TWO-COMPONENT INJECTION MOLDING:
STUDY ON THERMOPLASTIC AND RUBBER (T/R) COMBINATION

A Thesis
Presented in Partial Fulfillment of the Requirements for
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* * * * *

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ABSTRACT

A relatively new process in combining the hard/soft properties in one part is called Thermoplastic/Rubber (T/R) Combination processing. To gain an understanding on this new process, a study comprised of thermal simulation, adhesion characterization, and experimental investigations was done.

The thermal simulation studies done to evaluate the temperature distribution in the mold cross section showed the importance of having the heat transferred to most of the area of the elastomer. The adhesion characterization done using the Two-Step T/R Processing method through testing and examinations of the injection molded test parts consisted of 20% wt glass-fiber-reinforced PA612 and XNBR (carboxylated NBR) based rubber pairs.

The adhesion strengths were obtained by using the roll peel test (DIN 53 289 and DIN 53 350, which are similar to the ASTM D 3167-93). The light filler used (Vulkasil C and Polestar 200 R) and Carbon Black 1 (proprietary) seemed to be the important ingredient causing the good adhesion.

Two trends correlating the light filler amount as well as the carbon black filler amount with the adhesion strength. In the systems investigated, increasing the light fillers
(Vulkasil C and Polestar 200R) has a positive effect on the adhesion strength, while when used as the only filler in the compound, the carbon black with higher activity tends to lower the adhesion strength.
To Papah, Mamah, Otip, Weni, Ivar, and Williamsyah,

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CHAPTER 1

INTRODUCTION

In addition to the combination of metal and elastomer (familiarly known as rubber) to combine different properties of materials into one part (as a corrosion protection or as a method to join the metal parts), the plastic and elastomer combination is known as the other alternative.

In this regard, among other mechanical means (screws, rivets, clamps, etc.), the application of an adhesive gives more benefits (relatively uniform load distribution in the direction perpendicular to the applied load, the ability to join relatively thin material, the ability to save weight [21], and the preservation of the part surface [69], among others). However, the necessary preparation steps before the product is finished (temporary storage, surface preparations, addition of adhesives, drying, vulcanization, and cleaning [52]), are environmentally unfriendly and time consuming, which directly translates to being expensive. The same problems are faced by the traditional thermoplastic and rubber combination by using adhesive.

For rubber processing itself, the injection molding process has been increasingly used in the industry, along with injection compression molding. Compared with the
injection molding of thermoplastic, the advancements (e.g. flow simulation and specialized processes) made in the elastomer injection molding field have not been as quick-paced. Many of the difficulties in obtaining the same advancements result from the fact that rubber is rarely used without compounding (literally hundreds of recipes exist in each company, mostly guarded as trade secrets), hindering a thorough understanding of the material properties and behaviors. Moreover, these compounds are mostly prepared on a batch-to-batch basis, which can make a fluctuation in the final product.

A relatively new process in combining the hard/soft properties into one part is called *Thermoplastic/Rubber Combination* processing (the term is directly translated from the German word, *Kunststoff-Kautschuk Verbundsystem*, and will be denoted T/R henceforth). This process makes it possible to produce parts made up of thermoplastic and rubber materials without thermoplastic pre-treatments and has a similarity with other hard/soft combinations using a thermoplastic and a thermoplastic elastomer material (T/TPE). This method is gaining popularity and has been able to eliminate most, if not all of the preparation steps previously needed. **Table 1.1** shows the comparison between the T/R combination and other traditional processes [64].

As an alternative to rubber, TPEs from various bases (urethane, olefin - uncured and semi-cured, styrene, ester, and amide) have also been used in the thermoplastic industry. Promoted by the thermoplastic processing ease along with the elastomer properties, an average yearly usage growth of about 6% in Europe (1991 - 1997) [17 in 12] signifies their potential use in the future.
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+ : Necessary  • : Possibly Needed  — : Not Needed

**Table 1.1: Manufacturing of Hard-Soft Combination [64]**

However, the nature of the rubber allows for lightly cross-linked nodes to join relatively distant molecule chains. This forms 3-dimensional network structures, which allow it to have a reversible high flexibility (up to several hundred percent elongation is not unusual), as well as excellent fatigue resistance, toughness, and energy absorption characteristics [61]. Moreover, rubber is also known to have more resistance to creep, chemical attack and abrasion, and stability in heat, in comparison with TPE materials. In fact, these characteristics have made rubber the material of choice in the automotive industry where chemical resistance (against gasoline and oil, for instance) and dynamic
load absorbability (as a damping element) are the main characteristics sought by the part designers.

Besides the difference in the soft material used, the other main difference between T/R and T/TPE combination can be found in terms of the processing parameter values involved (see also section 2.4.6.1). In the T/TPE processing, since TPE has processing parameters in the proximity of the ones for thermoplastic materials, overlapped values can be assigned into the process, easing the task of the processor (detailed information can be seen in the works by Zipp [77], Jaroschek [42], and Brinkmann [12]), although it also has its own difficulties. On the other hand, as will be explained in section 1.1, T/R processing is relatively more difficult.

1.1 Background of the Process

The processing of T/R combinations, compared with the combination between thermoplastic and thermoplastic elastomer, is a relatively unknown subject. Part of the difficulties in accessing the technology is the opposing nature of the material processing technique itself.

In the processing of thermoplastics, the resin material is fed into a hopper, where it is heated and sheared to a relatively high temperature (150 - 350 °C/302 - 662 °F) inside the barrel to melt it. At the same time, it is also being conveyed and measured by the screw and injected into the relatively cold mold (30 - 120 °C/86 - 248 °F) where the molten plastic is cooled.
On the contrary, in the processing of elastomer, the material compound stripe is fed into a relatively cold barrel (60 - 100 °C/140 - 212 °F), "melted," conveyed and measured by the screw, and injected into the relatively hot mold (140 - 200 °C/284 - 392 °F), where it becomes more rigid due to the vulcanization/curing reaction occurring in the part.

In terms of machinery, a similar machine can be employed, which is an injection molding machine utilizing a reciprocating screw (specially designed for the elastomer material to prevent heat buildup [24]) allowing a more homogeneous and precise shot measurement. This ensures the repeatability and quality of the part production. A schematic illustration of T/R process utilizing injection molding method is presented in Figure 1.1.

In the field of T/R Processing, one can distinguish, in more detail, two different ways to produce one final part: One-Step Processing and Two-Step Processing.

In the One-Step Processing, there are currently two definitions of the process. One definition of the process is than it can be approached by the processing with the same technique as in the sandwich injection molding process [28], where one unit injects the rubber as the skin component of the part followed by the injection of thermoplastic as the core of the part. It is mentioned [28] that the mold temperature needs to be below the hardening temperature of the thermoplastic to provide sufficient rigidity as the part is ejected. There’s no technical report known to exist in part production or research by utilizing this particular method.
The other definition of the One-Step T/R Processing was stated by Richter [64] where the part production, the thermoplastic and elastomer parts, happens in one mold. This second definition is basically another way to produce a T/R part in the Two-Step T/R Processing (see below). To avoid confusion, the One-Step T/R Processing definition that will be used in this report is the one used by Richter.

In principle, *Two-Step T/R Processing* consists of preparing a thermoplastic ‘insert’ and then injecting or compressing elastomer onto it, allowing the damping or sealing function of the rubber. As far as the preparation of the thermoplastic insert and final part production, they can be done either in the same or in different machine/processes (injection molding, compression molding, and extrusion [28]). A similar and a more familiar example of the process has been used in producing two-color, same material, automobile tail light covers.

Processing of the thermoplastic parts in different machines enables each part to be made by different processors. In this case contamination of the thermoplastic surface must be avoided [64], because even a fingerprint can cause poor adhesion. Surface treatments, mostly degreasing operations, are sometimes necessary.

In both cases of the T/R processing methods, as in other hard-soft combinations, the thermoplastic will serve as a backing for the relatively soft rubber, either bearing an assembly function integrating the part further to the larger scheme, or as a main load carrier.
1.2 Applications and Disadvantages

From the hard and soft combination point of view, the only limitations are probably the manufacturing techniques and economical constraints. The main usage of the combination can range from energy absorbing devices and sealing applications to a better-grip provider. A few of the possible applications are the elastomer-coated roller, flange, tube, strengthened rubber profile, pump housing, valves, shoe soles, etc.

