased up to the glass transition and started to decrease during the transition. The decrease reached a minimum value and then slightly increased with temperature forming a rubbery plateau as described in equation 7-2.\(^{146}\)

$$E' = 3 \nu_e RT \ (T >> T_g) \quad (7-2)$$

Where $\nu_e$ is the number of moles of elastically effective network chains per cubic meter of film and $E'$ is tensile storage modulus. This relationship is effective when $T >> T_g$, and for low crosslink density elastomers. For the highly crosslinked system, it can only be used to evaluate the relative density of crosslinking. Crosslink density was
calculated by this equation with the E' at corresponding temperature T (T > Tg + 50). The minimum of storage modulus, E'(min), was recorded as the minimum value in rubbery plateau. The Tg was obtained from the maximum of the α-transition. The Tg, minimum elastic modulus (E'), crosslink density (νe), breadth of tanδ transition, and maximum tanδ transition as a function of reactive diluents are summarized in Table 7-3.

### Table 7-3 Viscoelastic properties of UV cured coating as a function of reactive diluents type and content

<table>
<thead>
<tr>
<th></th>
<th>T for E'_{min} (°C)</th>
<th>E'_{min} (MPa)</th>
<th>νe (mol/m³)</th>
<th>Tg (°C)</th>
<th>Tan δ Breadth (°C)</th>
<th>Max. Tan δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>APE</td>
<td>91.17</td>
<td>4.92</td>
<td>541.66</td>
<td>43.10</td>
<td>24.99</td>
<td>0.91</td>
</tr>
<tr>
<td>EGDMA-10</td>
<td>179.48</td>
<td>12.33</td>
<td>1092.17</td>
<td>47.52</td>
<td>48.61</td>
<td>0.39</td>
</tr>
<tr>
<td>EGDMA-20</td>
<td>227.53</td>
<td>42.32</td>
<td>3388.86</td>
<td>52.21</td>
<td>71.66</td>
<td>0.25</td>
</tr>
<tr>
<td>EGDMA-30</td>
<td>239.61</td>
<td>63.26</td>
<td>4946.34</td>
<td>59.88</td>
<td>98.95</td>
<td>0.18</td>
</tr>
<tr>
<td>EGDMA-40</td>
<td>240.00</td>
<td>167.20</td>
<td>13063.53</td>
<td>61.59</td>
<td>123.19</td>
<td>0.13</td>
</tr>
<tr>
<td>EOAED-10</td>
<td>115.03</td>
<td>11.49</td>
<td>1186.74</td>
<td>55.41</td>
<td>45.28</td>
<td>0.48</td>
</tr>
<tr>
<td>EOAED-20</td>
<td>214.49</td>
<td>13.48</td>
<td>1108.31</td>
<td>61.80</td>
<td>68.38</td>
<td>0.36</td>
</tr>
<tr>
<td>EOAED-30</td>
<td>220.42</td>
<td>15.82</td>
<td>1285.07</td>
<td>75.45</td>
<td>101.64</td>
<td>0.27</td>
</tr>
<tr>
<td>EOAED-40</td>
<td>227.42</td>
<td>22.83</td>
<td>1828.56</td>
<td>127.83</td>
<td>131.21</td>
<td>0.23</td>
</tr>
<tr>
<td>POAED-10</td>
<td>134.53</td>
<td>12.33</td>
<td>1212.59</td>
<td>54.34</td>
<td>49.89</td>
<td>0.45</td>
</tr>
<tr>
<td>POAED-20</td>
<td>190.27</td>
<td>14.54</td>
<td>1257.94</td>
<td>61.16</td>
<td>74.85</td>
<td>0.32</td>
</tr>
<tr>
<td>POAED-30</td>
<td>232.40</td>
<td>25.09</td>
<td>1989.78</td>
<td>72.68</td>
<td>98.86</td>
<td>0.24</td>
</tr>
<tr>
<td>POAED-40</td>
<td>230.40</td>
<td>29.21</td>
<td>2325.72</td>
<td>97.41</td>
<td>123.82</td>
<td>0.20</td>
</tr>
<tr>
<td>POAPD-10</td>
<td>122.94</td>
<td>12.30</td>
<td>1245.03</td>
<td>53.91</td>
<td>39.74</td>
<td>0.59</td>
</tr>
<tr>
<td>POAPD-20</td>
<td>160.75</td>
<td>17.84</td>
<td>1648.44</td>
<td>69.69</td>
<td>64.68</td>
<td>0.38</td>
</tr>
<tr>
<td>POAPD-30</td>
<td>179.33</td>
<td>25.02</td>
<td>2216.95</td>
<td>79.92</td>
<td>86.86</td>
<td>0.29</td>
</tr>
<tr>
<td>POAPD-40</td>
<td>196.58</td>
<td>25.40</td>
<td>2167.97</td>
<td>103.81</td>
<td>116.43</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The storage modulus E' as a function of different reactive diluents of EGDMA, EOAED, POAED, and POAPD are shown in Figure 7-5. E'(min) and the crosslink density (νe) of the cured films increased with addition of the all four reactive diluents. At 10 wt % reactive diluents load, the storage modulus was doubled with the addition of each of the four reactive diluents. The storage modulus was increased from 4.92 MPa to 12.33 MPa for EGDMA system, 11.49 MPa for EOAED system, 12.33 MPa for POAED
system and 12.30 MPa for POAPD system. As comparing of the NUDMA system with the EGDMA system, the storage modulus of these three NUDMA systems is always lower than that of the EGDMA system at the same percent loading in the range of 20 – 40 wt %. Crosslink density (νc) of these four cured films exhibits the same trends as storage modulus.