Like the T/TPE combination, in essence, T/R processing offers the advantages of having greater functionality in one part, increase in quality [12], and minimization of cost through the reductions of assembly, logistics, and pre-treatments.

The disadvantages of this process are the relatively new technology still requiring know-how, the unavailability of an adhesion matrix (typically available for two-material injection molding but not for T/TPE although some efforts have been done in that area [12]), elastomer compounds with variability natures, unknown important process parameters affecting the process, and special mold requirements that can be expensive.

This situation has been made more complex by the fact that in the elastomer industry, as has been mentioned above, each company has its own recipes for material compounding, mostly guarded as trade secrets. Batch to batch variations, along with different effects that filler, additives, and even the elastomer basis combination itself, among others, have made it seem difficult for this technology to establish a solid ground.
1.3 Scope of Research

In order to get a maximum benefit of the process, the research focus was put on the adhesion characterization using the 2-Step T/R Processing method through testing and examinations of the test parts injection molded at one processing condition. They are composed with one type of thermoplastic (glass fiber-reinforced PA612) and thirteen types of rubber compounds with XNBR (carboxylated NBR) as their basis material. The effect of certain material in the compound on the adhesion strength was compared and evaluated, but the optimizations of and the correlation between the processing parameters were not done.

To obtain quantitative results, the roll peel test (DIN 53 289 and 53 350) was used. This enabled the evaluation and comparison between the compounds’ effect. It was also combined with light microscopic investigation and the Electrones Spectroscope for Chemical Analysis (ESCA) to complete the analysis on the fractured surface.

Additionally, since an earlier research performed by Dyckerheff and Sell [18] was able to correlate the interfacial surface tension at the failed interface with the adhesion strength of the thermoplastic and various adhesive systems, an investigation of the fractured surface’s surface tension was also carried out to see if such phenomena also exists in the T/R systems.

Seeing the potential usage of computer simulation application in a simultaneous part design process, thermal simulation using CADMould-3D/MEX was also done. The focus is on the temperature distribution in the mold. More significantly, it was used in the
part cross section for several part geometries that will likely be encountered in the product design. In addition to a concept analysis on mold combining cold and hot temperatures, from the simulation study performed, part design recommendations favorable from the processing point of view were then reviewed.
CHAPTER 2

LITERATURE RESEARCH

2.1 Mold Design Technique

Mold design techniques for T/R processing have not yet reached a similar level despite the relatively advanced level achieved in the mold technology for the similar two-color or two-material injection molding process utilizing rotating molds typically accompanied with slider mechanisms and even deep cooling at certain locations [43].

Due to the necessary high curing temperature for the elastomer mold, the T/R processing has been done with special thermoplastics that possess the stability at or near the rubber curing temperature; they are able to withstand the injection pressure of the uncured elastomer. These materials are engineering thermoplastics such as PPE, PA, and Polyester, along with the glass fiber-reinforced ones. Several patents [28 - 37] state in more detail the general material manufacturing methods and the tests conducted.

The stability of these thermoplastics has made it unnecessary to provide thermal insulation to the mold halves. They do not receive special design consideration other than being capable of providing enough cooling and heating necessary for each corresponding
material. The use of slides and/or rotating molds, however, has been mentioned to make it technically possible and a more economical operation [64]. Little has been published in this area.

Mold flushing with nitrogen gas has also been utilized [64] in conjunction with the usage of the thermoplastic materials showing the sensitivity to oxidation through an air exposure at high temperature (e.g. compressed air during elastomer filling - also called the Diesel Effect, or an exposure of an extrudate at a high temperature to the open air). The flushing has been shown to remedy the adhesion problem due to the thermoplastic oxidized surface which causes the curing and the degradation on the surface.

From the mold design point of view, the molds for thermoplastic and elastomer applications are nearly identical [48, 26], which will ease the mold designer in transferring the knowledge from one field to the other. Some minor differences are the heated molds, which can be achieved by means of oil or heat cartridges, and the runner systems, which have to be larger to avoid premature curing [67].

2.2 Mold Concept for T/R Processing

Despite the similarities possessed by both thermoplastic and elastomer processing which ease the task of the mold designer tremendously (viscoelastic behavior of the melt, shear thinning behavior, etc.), some differences still exist (runner size, undercuts, etc.). In designing the mold for T/R processing, a mold designer needs to take all of these factors into consideration.
Kohlmann [50] mentioned the drawback of the two-step T/R process by putting a thermoplastic insert into the mold. High tolerance parts, using a core to hold a circular part, for example, necessitate the insert to be produced at a slightly larger dimension compared to the core. However, the high temperature imposed on the thermoplastic (high enough to soften the thermoplastic - see section 6.2), can result in parts with unacceptable tolerances, e.g. the part might no longer be circular because of unequal pressure distribution on the thermoplastic insert. For this reason, it is noted to be more reasonable and economical to produce the insert at the elastomer cure temperature [50] using the same mold. In this way, the parts can still be in the core while the rubber is injected, resulting in a more acceptable tolerance. Two methods of approaching this, by utilization of a rotating mold and platen, are represented in Figure 2.1 and Figure 2.2, respectively.

Figure 2.3 illustrates the mold setup for the rotating platen mechanism. While the curing temperature has to be fixed at $T_c$, three general possibilities of assigning mold temperatures $T_1$ and $T_2$ are:

- Assigning $T_1$ at a certain cooling temperature less than the curing temperature and $T_2$ at the intermediate temperature between $T_1$ and $T_c$ (e.g. $T_2 = (T_1 + T_c) / 2$)

- Assigning $T_1$ at a certain cooling temperature less than the curing temperature and $T_2$ at elastomer curing temperature

- Assigning $T_1$ and $T_2$ at elastomer curing temperature

The first and second possibilities have the disadvantage caused by the different mold halves' temperatures. Since curing takes a relatively long time, the cooler
1. T/R Part is ready for removal
   Thermoplastic part is made

2. Middle mold rotates

3. Molds close
   Elastomer is injected
   Thermoplastic is injected

4. Elastomer curing
   Thermoplastic cooling

T : Top Mold
M : Middle Mold
B : Bottom Mold

Figure 2.1: Rotating Mold Concept for T/R Process
1. T/R Part is ready for removal
   Thermoplastic part is made

2. T/R Part is ejected
   Mold platen rotates

3. Elastomer injection
   Thermoplastic injection

4. Elastomer curing
   Thermoplastic cooling

Figure 2.2: Rotating Platen Concept for T/R Process
Figure 2.3: T/R Mold Temperature Variance Concept

- $T_c$: Elastomer Curing Temperature
- $T_1$: Thermoplastic Temperature 1
- $T_2$: Thermoplastic Temperature 2
- $M_c$: Mold for Elastomer Curing
- $M_1$: Mold for Thermoplastic Cooling
- $M_2$: Mold for Thermoplastic Holding

Diagram:
- Stationer and Injection Side
- Moving and Rotating Side
- Insulator
- Schematic showing temperature and mold sections.
mold can act as a heat sink during elastomer curing, causing a non-uniform temperature distribution that can affect the curing performance of the rubber compound, which was also shown by a simulation study [46]. Furthermore, controlling an exact temperature in the mold cavity can also be a difficult issue since the temperatures that will be used for the part production have to be measured upon their reaching quasi stationary values.

The third possibility seems to be the best since the heat sink effect does not occur. Moreover, the curing process can benefit from the relatively hot thermoplastic part. However, this last method requires stability in the thermoplastic form and against the long heat exposure at the curing temperature and more importantly inside the barrel. This is where the possibility of using LSR, liquid silicone rubber, can make a difference. Having a curing time significantly lower than a typical rubber means less residence time in the hot mold and barrel for the thermoplastic.

Since at the elastomer curing temperature the thermoplastic can be considered soft, part removal has to proceed carefully as well. Since the part handling in the elastomer processing industry is mostly done manually, ejection can probably be eliminated. In this regard, a generous draft angle might help in releasing the part.

2.3 Importance of Thermoplastic Part Stability

To illustrate the thermoplastic form heat stability, two standard measurements were usually displayed at the material data sheet, ISO 75 and ISO 306 (DIN 53 461 and DIN 53 460, respectively). In T/R processing, ISO 75 consisting of three point bending
test of a sample under certain temperature and load, can be seen as inappropriate because
the thermoplastic part has to withstand a distributed pressure from the elastomer melt at
elastomer curing temperature.

In this respect, the Vicat softening temperature (ISO 306) can be a more
appropriate measure. The test consists of giving a certain load (10 N for Process A, 50 N
for Process B) to a certain area (1 cm²) on a sample in the tempered oil bath heated at
50 °C/hour or 120 °C/hour. Sample dimensions were mentioned to be 10 x 10 x (3 - 6.4)
mm³. The temperature at which the deformation is 1 mm is then recorded as the material's
Vicat softening temperature. For the thermoplastic used, ISO 306 results were listed as
215 °C for Process A, and 205 °C for Process B. Naturally, it has to be noted if this test is
applicable to the application intended.

2.4 Adhesion between Rubber and Thermoplastic

2.4.1 Introduction

Adhesion, the force that holds two forms at the interface [67], between rubber and
thermoplastics has been widely discussed in terms and in the field of adhesive application.
The focus has been in the usage of the rubber adhesive for the thermoplastic materials due
to adhesion importance in transmitting a force across a joint properly.

Little exists in the literature about the adhesion mechanism at the
thermoplastic/rubber interface without the presence of solvent or adherend surface pre-
treatment except in the application of the “adhesion compound” (see section 2.4.5.3 - Rubber and Thermoplastic Cords or Fabric Adhesion), where thermoplastic cord or fabric is used as the reinforcement for rubber products.

Regardless of the importance of the adhesion, it also has to be noted that the strength of a joint, often measured by destructive adhesion strength tests (see section 2.5), doesn’t always depend on the adhesion itself to support the load. More important is the cohesion of each part making up the system itself.

2.4.2 Interaction Forces between the Polymer Molecule Chains

Covaient bonding is known as the strongest bonding holding together the polymer atoms. Its significance lies in the fact that when this bonding is destroyed through heat or chemicals, the polymer degrades. For the thermoplastic itself, the force that holds polymer chains together determining its physical characteristics such as strength, comes from van der Waal’s force [56] which is proportional to the various power of the distance between the molecule chains. It consists of dispersion bonding, dipole bonding, hydrogen bonding, and ion bonding, each with its own level of bonding energy.

Referring to the covalent bonding as the intramolecular force and van der Waal’s force as the intermolecular force, Möhier [60] depicted the bonding energy ranges illustrated in Figure 2.4 (with metallic and ionic forces especially reserved for metals).

In the polymer systems, these are the forces that give the polymer its physical and chemical characteristics, including the cohesion and the adhesion.
2.4.3 Theories of Adhesion

The division of various theories of adhesion, which can be seen in Figure 2.5, have been reviewed by many authors (among others [72], [71], and [44]). In essence, it is agreed that the adhesion phenomena can not be simply explained by only one theory.
Figure 2.5: Adhesion Theories [69]
In this section, a brief explanation serving mainly as an overview is presented in Table 2.1.

<table>
<thead>
<tr>
<th>Theory</th>
<th>General Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mechanical Adhesion</strong> (McBain)</td>
<td>Adhesion interpreted as mechanical interlocking of the adhesive to the surface pores and dents.</td>
</tr>
<tr>
<td><strong>Specific Adhesion</strong></td>
<td></td>
</tr>
<tr>
<td>• <strong>Diffusion</strong> (Voyutskii)</td>
<td>Adhesion interpreted as a result from interdiffusion of the macromolecule chains.</td>
</tr>
<tr>
<td>• <strong>Thermodynamic Adsorption</strong></td>
<td>Adhesion interpreted as a result from the intermolecular forces between the adhesive and adherend.</td>
</tr>
<tr>
<td>(Sharpe &amp; Schornhorn)</td>
<td></td>
</tr>
<tr>
<td>• <strong>Polarization</strong> (de Bruyne)</td>
<td>The adhesive and adhesion must have similar polarity to achieve adhesion.</td>
</tr>
<tr>
<td>• <strong>Electrostatic Theory</strong></td>
<td>Adhesion phenomena is explained in terms of charge transfer across the interface, resulting in the formation of an electrical double layer. Adhesive-substrate system behaves then like capacitor plates having different charges, causing the adhesion.</td>
</tr>
<tr>
<td>(Deryagin &amp; Kortova)</td>
<td></td>
</tr>
<tr>
<td>• <strong>Chemical Reaction</strong></td>
<td>Adhesion is caused by chemical reaction at the interface</td>
</tr>
</tbody>
</table>

Table 2.1: Various Adhesion Theories

2.4.4 Process Physics of Adhesion

2.4.4.1 General Concept of an Adhesion Process

In the adhesive application, Walter [72] mentioned that there were several factors affecting adhesion such as wetting characteristics, temperature and viscosity at application, curing speed of the adhesive, and also surface structure, porosity, crystallinity of the adherend, and cohesion of each part.

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Despite the above mentioned complexity in determining the factors that affect the adhesion, one can look at the basic adhesive application process which can be seen in Figure 2.6. First, a form of adhesive has to be brought to a liquid form so it can be applied readily, benefited from a wetting mechanism. Schlegel [65] mentioned the wetting importance by stating that “if the fluid wets the surface, whereupon it was transformed into a tough substance, it has to be considered as the adhesive for the corresponding surface.”

There are three general ways to liquefy an adhesive [54], which are by applying heat (as in hot melt adhesive), adding solvent (as in most of the adhesive application), and applying heat (as in rubber component). After the fluid wet all the solid surface, it has to be turned into a solid form, so it can have the strength needed to properly function in transmitting the force. There are also three general ways to do this [54], which are by cooling, removing the solvent, and applying more heat, each corresponding to the three above-mentioned “melting” methods.

From the above mentioned theories and by considering the basic adhesion mechanism process, it can be concluded that there are three general adhesion mechanisms that can also apply in the polymer adhesion process:

- adhesion through chemical reaction
- interdifussion mechanism
- intermolecular force (van der Waal’s force)
Figure 2.6: Basic Scheme of an Adhesion Process
2.4.4.2 Wetting Phenomena

As mentioned before, wetting can be related to the adhesion tendency of a condensed phase to attract foreign material to its surface [49]. It is required for adhesion to occur because it promotes good contact between the elastomer and the thermoplastic molecules. In fact, several factors causing poor paint adhesion [72], which are not necessarily encountered in the multi-component injection molding processes, such as water layer, oil or plasticizer in interface, chemical change or destruction through oxidation, presence of wax at interface, dust particles, etc., can be interpreted as factors prohibiting molecules to be near one another.

On a simple system consisting of a liquid and a solid surface, when a drop of the liquid with surface tension \( \gamma_{lv} \) is deposited on the solid with a surface energy \( \gamma_{sw} \), the drop will try to minimize its surface on its given volume, i.e. it tries to form a sphere (a physical characteristic of liquid or solid called surface tension or surface energy, respectively, is defined as force per unit length in the surface \( \text{[mN/m]} \)). On a solid surface, the drop will have a parabolic shape with an angle \( \Theta \), as illustrated in Figure 2.7.

Young’s equation (Equation 2.1), relates the force balance between the above-mentioned surface tensions and the angle formed by the liquid.

\[
\gamma_{sw} = \gamma_{sl} + \gamma_{lv} \cos \Theta
\]  

(2.1)

where:  
\( \gamma_{sw} \) = Surface energy between solid and vapor phase \([\text{mN/m}]\)  
\( \gamma_{sl} \) = Surface tension between solid and liquid phase \([\text{mN/m}]\)
\( \gamma_{lv} \) = Surface tension between liquid and vapor phase [mN/m]

\( \Theta \) = Wetting angle formed [\(^{\circ}\)]

Roughly, it can be said that poor, good, and complete wetting is achieved when

\( \Theta > 90^{\circ} \), \( \Theta < 90^{\circ} \), and \( \Theta = 0^{\circ} \) (spreading), respectively [12].