Figure 7-5 Modulus (E’) as a function of temperature of the UV curable coating with different reactive diluents of (a) EGDMA; (b) EOAED; (c) POAED; and (d) POAPD.

The tanδ as a function of different reactive diluents of DGEMA, EOAED, POAED, and POAPD are shown in Figure 7-6. Tg and breadth of tanδ transition of the cured films increased with addition of the all the four reactive diluents. The maximum of tanδ transition of the cured films decreased with addition of the all the four reactive
diluents. At the same percent loading in the range of 10 – 40 wt %, $T_g$ and maximum of tanδ transition of all three NUDMA system is higher than that of the EGDMA system, and breadth of tanδ transition of all four cured films shows similar values with each other.

Figure 7-6 Tan δ as a function of temperature of the UV curable coating with different reactive diluents of (a) EGDMA; (b) EOAED; (c) POAED; and (d) POAPD

7.7.3 Thermal properties

The thermal properties of the UV cured coatings were further investigated using DSC and thermal gravimetric analysis (TGA). The DSC thermograms as a function of reactive diluents are shown in Figure 7-7. The corresponding $T_g$ and $\Delta C_p$ derived from the DSC data are summarized in the Table 7-4.
Figure 7- 7 DSC thermograms as a function of temperature of the UV curable coating with different reactive diluents of (a) EGDMA; (b) EOAED; (c) POAED; and (d) POAPD
Table 7-4 DSC data of UV cured coating as a function of reactive diluents type and content