![Diagram of liquid drop on solid surface]

**Figure 2.7: Liquid Drop on a Solid Surface**

Between the solid and the liquid itself exists a work of adhesion which can be described by Dupré’s equation (Equation 2.2).

\[
W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} 
\]  

\( (2.2) \)

where: \( W_a \) = Work of adhesion [mN/m]
Introducing the interface energy between solid and vapor, the surface energy of the solid $\gamma_s$ (between solid and vacuum) is distinguished by $\gamma_{sv}$ by Equation 2.3 [19]:

$$\gamma_{sv} = \gamma_s + \Pi$$  

(2.3)

where:  
$\gamma_s$ = Surface energy of solid in vacuum [mN/m]  
$\Pi$ = Spreading pressure [mN/m]

Combining Equation 2.1 and Equation 2.2, and neglecting $\Pi$ (which can be done for low energy surfaces [71]) results in Equation 2.4, also called thermodynamic work of adhesion, by which the work of adhesion can then be estimated by measuring $\Theta$ and $\gamma_v$.

$$W_s = \gamma_v (1 + \cos \Theta)$$  

(2.4)

As a criteria of wetting, a concept of critical surface tension $\gamma_c$ was first introduced by Zisman [78]. By measuring various values of the wetting angle $\Theta$ for a series of liquids with a known surface tensions $\gamma_v$ on the thermoplastic surface at the operating temperature, a plot between $\gamma_v$ and the corresponding value of $\cos \Theta$ can be made. Extrapolating to $\cos \Theta = 1$ gives us the $\gamma_v$ value of a fictitious liquid that will give a complete wetting characteristic to the thermoplastic surface [79]. To ensure optimal wetting upon which an optimal adhesion can also be expected, $\gamma_v$ needs to be less than or equal to $\gamma_c$.  

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Further evaluations on the surface tension showed that one can divide surface energy into its components, which are, for simplicity, $\gamma^p$ for the polar forces (including various dipole interactions and hydrogen bonding [78]) and $\gamma^d$ for the dispersion forces. Between the substrate and adhesive, Wu [78] stated that the optimum thermodynamic wettability condition would be reached when both polarities (evaluated at melt condition) are the same.

He also stated that:

"When the surface tensions of the two phases have similar values, matching of the polarity is very important. But, when the surface tensions of the two phases are widely different, matching of the polarity becomes less important. In this case, the system can tolerate a greater disparity in the polarity and still wet each other well."

Unfortunately, for practical application (see also section 2.5) the work of adhesion is not directly reflected in the adhesion strength measurement of the joint, as stated by several authors (among others Dyckerhoff and Sell [18], and Wu [78]).

Wetting, therefore, only shows the possibility of forming an adhesive joint [44], but it doesn’t necessarily mean strong adhesion strength [18], since the latter depends on various factors. Wu [79] further emphasized that the fracture strength of an adhesive joint cannot simply be related to wettability or surface chemical composition alone. An optimal wetting might not give optimal joint strength, but an interface unwet properly can lead to a joint failure by fracture mechanism.

Complete wetting, however, is important in making the strong adhesion possible. After all, it can bring an intimate contact between the elastomer and thermoplastic molecules in the order of molecular dimensions (<1 nm). Assuming that only van der
Waal's force was taking place, it was mentioned that at around that range of closeness it can give its effect (from de Bruyne's polarization theory [16], Walter [72] mentioned that less than 5 nm was necessary for the dipole molecules, or inducted ones, to make the dipole bonding force become effective).

Another approach has therefore been taken to correlate the adhesion strength to the wetting phenomenon; Dyckerhoff and Sell [18] stated (from the work of Hellwig et al. [23] and Wolf et al. [76]), that one can consider the interface tension, represented by Equation 2.5, as an energy discontinuity between the joining part, which makes it plausible for the adhesion strength to increase as this energy discontinuity, i.e. the interface tension, decreases. They stated that the adhesion strength showed “a maximum value when the surface energy of the hardened adhesive is equal to that of the substrate, i.e. when the interfacial energy adhesive/substrate is a minimum.” They also found that in the event of bad wetting and correspondingly increasing $\gamma_{d}$, the adhesion strength was found to decrease more. Their results are represented in Figure 2.8.

$$\gamma_{b} = \gamma_{l} + \gamma_{s} - 4\gamma_{l}^{d}\gamma_{s}^{d}/(\gamma_{l}^{d} + \gamma_{s}^{d}) - 4\gamma_{l}^{p}\gamma_{s}^{p}/(\gamma_{l}^{p} + \gamma_{s}^{p})$$  \hspace{1cm} (2.5)

Equation 2.5 is called harmonic-mean equation, which is preferred for low energy systems (organic liquids, water, polymers, and organic pigments). Its derivation can be seen in the work of Wu [78].
Figure 2.8: Adhesion Strength Relationship with Interfacial Tension [18]
Later, Michel [58] stated in his review that the measurable adhesion value on the polymer surfaces can be achieved when the $\gamma_{sl}$ is under 3 mN/m and at its best when it is under 1 mN/m.

$$\gamma_{sl} < 1 \text{ (max. 3) mN/m} \quad (2.6)$$

Brinkmann [12] correlated the ratio between surface energy of the solid (both $\gamma_s$ and $\gamma_s^p$) and the adhesion strength via a tensile test of T/TPE material combinations. Generally it can be said that the adhesion strength has a tendency to increase as the ratio from the whole - $\gamma_{s,T}/\gamma_{s,TPE}$, and the polar part only - $\gamma_{s,T}^p/\gamma_{s,TPE}^p$, approaches 1, with some exceptions for the polyolefin combinations.

2.4.4.3 Surface Treatment Effects on Adhesion Strength

From previous sections, it is clear that the importance of surface condition can’t be taken lightly. In fact, since the bonding process could be derived from physical and chemical properties at the interface [49], in order to achieve a successful application of rubber adhesive as one of the methods of joining thermoplastic materials. It is not uncommon to modify the relative inert surface of the thermoplastics and its known low surface energy. Wu [79] mentioned that surface treatments are used to change the chemical composition, increase the surface energy, modify the crystalline morphology and
surface topography, or remove the contaminants and weak boundary layers within 100 Å to 100 µm thick on the surface layer without affecting the bulk properties.

The typical first step is surface degreasing with organic or alkali soaps followed by surface roughening to *remove the layer causing poor adhesion*. Roughening has been known to *increase the adhesion contact area* also, so better bonding can be achieved. However, not all organic and alkali cleaners can be accepted by the adherend due to the risk of cracking and discoloration of the adherend.

The next step is changing the thermoplastic surface structure either by chemical, thermal, or electrical means. The latter is usually achieved through corona discharge, plasma modification, or treatment with an oxidizing acid to make the unpolar macromolecules to accumulate polar groups, what roughly can be considered as oxidation or exchange reaction [13], *increasing its polarity*. The end results are better wetting characteristics and adhesion properties.

Application of primer is also typically done before adhesive application. As indicated by a study done by Yang and Garton [81], one of its functions, in an application of triphenylphosphine or cobalt acetylacetonate as primer to LDPE and PP respectively, is to *enable the interpenetration into the adherend* by the ethyl cyanoacrylate adhesive.

*In summary, in traditional adhesive applications, polarity, good wettability and solubility were mentioned to favor the adhesion* [57].
2.4.5 T/R Adhesion Process

Looking back to section 2.4.4.1, it can be said that for the T/R processing, the adhesion mechanism between the thermoplastic and the rubber material can also be divided into 3 steps, as illustrated in Figure 2.9. In this case, the solid adherend is the thermoplastic, produced either as insert from other machine, or directly produced by the same machine by utilizing a two-plastification-unit injection molding machine.

The rubber compound is first melted by heating it between 60 - 100 °C, then “applied” to the thermoplastic adherend by using the injection molding machine. The next step will be the wetting of thermoplastic surface by “molten” elastomer compound. As discussed above, criteria of wetting has to be fulfilled in order for the elastomer to wet the thermoplastic surface properly if good adhesion is to be obtained.

Thereafter, the solidification of the elastomer proceeds through the curing reaction, which starts after the Scorch Index $S_i$ of the rubber reaches 1. Thereafter, three-dimensional net structures are formed and the elastomer obtains its physical properties.

The sufficient adhesion strength will be formed after sufficient bonding (interfacial bonding, adhesion) and the strength of the elastomer and/or the thermoplastic (cohesion) reach a necessary value. Optimal adhesion strength can be said to be reached when a cohesive failure occurs, so the product can be designed according to the bulk materials properties [50].
Figure 2.9: Basic Scheme of the T/R Adhesion Process

- Interdiffusion Mechanism - Chemical Reaction - Intermolecular Force

Symbols:
- L: Liquid
- S: Solid
- F: Force
- v: Velocity
Presently, there still exists a lack of knowledge of what happens as the rubber melt wets the thermoplastic and solidifies. In the following sections, a literature review on the subject of the adhesion between thermoplastic and rubber will be presented.

2.4.5.1 Elastomer Melt

During T/R processing, elastomer melt at operating temperature and pressure is supposed to wet the thermoplastic adherend. The fact that the elastomer is still in the melt condition is beneficial to the wetting since as the melt viscosity gets higher, the harder it gets to ‘wet’ the adherend. Good wettability of the elastomer melt will hence depend on the chemical and physical (such as viscosity) conditions of the melt. Fortunately, at melting temperature, the rubber compound has already some tack to it, so it can be assumed that it wets, or at least tacks, the thermoplastic insert interface.

Schlegel [65] mentioned some factors affecting the wetting for the polymeric systems are the size and structure of the molecules, sterycal hindrance, polarity, molecular weight distribution, content of solvent, plasticizer, and fillers. Obviously, for the elastomer compound, the effect of each compound’s components needs to be considered.

What is important for the T/R process is that the elastomer melt, especially for the highly reactive compound, has not yet cured upon wetting the thermoplastic. Kriesten [52] mentioned the expectation of better wetting with increasing curing temperature due to lower viscosity and the diffusion possibility enhancement at higher temperatures.
2.4.5.2 Thermoplastic Solid

The material stages of an amorphous or a semi-crystalline thermoplastic undergoing a temperature increase can be seen in Figure 2.10 and explained in Table 2.2. These stages of molecular chain activities were discussed further in their relations with the interdiffusion possibility in section 2.4.5.4.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Condition [21]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass-like</td>
<td>The material behaves elastically with relatively high modulus; it is brittle. Physical and mechanical properties are less temperature dependent, and micro- and macro-brownian movements are not present.</td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>Micro-brownian movements, where rotation and translation with respect to the bonding axis in the molecules exists, allowing chain segments or side chains movement without moving the whole chain.</td>
</tr>
<tr>
<td>Entropy elastic</td>
<td>Molecule chains move more freely. The material can be described as rubbery elastic. Translation movement mechanism without moving the whole chain.</td>
</tr>
<tr>
<td>Crystalline melting temperature</td>
<td>The crystalline region melts. This stage is signalized by sharp change in mechanical properties.</td>
</tr>
<tr>
<td>(only for semi-crystalline)</td>
<td></td>
</tr>
<tr>
<td>Molten</td>
<td>Macrobrownian movement, where the free movements of the whole molecule chains take place. Molecule chains move freely and can slip on top of each other.</td>
</tr>
<tr>
<td>Degradation</td>
<td>Signalized the destruction of the covalent bonding within the macromolecule.</td>
</tr>
</tbody>
</table>

Table 2.2: Thermoplastic Material Stages
Temperature Dependence of Mechanical Properties for Thermoplastics [56]

Stages

1. Glass-like
2. Glass Transition Temp.
3. Entropy Elastic
5. Molten State
6. Degradation
2.4.5.3 Previous Rubber and Thermoplastics Adhesion Studies

Rubber and Thermoplastic Cords or Fabric Adhesion

Adhesion between rubber and fabric made from cotton, rayon, polyamide, polyester with "Spin Finish," polyvinylakohol, glass cord, glass fabric, as well as metals as rubber reinforcement materials without pretreatment have been known in the rubber industry since 1965 [25] with the so called "adhesive compound."

With the adhesive compound known as the RFK system (Resorcinol - see Equation 2.7, Formaldehyde - see Equation 2.8 - donor, and Kieselsäure (Silicic acid - see Equation 2.9), the previous difficulties dealing with RFL öip (Resorcinol Formaldehyde Latex) (special aggregates and the expensive machines for impregnation and drying of the fabrics) can be eliminated [25].

\[ \text{C}_6\text{H}_{12}(\text{OH})_2 \quad (2.7) \]
\[ \text{OCH}_2 \quad (2.8) \]
\[ \sim\text{Si(OH)}_2-\text{O}~ \quad (2.9) \]

The adhesion was mentioned to originate from the resorcinol formaldehyde resin, while the role of silicic acid hasn’t been able to be explained beside its function as a catalyst for the resin forming. Its importance, however, is clear that it was stated that only at its existence, that the high bonding level could be obtained (the more active it is, the better the bonding is [27]). It was also shown by Albrecht [1] that the adhesion between
rubber and the thermoplastic cord/fabric can reach a significant value only in the presence of the three main combination.

In the RFK system, the resorcinol component, also known as Cohedur RS, consists of homogenous hardened melt from resorcinol and stearic acid (see Equation 2.10) with a ratio of 2:1.

\[ \sim \text{C}_{17}\text{H}_{35}\text{COOH} \]  \hspace{2cm} (2.10)

It was mentioned that for the formaldehyde donor, a product from Bayer, Cohedur A or Vulkacit H 30 (a relatively slow amine accelerator - 97% Hexamethylentetramine) can be used, while for silicic acid, either Vulkasil S or Vulkasil C (Vulkasil S being more reactive than Vulkasil C; see section 5.1.1.1 for an explanation on Vulkasil C) can be used. Table 2.3 shows the mixture combinations that can be added to the rubber compound [27].

<table>
<thead>
<tr>
<th>Component</th>
<th>Combination A</th>
<th>Combination B</th>
<th>Combination C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resorcinol</td>
<td>Cohedur RL</td>
<td>Cohedur RS</td>
<td>Cohedur RS</td>
</tr>
<tr>
<td>Formaldehyde Donor</td>
<td>(Resorcinol in Cohedur A)</td>
<td>Cohedur A</td>
<td>Vulkacit H 30</td>
</tr>
<tr>
<td>Silicic Acid</td>
<td>Vulkasil S</td>
<td>Vulkasil S</td>
<td>Vulkasil S</td>
</tr>
</tbody>
</table>

Table 2.3: Filler Combination for Rubber Adhesive Compound

For vulcanization, it was mentioned that it should proceed so that the flow time gives enough time for the forming of the resorcinol formaldehyde resin (Scorch time > 39
resin building time). Stearic acid was mentioned to be important to achieve optimal bonding (for NBR, a higher content tends mostly to yield better bonding). Furthermore it was mentioned that:

- Carbon black (active and inactive) does not affect the adhesion system, yet through the compound stretching effect might give better or worse result.

- Other light fillers, as long as the content is less than the Vulkasil S, react well to the adhesion, for quartz flour, silica, and chalk, or poorly for hard kaolin, soft kaolin, aluminum silicate gel.

- Plasticizer (an aromatic and a napthenic one; paraffin oil is not recommended) does not affect the adhesion essentially unless exceeding 20 phr.

As a summary of the adhesion from rubber to textile, metals, thermoplastics, or other substances, it can be summarized that the effect of the compound is also important [25]:

- Softer compounds (e.g. <50 Shore A) are essentially more difficult to adhere than the harder ones.

- Plasticizer, sulfur, wax, or other product migration can lead to adhesion loss.

- It is required that the vulcanization time be long enough so the adhesion can be built (Albrecht [1] mentioned that the use of ultra accelerator give only little, if not at all, adhesion).

- Certain aging protection components, such as MBI, can lessen or even destroy the adhesion

- Filler can also affect the adhesion
• The rubber basis type also influences the adhesion. From the highest to the
   lowest adhesion: NBR > CR > NR > SBR > BR > EPDM > IIR

**Fusion Bonding**

With a process called *Fusion Bonding*, Wragg *et al.* [72] mentioned the reversed
step from T/R processing consisting of the thermoplastic injection following that of the
elastomer. They discussed the occurrence of adhesion between the rubber, whether cured
or not, and the thermoplastic melt without surface treatment or the usage of solvent. They
found that

"... if, under certain conditions, the molten surface of a plastic material is
brought into contact with a compatible rubber compound, either during the
vulcanization process or afterwards, then spontaneous adhesion occurs to
produce, upon cooling, a strongly bonded composite."

To bring the molten polymer into contact with the elastomer part, various
methods, such as compression molding, injection molding, extrusion bonding, and friction
bonding, were utilized.

Their investigations showed that for a combination of various rubber (and also
depending on the rubber content in the compound for a pre-cured compound) with the
same type of thermoplastic, the adhesion strength (measured with peel test) will be
different, and vice versa.