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tg (°C)</th>
<th>Delta Cp (J/(g·°C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>APE</td>
<td>-18.01</td>
<td>0.53</td>
</tr>
<tr>
<td>EGDMA-10</td>
<td>-12.40</td>
<td>0.43</td>
</tr>
<tr>
<td>EGDMA-20</td>
<td>-13.06</td>
<td>0.40</td>
</tr>
<tr>
<td>EGDMA-30</td>
<td>-13.15</td>
<td>0.36</td>
</tr>
<tr>
<td>EGDMA-40</td>
<td>-13.05</td>
<td>0.29</td>
</tr>
<tr>
<td>EOAED-10</td>
<td>-9.88</td>
<td>0.51</td>
</tr>
<tr>
<td>EOAED-20</td>
<td>-4.22</td>
<td>0.42</td>
</tr>
<tr>
<td>EOAED-30</td>
<td>1.09</td>
<td>0.40</td>
</tr>
<tr>
<td>EOAED-40</td>
<td>3.43</td>
<td>0.27</td>
</tr>
<tr>
<td>POAED-10</td>
<td>-10.63</td>
<td>0.49</td>
</tr>
<tr>
<td>POAED-20</td>
<td>-9.22</td>
<td>0.45</td>
</tr>
<tr>
<td>POAED-30</td>
<td>-3.80</td>
<td>0.30</td>
</tr>
<tr>
<td>POAED-40</td>
<td>-2.87</td>
<td>0.25</td>
</tr>
<tr>
<td>POAPD-10</td>
<td>-10.33</td>
<td>0.54</td>
</tr>
<tr>
<td>POAPD-20</td>
<td>-9.42</td>
<td>0.51</td>
</tr>
<tr>
<td>POAPD-30</td>
<td>-6.88</td>
<td>0.51</td>
</tr>
<tr>
<td>POAPD-40</td>
<td>2.33</td>
<td>0.34</td>
</tr>
</tbody>
</table>

For EGDMA system, the Tg increased with initial addition of 10 wt % reactive diluent, and kept at the same level with reactive diluent further increasing to the load range of 20-40 wt%. For all three NUDMA systems, the Tg kept continuously increasing with the addition of the reactive diluents in the load range of 10-40 wt%. For all the four systems, the ∆Cp decreased with the addition of the reactive diluents. As a comparison, the Tg of the NUDMA system is always higher than that of the EGDMA system at the same reactive diluents content.

Thermal gravimetric analysis (TGA) was used in this study to evaluate the thermal decomposition of these UV cured coatings as a function of reactive diluent type.
and content. Representative dynamic TGA curves for UV cured coatings with various compositions are shown in Figure 7-8. The TGA data are summarized in Table 7-5.

Figure 7-8 TGA thermograms as a function of temperature of the UV curable coating with different reactive diluents of (a) EGDMA; (b) EOAED; (c) POAED; and (d) POAPD
Table 7- 5Thermogravimetric Analysis (TGA) data of UV cured coating as a function of reactive diluents type and content

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C) required to produce % weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5%</td>
</tr>
<tr>
<td>APE</td>
<td>307</td>
</tr>
<tr>
<td>EGDMA-10</td>
<td>319</td>
</tr>
<tr>
<td>EGDMA-20</td>
<td>314</td>
</tr>
<tr>
<td>EGDMA-30</td>
<td>313</td>
</tr>
<tr>
<td>EGDMA-40</td>
<td>316</td>
</tr>
<tr>
<td>EOAED-10</td>
<td>291</td>
</tr>
<tr>
<td>EOAED-20</td>
<td>279</td>
</tr>
<tr>
<td>EOAED-30</td>
<td>270</td>
</tr>
<tr>
<td>EOAED-40</td>
<td>256</td>
</tr>
<tr>
<td>POAED-10</td>
<td>298</td>
</tr>
<tr>
<td>POAED-20</td>
<td>295</td>
</tr>
<tr>
<td>POAED-30</td>
<td>290</td>
</tr>
<tr>
<td>POAED-40</td>
<td>279</td>
</tr>
<tr>
<td>POAPD-10</td>
<td>291</td>
</tr>
<tr>
<td>POAPD-20</td>
<td>279</td>
</tr>
<tr>
<td>POAPD-30</td>
<td>262</td>
</tr>
<tr>
<td>POAPD-40</td>
<td>251</td>
</tr>
</tbody>
</table>

For the most part, reactive diluent concentration had no major impact on the films thermal stability until higher temperatures (>300°C) were achieved. Figure 7- 8a shows the TGA data for EGDMA systems. It was found that the sample degradation of 5% took place at 307°C for neat polyester coating, between 313-319 °C for coating containing 10-40 wt. % EGDMA reactive diluent. It indicated that the thermal stability of the UV cured polyester coatings was slightly increased with the addition of the EGDMA reactive diluent. Figure 7- 8b shows the TGA data for EOAED systems. It was found that there was a shift to slightly lower temperatures as the EOAED reactive diluent loading
increased. The sample degradation of 5% took place at 291°C with 10 wt % reactive diluent content, at 279°C with 20 wt% reactive diluent, at 270°C with 30 wt% reactive diluent, and at 256°C with 40 wt% reactive diluent. It indicated that the thermal stability of the UV cured polyester coatings was kept decreasing with the addition of the EOAED reactive diluent. The other POAED and POAPD system exhibit similar trends as EOAED system. The shapes of the weight loss curves of all NUDMA system are almost identical, and overall differences in thermal stability appear to be small.

7.7.4 Gel content properties

In order to further investigate the crosslink properties of the cured coating films, the gel content measurements were performed. The gel content as a function of the different reactive diluents is shown in Figure 7-9. The gel contents of the cured films increased with addition of all the four reactive diluents, and show similar values at the same percent loading in the range of 10 – 40 wt %. For all of these four cured coating films, the gel contents were increased from 88% initially to 90% at 10 wt %, to 91 % at 20 wt %, to 92% at 30 wt %, and to 93% at 40 wt % reactive diluents load.
7.7.5 Water absorption properties

The effect of the reactive diluents on cured film was further verified in terms of water adsorption\textsuperscript{209}. In Figure 7-10, it is shown that the water absorption of the cured films increased with addition of all the four reactive diluents, and the water absorption of EGDMA system was found to be slightly lower than other three NUDMA system.
Figure 7-10  Effect of the reactive diluent type and content on the water absorption properties of UV cured coatings

7.7.6 General coating properties

A summary of the cured coating properties is found in Table 7-6. After complete UV curing, several film properties were evaluated: pencil hardness, impact resistance, gloss, and solvent resistance. It was found that the pencil hardness did not change with the addition of 10 wt% reactive diluents, and increased from 2B to HB with the addition of 20-40 wt% reactive diluents for all systems. The impact resistance of the EGDMA system was decreased with the addition of reactive diluents in the load range of 10-40 wt%. The impact resistance of the three NUDMA systems was increased with addition
of 10-20 wt % reactive diluents, and decreased with addition of 30-40 wt % reactive
diluents. The methyl ethyl ketone (MEK) solvent resistance was increased with the
addition of reactive diluents in the load range of 10-40 wt % for all systems. It was found
that there was no effect on the gloss with the incorporation of the reactive diluents for all
systems.

Table 7-6 General coating properties as a function of reactive diluents type and content

<table>
<thead>
<tr>
<th>Samples</th>
<th>Direct impact (kg/cm)</th>
<th>Reverse impact (kg/cm)</th>
<th>Pencil hardness</th>
<th>MEK double rubs</th>
<th>60°C Gloss</th>
<th>20°C Gloss</th>
</tr>
</thead>
<tbody>
<tr>
<td>APE</td>
<td>64</td>
<td>56</td>
<td>2B</td>
<td>16</td>
<td>181 ± 3</td>
<td>142 ± 2</td>
</tr>
<tr>
<td>EGDMA-10</td>
<td>55</td>
<td>52</td>
<td>2B</td>
<td>20</td>
<td>187 ± 4</td>
<td>148 ± 7</td>
</tr>
<tr>
<td>EGDMA-20</td>
<td>50</td>
<td>40</td>
<td>HB</td>
<td>60</td>
<td>185 ± 2</td>
<td>146 ± 7</td>
</tr>
<tr>
<td>EGDMA-30</td>
<td>44</td>
<td>42</td>
<td>HB</td>
<td>&gt;200</td>
<td>184 ± 4</td>
<td>144 ± 7</td>
</tr>
<tr>
<td>EGDMA-40</td>
<td>26</td>
<td>7</td>
<td>HB</td>
<td>&gt;200</td>
<td>183 ± 2</td>
<td>131 ± 18</td>
</tr>
<tr>
<td>EOAED-10</td>
<td>92</td>
<td>87</td>
<td>2B</td>
<td>36</td>
<td>189 ± 2</td>
<td>149 ± 2</td>
</tr>
<tr>
<td>EOAED-20</td>
<td>90</td>
<td>71</td>
<td>HB</td>
<td>44</td>
<td>182 ± 2</td>
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7.8 Discussion