However, the mechanism of the bonding process was not completely understood.
The wetting criteria was mentioned to be fulfilled by comparing the surface tension of the
rubber vulcanisates (EPDM) and the molten thermoplastics (linear HDPE and branched
LDPE).
By focusing their work on the fusion bonding between polyolefin thermoplastics (polyethylene, polypropylene, ethylene propylene copolymer and ethylene vinyl acetate copolymer) and polyolefin elastomers (EPDM, EPM, and blends between EPDM or EPM with SBR, polybutadiene or polyisoprene), they found that:

- when a combination of rubber basis was used, good adhesion depends on the amount of a certain rubber content in the compound
- adhesion strength depends on rubber content, type of thermoplastic material used, and the presence of a barrier preventing adhesion such as low concentrations of ozone
- highly branched thermoplastics are more sensitive to rubber volume than the linear ones.

When the thermoplastic melt is injected during rubber curing, some degree of bonding occurred, irrespective of rubber compound composition. This happens provided that the cure temperature is at or above the melting point of the plastic, while when the melt is delivered after elastomer curing, bonding appears to be confined to certain volumes of rubber content in the compound (the lesser the better).

They also found that the type of unsaturation in the rubber and the nature of the subsequent crosslink are irrelevant with respect to bonding. Oil migration was mentioned because of its ability to cause a problem with the adhesion. As injection temperature increases, better bonding was observed.

It was also found that no pre-bonding treatment to the rubber is necessary. If the adhesion is inherently poor, surface roughening can improve it, but if the adhesion is
already good, surface roughening can worsen it. Air trapping and stress concentration were suspected to be the cause.

**T/R Adhesion Studies**

Kriesten [52] investigated the adhesion between a modified poly(2,6-dimethyl-1,4-phenyleneether) (PPE) toughened with fine elastomer particles and a glass-fiber-reinforced SBR. An oxidation layer formed when PPE is exposed to air at high temperature was found to be the cause of the poor bonding, so a vacuum-equipped mold was necessary to produce the PPE part.

Exposure to high temperatures along with the effect of exposure time was observed to reduce adhesion strength until adhesive failure (interfacial failure), an occurrence which was related to the presence of an oxidation layer. Antioxidant was found to retard the forming of this layer, and an addition of plasticizer was also found to promote the adhesion on the oxidized surface.

Using the peel test (DIN 53 531), three types of failures were observed within the experiment window, which are:

- cohesive failure in rubber (30 - 50 N/mm)
- cohesive-adhesive failure (10 - 30 N/mm)
- adhesive failure (0 - 10 N/mm).

Supported by his work [64] using PPE and a styrene-butadiene two-block copolymer (as a sulfur-cured rubber model) system, Richter claimed that the interdiffusion mechanism existed between PPE and SBR compounds (styrene molecules moving from
SBR into PPE). Using an electronic microscope, an interdifussion zone as wide as 100 nm was detected.

**Table 2.4** shows the list of rubber that can be paired with the modified PPE. All fillers were mentioned to be able to be used as usual, except when a peroxide is utilized, filler with low specific surface value should be used to prevent the peroxide being attracted by the filler (see section 4.1.2), making it less effective.

As for the PPE and EPDM compounds combination, the adhesion mechanism was caused by the peroxide curing agents causing the rubber to be cured with the thermoplastic surface radically [64]. Incompatibility noted from this component was shown from the insufficient existence of the penetration depth [75].

<table>
<thead>
<tr>
<th>Thermoplastic (modified PPE)</th>
<th>Base Rubber</th>
<th>Base Rubber (+ 5 phr SBR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vestoran 2000, 1900, X4880</td>
<td>SBR, BR, SBS, SEBS, EPDM^</td>
<td>NR, IR, IIR, PNR</td>
</tr>
</tbody>
</table>

^Vulcanized with Peroxide; all others with sulfur

**Table 2.4: T/R Combination Pairs investigated by Richter [64]**

2.4.5.4 The Possibility of Interdiffusion Mechanism

The interdiffusion mechanism is often associated with the movement or reptation of the polymer molecule chains across the interface into another matrix material and has been described using a *reptation model*. Factors that promote these crossings, such as low molecular weight, presence of solvents, plasticizers, etc., are hence important in
strengthening the adhesion, in addition to the processing parameter time, pressure, and temperature.

To illustrate the importance of this interdiffusion mechanism in governing adhesion, in his review on adhesive application Wuich [80] stated that:

- When the polymer is polar or unpolar and has good solubility, good adhesion can be expected.
- When the polymer is polar but has poor solubility, it is hard to adhere.
- When the polymer is unpolar but partially soluble, it is hard to adhere without pre-treatment.
- When the polymer is unpolar or polar and not soluble, it will not adhere without pre-treatment.

The interdiffusion mechanism across the interface requires polymer compatibility, which consists of a kinetic requirement (mobility) and thermodynamic requirement (compatibility), although according to Wu [79], theoretically and experimentally, local segmental diffusion is known to occur readily, forming a diffuse interfacial layer of 10 - 100 Å between two incompatible polymers. From the work of Jabbari and Peppas [40], Brinkmann [12] mentioned that in a compatible system, the area of diffusion layer was found in the area of several micrometers, while in the semi-compatible system, the diffusion layer was found to be in the area of several Å, although this was observed by using the material combinations that were not used in practical applications.

For the diffusion mechanism to occur between polymers, however, the temperature must be above the polymers' glass transition temperature, along with
thermodynamic compatibility existence at least at the interfacial region of the components [44].

In the thermoplastic welding, as also in the weld line strength studies, where two molten surfaces are brought together, the interdiffusion mechanism has been proposed as a mechanism that allows the bonding between two interfaces having a high degree of molecular chain movements, i.e. in fluid condition, a similar condition that also applies to T/TPE processing as will be mentioned in section 2.4.6.1.

In the case of T/R processing, since one of the requirements for the interdiffusion is the polymer's ability to move the molecule chains and the thermoplastic part is in solid form at elastomer curing temperature and below its glass transition temperature for amorphous and a little bit above the glass transition temperature for semi-crystalline material (to preserve its form during elastomer injection), the only molecules that have the ability to move or reptate are the elastomer molecule chains before it is cured.

Especially for the semi-crystalline thermoplastics, the presence of crystalline regions make it seem rather unlikely for the elastomer molecule chains to reptate, by macrobrownian movement, into the semi-solid thermoplastic. Unless the thermoplastic surface is melted either by the elastomer melt temperature above thermoplastic melt temperature or by heat released by elastomer during curing reaction, it can be argued that the interdiffusion mechanism will probably not occur.

This is supported by Sung's study [68] which showed that the peel strength, measured at the room temperature, undergoes a sharp transition from its low values (about 1 N/mm) to higher values (about 2.5 N/mm) as the bonding temperature is changed
from below to above the melting point of the substrate. This increase in peel strength is accompanied by changes in failure mode from the apparent interfacial failure to cohesive failure through the adhesives. Interference microscopy revealed the interdiffusion layer (observed as a gradient of the interference fringe pattern across the interface) between the HDPE and EVA interfaces at higher temperatures. Sung also noted that at lower bonding temperatures, the adhesion is present, however weak (in the order of 1 N/mm).

Due to the absence of solvent in the elastomer system, which has the purpose of enabling molecule mobility in the adherend, interdiffusion can occur [49]. The primer that is applied to the thermoplastic surface allows the adhesion mechanism to then result either from the chemical reaction or from the intermolecular forces between the molecules of both components.

2.4.5.5 The Possibility of Chemical Reaction

The classical example of the chemical reaction occurring at the bonding interface is probably between glass fibers with their thermoplastic matrix through an application of a silane adhesion promoter or a primer which can be put on the adherend or into the adhesive material itself. This silane adhesion promoter has a function of bridging the surface of the glass and the matrix material with either chemical or hydrogen bonding through its bifunctional molecules so that the adhesion strength is improved.

Although Kammer [44], among others, mentioned that thermodynamically, it is unfavorable for most polymers to mix, i.e. forming chemical bonding, the possibility still
remains open. The presence of functional groups in the material might induce the occurrence of this chemical reaction, as the experimental data of Pritchard [62 in 44] shown that several reactive functional groups such as amino (NH$_2$-), hydroxyl (OH-), carboxyl (COOH-), and also H-bond formation tend to increase adhesion.