Generally, the UV-curable PU coatings were formulated using the urethane
acrylate oligomers and (meth) acrylate reactive diluents. The urethane acrylate oligomer
was prepared from the reaction of a polyol with a diisocyanate followed by the reaction with hydroxyl acrylate monomer \(^{171}\). The drawback of the urethane acrylate oligomer is the use of the toxic isocyanate starting material. In this study, UV curable PU coating were prepared by using acrylated polyester (APE) as oligomer, and non-isocyanate urethane dimethacrylate (NUDMA) as reactive diluents. The UV curable PU coating prepared by this new method shows more environmental friendly compared with conventional UV curable PU coatings.

The tensile modulus of UV cured coating increased with the addition of the reactive content. This result is attributed to intra/inters molecular reaction between APE oligomer and reactive diluent, and the increase in crosslink density with the addition of reactive diluents. The tensile modulus of the NUDMA system is lower than that of the EGDMA system with the same content of reactive diluent, this may due to the fact that NUDMA system provide lower crosslinking sites for the coatings. The trend in the storage modulus mirrored the trend in tensile strength. The increase in tensile and storage modulus as the concentration of reactive diluents increased corroborated the crosslink density, Tg, impact resistance and gel content data. For EGDMA system, flexibility of the film was reduced as measured by elongation at the moment of breakage. Such reduction in elongation was expected due to higher concentration of joint site between polymer chains, which restrict the polymer movement upon stretching\(^{147}\). More interestingly for NUDMA system, the elongation at break increased with addition of the 10-20 wt% reactive diluent, and decreased with further increasing reactive diluent to 30-40 wt%. Such behavior might be the results of increasing physical interaction forces from the hydrogen bonding among urethane groups. The effect of the reactive diluent type and
content on the impact properties exhibits the similar trends as elongation at break properties. That is another evidence of improvement of the flexibility achieved through physical interaction forces via the hydrogen bonding in the NUDMA system.

The dynamic mechanical analysis of UV cured film with increasing reactive diluent concentrations showed two major trends. One corresponded to broadening of the transition region and the other represented the shift of the maximum tan δ value toward lower numbers and higher temperatures. The breadth of a transition region is closely related to the degree of heterogeneity. As given in Table 7-3, tan δ transition breadths was increased with the content of the reactive diluent, but independent of type of the reactive diluent, which suggested that the extent of reactive diluent has major impact on the heterogeneity, and higher amount of urethane group incorporation not necessarily cause more heterogeneous systems. The crosslink density has a direct impact on the tan δ such that it reduces long range segmental motion required for viscous flow behavior. As a result, the maximum tan δ can be used to compare the extent of cure. The maximum tan δ decreases as the extent of reactive diluents. This indicates that the crosslink density of the UV cured films increases with reactive diluent content. The maximum tan δ of the EGDMA system is lower than that of the NUDMA system at the same reactive diluent content. This is another evidence to show that the EGDMA system has a higher crosslink density, and higher tensile and storage modulus. The Tg was obtained as the maximum of tan δ. It was found the Tg increased with the content of the reactive diluent, and the Tg of NUDMA system is higher than that of the EGDMA system. On the molecular scale, the glass transition temperature of a polymeric material is the temperature at which the micro-Brownian movements of the molecular chain segments become significant.
Therefore, any responses of the material to a chemical and physical environment only occurs at or above the glass transition temperature. An increase in \( T_g \) corresponded to a decrease in mobility in the polymer. The formation of the crosslinking networks between the reactive diluent and acrylated polyester oligomers would hinder the movement of the polymer chains, resulting in the increase of the \( T_g \). It indicates that with the increase of reactive diluent content, the crosslink density of UV cured coating enhanced, leading to the increase of \( T_g \) of the coating. The \( T_g \) of the NUDMA system is higher than that of the EGDMA system. This can be attributed to the additional physical crosslink density formation via the hydrogen bonds between the urethane groups in the NUDMA system. As a comparison, the \( T_g \) measured by DSC exhibited the same trends as the \( T_g \) measured by DMTA. But the \( T_g \) measured by DSC were lower than the \( T_g \) measured by DMTA. This result can be due to a fact that the glass transition temperature of a polymeric material is a kinetic parameter which is affected by the time scale of the measurements.

The thermostability of UV cured coating is independent on the content of the EGDMA reactive diluent, but decreased with the extent of the NUDMA reactive diluent. This is attributed to the fact that the degradation process is caused by the dissociation of the ester bond in the EGDMA system, and the degradation process is caused by the dissociation of the urethane bond and ester bond in the NUDMA system. The urethane bond was known to be relatively thermally unstable materials, and decomposition of the urethane bond starts at about 150–200°C. This suggests that degradation starts at the urethane bond in the NUDMA system.
The gel is the portion of a material that does not dissolve in a solvent. Given a proper solvent, the gel content is primarily determined by the molecular weight and the geometry of the molecules. After crosslinking, the molecules of the coatings are formed into a three dimensional network and the entropy of the molecules was reduced. Consequently, the material dissolved less in the solvent and resulted in higher gel content. Thus, the gel content is proportional to the crosslink density. The gel contents of all the cured films increased with addition of reactive diluents, this indicates that the crosslink density increased with the addition of the reactive diluents.

The properties of water absorption by polymers have received considerable attention, due to the importance of these phenomena in the case of environmental ageing of polymers. Certain authors have found that the water absorption of polymers is directly related with their free volume fraction, while others have found that it is linked to the presence of polar groups capable to form hydrogen bonds with water molecules, and there is no apparently influence of the large-scale structure (crosslinking) of the polymer on water absorption. The water absorption of the cured films increased with the content of reactive diluents. It could be attributed the fact that the increase of the reactive diluent leads to the increase of the ester/urethane polar groups in the APE polymer matrix, increasing the interaction of the APE polymer and water, resulting in the increase in the total water absorption. It is known that the urethane group shows more polarity than the ester group. This results in the higher total water absorption of the NUDMA systems comparing with the EGDMA system.

Improvement of pencil hardness and MEK chemical resistance can be anticipated with the amount of reactive diluents incorporated into the system. This can be attributed
to the increase in crosslink density of the UV cured films which reduced the flexibility of the coating system. Similarly, the decrease in impact resistance with an increase in the concentration of EGDMA can also be attributed to the increase in crosslink density. But for NUDMA system, the increase in impact resistance with the addition of 10-20 wt % reactive diluent, and decreased with further increasing reactive diluent to 30-40 wt%. This phenomenon can be attributed to combined effects of two factors: the physical interaction force via hydrogen bonds in the urethane groups and crosslink density. At the low reactive diluent load, the physical interaction force via hydrogen bonds plays the dominant role in the effect of the impact resistance which favors the improvement of the impact resistance; while at the high reactive diluent load, the crosslink density factor plays the dominant role in the effect of the impact resistance which leads to the decrease in the impact resistance.