Moffett and Dekkers [59] investigated the polymer blends and found that there exists a reaction of functional groups between thermoplastic (PBT with carboxylic acid endgroups) and rubber (EPDM-g-GMA, which is an EPDM grafted with glycidyl methacrylate, with the reactive epoxy endgroups) upon melt mixing of the two.

According to Elias [19], two components can mix with each other when two thermodynamic requirements are fulfilled. The first one is when the Gibbs free energy of mixing is negative, represented in Equation 2.11, where $\Delta G_{\text{mix}}$ is the Gibbs free energy of mixing, $\Delta H_{\text{mix}}$ is the enthalpy of mixing, $T$ is the temperature, and $\Delta S_{\text{mix}}$ is the entropy of mixing. The second one is when the first derivation of the chemical potential $\Delta \mu_A$ of the component A to the volume part $\phi_B$ of the component B is positive, represented in Equation 2.12.

\[
\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} < 0
\]

(2.11)

\[
(\partial^2 \Delta G_{\text{mix}}/\partial \phi_B^2)_{T, \phi} = \partial \Delta \mu_A / \partial \phi_B > 0
\]

(2.12)

Polymer incompatibility arises from the very small amount of entropy gained by mixing different kinds of long chains [53], while enthalpy of mixing is often a positive
quantity or, at best, zero [45]. A study of compatibility at highly diluted solution has shown that even at 5 - 10% of polymer concentration, phase separation occurs [53].

Wu [79] mentioned in comparison with the interdiffusion's diffuse interface, interfacial attraction or chemical reaction yields in a sharp interface, one can detect its presence within reasonable means. Furthermore, by comparing the adhesion strength value, a distinction between the chemical reaction and the interfacial attraction can be made.

2.4.6 Similar Process Combination

2.4.6.1 Thermoplastic/Thermoplastic Elastomer

Although having similar physical characteristics as rubber, the nature of TPE in adhesion of TPE and thermoplastic plays a significant role. Since TPE is also a thermoplastic material, the processing temperatures of TPE can be similar to the corresponding thermoplastic material pair. Overlapped processing conditions and material properties, such as shrinkage, melt and mold temperatures, can be chosen to minimize the difficulties in combining both materials. The melt temperature of the latter injected material can be advantageously used to melt the first injected thermoplastic interface so better bonding can be obtained, as investigations by Jaroschek [42] showed.

This was confirmed later by Brinkmann [12] in an attempt to predict the adhesive strength of T/TPE parts by monitoring the temperature near the interface. The effect of
surface roughness depends on the material and only within a small range (investigated average roughness lied between 0.43 - 27.3 μm).

2.4.6.2 Polymer Blends and Copolymers

The rubber particles within the thermoplastic matrix is not a recent phenomenon. In producing thermoplastic elastomers, polymer blends (defined as intimate mixtures of two kinds of polymers, with no covalent bonds between them, although interdiffusion was mentioned to be an expected mechanism in polyblends exhibiting limited compatibility [53]), are produced through intensive mixing between both components, producing impact-resistant plastics or reinforced elastomers. Since the adhesion at the interface between elastomer and thermoplastic phase define the mechanical properties of the blends, compatibility is often reached by means of compatibilizer or elastomer oligomere [12].

However, the nature of T/R and polymer blends are somewhat different. First, the melt mixing doesn’t happen in the T/R, and second, contact surface between thermoplastic and rubber consists solely in the form of relatively large interface between thermoplastic and rubber, instead of through many small interfaces for polyblends.

As for graft and block copolymers, they are made directly in the polymerization reaction, consisting of two different polymer chains in combination with each other linked with covalent bonds. Interpenetrating Polymer Networks prepared a crosslinked polymer network, swelled in a second monomer together with activator and crosslinking agent, and
polymerized in situ. This second reaction forms a crosslinked polymeric network that interpenetrates the first network [53].

It can be said that all of the three systems mentioned above have a different nature with T/R processing and will not be discussed further.

2.5 Testings

As mentioned in the previous section, although theoretical work of adhesion between two interfaces exists, it is rarely used to judge the joint or adhesion strength, the failure mechanism of which can depend upon various factors, among others rate of test and defects at the interface. Therefore, indirect methods are often used to give quantitative values needed to judge the effect of processing conditions or additives on the adhesion strength between two materials which can also be used to optimize the process and to relate various processing parameters.

As Bischof et al. [11] mentioned, no general test method exists. Each test has to be directed toward a specific application, which is still probably the best adhesion estimation of the system. It was furthermore stated that since each phase of material has its own tension-deformation relationship, it was also difficult to compare one combination with the other.

Using a standardized sample shape for thermoplastic testing (DIN 53 455), Brinkmann [12] performed tests of T/TPE combination. To be able to incorporate the TPE yet still allow a secure grip by the machine, both shoulders were designed to be
thermoplastic while the middle area of the sample was changed to TPE material. The geometry leads to necking in the TPE area, leading to a complex 3-D state of stress, and making it difficult for the results to transfer directly to the application. A study using the finite element method indicated that in such geometry, a maximum state of stress can be expected at the outer edge of the interface.

The tests used to investigate the adhesion strength between elastomer and thermoplastic can be derived or taken from various adhesion tests originally intended to test the adhesion between elastomer and metal, or between rubber and textile. To test the adhesive strength between metal and elastomer, and between rubber and textile under static conditions, standardized tests consisting principally of peeling, shear, and tension tests are available.

A non-destructive test using ultrasonic waves to detect flaws at the interface is also available. However, in practicality, these tests have been noted [14] to have a number of difficulties limiting their application, one of which originates from the fact that even the detection of a complete disbond is hard to perform.

In all of the testing systems mentioned above, it is clear that when one talks about the strength of a product made of different components in a series system, its strength will be determined by the strength of each component, especially the weakest one.
2.6 Summary

This chapter gives an overall background on the process physics of the adhesion phenomena, and a review on the processes similar to the T/R processing with the emphasis on the aspects governing their adhesion mechanisms, along with an overview on the subject of adhesion strength testing for the parts consisting of two materials.

It was further proposed that the adhesion mechanism for the T/R material combination can consist of intermolecular interaction, chemical reaction, and interdiffusion at the interface between the thermoplastic and the rubber. From the characteristics of the T/R process, it was hypothesized that the possible mechanism governing the adhesion process in the T/R combination pair is caused by the intermolecular interaction at the interface.
CHAPTER 3

THERMAL SIMULATION USING CADMOULD-3D/MEX

3.1 Introduction

For the two-step T/R process, it is important to know the temperature distribution in the thermoplastic part to avoid its thermal degradation and deformation. To achieve this, a 2-D thermal simulation was done utilizing the MEX module from the software CADMOULD-3D from SIMCON/IKV, Aachen. The program simulates the temperature distribution in the part and the mold upon the constrains of boundary and initial conditions.

The thermal investigation using a simulation program has two benefits. First, the simulation allows the study of the thermal distribution inside the part which will be otherwise difficult to ‘see’. Since the elastomer curing is related to the temperature, the curing stage in the elastomer part can be calculated and proper heating time can be assigned. Second, as a part of the simultaneous engineering process, it assists the task of mold designer in assigning and studying the feasibility of a certain part geometry before the mold steel is cut.

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In this program, each material was assigned to a layer (group), to which corresponding constant material properties (thermal conductivity $\lambda$, density $\rho$, and specific heat capacity $c_p$), were assigned. Further detail about CADMESH, and CADMOULD-3D and their modules can be seen in [10] and [2], respectively.