7.9 Conclusions

The new type and more environmental friendly UV curable polyurethane coatings were formulated using the acrylated polyester (APE) as oligomer and non-isocyanate urethane dimethacrylates (NUDMA) as reactive diluents. The UV-cured coatings properties were dependent on the reactive diluents type and content. Crosslink density, storage and tensile modulus, pencil hardness, chemical resistance, gel content, total water absorption, and Tg were proportional to the content of the reactive diluents. Comparing with traditionally used ethylene glycol dimethacrylate (EGDMA) reactive diluent, these new type non-isocyanate urethane dimethacrylates (NUDMA) reactive diluents shows significant improvements in impact resistance and elongation at break properties. This improvement in toughness is presumably the result of hydrogen bonds formation in the
urethane groups. It was found that the optimum level of the NUDMA reactive diluents concentration is between 10-20 wt %.
CHAPTER VIII

CONCLUSIONS

In this dissertation, four types of organic coatings based on polyester polyols were prepared: UV-curable unsaturated polyester/poly(meth)acrylate block copolymers, thermal curable long pot life polyester based polyurethane-urea coatings, thermal curable non-isocyanate polyurethane coatings, and UV-curable non-isocyanate polyurethane coatings.

A series of novel saturated polyester (SPE)- and unsaturated (UPE)-based block copolymers of (meth)acrylates were accomplished by the combination of condensation polymerization and ATRP. The polymerizations were well controlled and the main chain double bonds in the unsaturated polyester backbones remained almost unaffected during polymerization. Because of network formation upon irradiation the UPE-based block copolymer could be suitable candidate for solvent resistant coating material with superior properties.

Thermal curable polyester based polyurethane-urea (PUU) coating was successfully prepared. During the formulation, four different polyester polyols were chosen as the binders, isophorone diamine (IPDA) was chosen as the chain extender and also as the reactant for the formation of urea units, and the partially blocked
HDI isocyanurate (PBH) was chosen as crosslinker to increase pot life and reduce the loss the IPDA. As a comparison, the polyurethane coatings (PU) without adding IPDA were also prepared. With the incorporation of the IPDA, the tensile modulus and tensile strength of PUU coating showed higher values than those of the corresponding PU coatings due to the formation of the urea unit and extra physical interaction forces from the hydrogen bonding among urea groups. With the incorporation of the IPDA, PUU coating exhibited higher crosslink density and Tg than the corresponding PU coating.

The hydroxyl terminated, epoxidized, and cyclic carbonate terminated polyesters were synthesized and characterized by FTIR and NMR. The cyclic carbonate terminated polyester formation with time was monitored by using IR spectroscopy. Non-isocyanate polyurethane coatings were prepared by the thermo-curing of the cyclic carbonate terminated polyester and polyamine.

Three urethane dimethacrylate monomers were synthesized via a non-isocyanate route. The addition of the non-isocyanate urethane dimethacrylate could reduce the viscosity of the acrylated polyester (APE) oligomer. The urethane dimethacrylates could use as reactive diluents for UV-curable coating. Photopolymerization kinetics of non-isocyanate urethane dimethacrylates was studied. PI Darocur 4265 shows highest overall conversion and maximum polymerization rate, it was chosen as the PI for photopolymerization kinetics of reactive diluents and its formulation with APE oligomer. The polymerization conversion and maximum polymerization rate increase with increasing initiator concentration in the range from 0.5 % to 4.0 %. The reactive diluents non-isocyanate urethane dimethacrylate showed lower polymerization overall conversion and maximum polymerization rate than APE oligomer. But formulation system showed
higher polymerization overall conversion and maximum polymerization rate than APE oligomer.

The new type and more environmental friendly UV curable polyurethane coatings were formulated using the acrylated polyester (APE) as oligomer and non-isocyanate urethane dimethacrylates (NUDMA) as reactive diluents. The UV-cured coatings properties were dependent on the reactive diluents type and content. Crosslink density, storage and tensile modulus, pencil hardness, chemical resistance, gel content, total water absorption, and Tg were proportional to the content of the reactive diluents. Comparing with traditionally used ethylene glycol dimethacrylate (EGDMA) reactive diluent, these new types of non-isocyanate urethane dimethacrylates (NUDMA) reactive diluents showed significant improvements in impact resistance and elongation at break properties. This improvement in toughness is presumably the result of hydrogen bonds formation in the urethane groups. It was found that the optimum level of the NUDMA reactive diluents concentration is between 10-20 wt %.
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