### 3.2 Process Cycle Description

**Figure 3.1** represents the illustration of the two-step T/R molding in general. During the beginning of the process, the molds are brought together and heated to the processing temperature taken from the mold cavities surface which can be measured in practice by using a surface pyrometer. The time until the processing temperature is reached, $t_{heating}$, will characterize the mold start up time in the production. Cycle time can be calculated using **Equation 3.1**.

$$t_{cycle} = t_{open1} + t_{handling} + t_{insert} + t_{close1} + t_{elastomer injection} + t_{cure}$$

(3.1)

where:

- $t_{cycle}$ = Total production cycle time [s]
- $t_{open1}$ = Mold opening time [s]
- $t_{handling}$ = Part removal time [s]
- $t_{insert}$ = Insert placement time [s]
- $t_{close1}$ = Mold closing time [s]
- $t_{elastomer injection}$ = Elastomer injection time [s]
- $t_{cure}$ = Elastomer curing time [s]
1. Mold Heating
2. Mold Opening
3. Insert Laying
4. Mold Closing
5. Elastomer Injecting
6. Elastomer Curing
7. Mold Opening
8. Part Handling

Figure 3.1: T/R Process Cycle
If the insert is produced at the same mold, $t_{\text{insert}}$ will consist of time to inject the thermoplastic - $t_{\text{thermoplastic injection}}$, to cool the thermoplastic - $t_{\text{cool}}$, to open the mold - $t_{\text{open2}}$, move the slider or rotate the mold - $t_{\text{mold}}$, and close the mold again - $t_{\text{close2}}$, until the insert is ready to be injected by elastomer, as indicated by Equation 3.2.

$$t_{\text{insert}} = t_{\text{thermoplastic injection}} + t_{\text{cool}} + t_{\text{open2}} + t_{\text{mold}} + t_{\text{close2}}$$ (3.2)

In the cycle scheme mentioned above, the cycle time will be mostly governed by the elastomer curing time. Generally, it can be said that the thermoplastic injection molding cycle typically runs in seconds, while the elastomer injection molding cycle runs in minutes).

3.3 Simulation Scheme for Geometry I

The part geometry, Geometry I, used in the first thermal study can be seen in Figure 3.2. It was the geometry used to study the adhesion strength between metal and rubber [47] and was also used to perform the T/R processing experiment in this report. To study the temperature distribution in the part and correspondingly in the mold, data corresponding to the thermoplastic and elastomer were assigned. Two materials, which were not used in the real experiment, were chosen to represent the thermoplastic and the elastomer (POM and EPDM, respectively).
Figure 3.2: T/R Part Geometry 1

Original Part Geometry
Scale 1:2

Units in mm
Table 3.1 lists the assigned thermal property values to each material group, while Table 3.2 lists the reaction kinetic data for the EPDM compound. It has to be realized that the value used in the real experiment will vary depending on the compounds' content, especially for the rubber.

By using a computer simulation, a parameter variation study could be done in a relatively short time. To see the effect of mold material, one simulation was done by varying the mold material from a high-alloyed steel mold, Case 1, \((\lambda_1 = 30 \text{ W/(m K)}, c_p = 0.477 \text{ kJ/(kg K)}, \rho = 7900 \text{ kg/m}^3)\) to a low-alloyed steel mold, Case 2, \((\lambda_2 = 50 \text{ W/(m K)}, c_p = 0.477 \text{ kJ/(kg K)}, \rho = 7900 \text{ kg/m}^3)\). Since generally both mold halves are made with low-alloyed steel, the rest of the simulation variation study was done using the low-alloyed steel mold. Case 2 was then used as a reference to see the effect brought by parameter variations.

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat Conductivity (\lambda) [W/(m K)]</th>
<th>Specific Heat Capacity (c_p) [kJ/(kg K)]</th>
<th>Density (\rho) [kg/m(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mold Steel</td>
<td>30 (50)</td>
<td>0.477</td>
<td>7900</td>
</tr>
<tr>
<td>Insulator Plates</td>
<td>0.21</td>
<td>0.75</td>
<td>1500</td>
</tr>
<tr>
<td>POM</td>
<td>0.275</td>
<td>1.46</td>
<td>1410</td>
</tr>
<tr>
<td>EPDM</td>
<td>0.26</td>
<td>1.789</td>
<td>1596</td>
</tr>
</tbody>
</table>

**Table 3.1: Thermal Properties Assigned to Each Material**

In order to see the effect of increasing insert temperature on enhancing the curing ratio of the elastomer, a simulation was done by using a 100 °C insert temperature,
so that by heating the insert, the mold does not need to bring the insert temperature to 100
°C from 25 °C first, whereby more heat can be supplied to the elastomer.

\[
\begin{array}{|c|c|}
\hline
E_a & [J/mol] \\
\hline
214073 \\
\hline
n & [-] \\
2.36672 \\
\hline
\log K_a & [1/min] \\
24.70126 \\
\hline
\log t_0 & [min] \\
-10.225141 \\
\hline
T_0 & [K] \\
10211.65 \\
\hline
\end{array}
\]

$E_a$ Activation energy  
$n$ Reaction order  
$K_a$ Temperature independent reaction speed constant  
$T_0$ Temperature constant  
$t_0$ Time constant

**Table 3.2: EPDM Reaction Kinetic Data**

Furthermore, different **elastomer melt temperatures** were also simulated to see their effect. Two melt temperatures, 100 °C and 120 °C, were used as the melt temperature entering the cavity. As with the **mold temperature**, 160 - 200 °C being the most common mold temperature range encountered in the rubber processing, 160 °C was constantly used.

These variation studies were done separately to see what effects they brought to the part, especially to the elastomer curing at the thermoplastic-elastomer interface, a very important factor to consider since without the necessary curing ratio to withstand the movement during part removal, good adhesion strength will be destroyed. **Table 3.3** summarizes the above-mentioned study.
<table>
<thead>
<tr>
<th>Simulation Case</th>
<th>$\lambda$ [W/(m K)]</th>
<th>$\theta_{POM}^0$ [°C]</th>
<th>$\theta_{EPOM}^0$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>25</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>100</td>
<td>120</td>
</tr>
</tbody>
</table>

Table 3.3: Parameter Variation Study

3.4 Initial and Boundary Conditions

Before the simulation cycle was started, the heating of both mold halves and the rest of the groups was done from room temperature (25 °C) and then by putting the thermoplastic insert in the mold.

As boundary conditions, Figure 3.3 is a representation of the simplified mold. As the mold was heated using heat plates, metal plates containing heat cartridges maintained at a constant temperature, the mold sides in touch with the heat plates were constrained by constant temperatures. The top and bottom of the molds were exposed to the open air.

For the simulations performed, the time for elastomer curing was taken so that the elastomer skin was not overcured for too long. Upon setting the temperature long enough (e.g. 1000 seconds), 450 seconds were taken as a common heating time for the elastomer curing process.
A : Heating Plates  
B : Insulator Plates  
C : Mold Cavity  
D : Mold Halves

1 : Convective Cooling  
\[ \alpha = 15 \, \text{W/m}^2\text{K}, T_u = 30 \, ^\circ\text{C} \]
2 : Constant Temperature  
160 \, ^\circ\text{C}

Figure 3.3: Boundary Conditions assigned to the Mold
3.5 Simulation Assumptions

Although thermal properties for materials depend on the pressure and temperature, the software only allows those with constant values. Therefore, they were assumed to be constant during the course of the process due to the purpose of the experiment. For known properties across the range of temperature and pressure, the constant, averaged values can be used for practical purposes.

For the initial temperature of the elastomer, the melt temperature as it entered the mold cavity was used since the program module only allowed for the uniform melt temperature. In reality, one needs to consider viscous dissipation of the melt as it enters the cavity, which can be calculated using Equation 3.3 to be roughly about a 5 °C/100 bar pressure drop for most elastomer compounds [73].

\[
\Delta \theta = \Delta p / (\rho c_p)
\]  

(3.3)

where: \(\Delta \theta\) = Temperature increase [°C]  
\(\Delta p\) = Pressure drop [bar]  
\(\rho\) = Density [kg/m³]  
\(c_p\) = Specific heat capacity [kJ/(kg K)]

In the study performed in this paper, the effect of imperfect contact between the mold plates was neglected. Putsch [63] showed that by taking into account the fact that mold halves were not perfectly in contact with one another, the temperature drop
encountered at the interface caused only a 5°C drop for 10 μm of average surface roughness.

During the opening, putting in the thermoplastic inserts, and closing the molds (see Figure 3.1), convective cooling occurs at the surfaces of the molds. Separate simulation by creating new mesh geometry was also done to investigate the temperature drop in the cavity. A uniform starting temperature of 160 °C was assigned to both mold halves, and temperatures at the surface were calculated for the estimated 15 - 30 seconds of convective cooling period. The calculated temperature was found to decrease only by 0.5 - 1.5 °C; a similar temperature drop value founded by Putsch [63]. Figure 3.4 shows this for both values λ, which also indicates that the assumption of eliminating the cooling effect during mold opening phase can be more justified when using a higher λ value. Apparently, air surrounding the mold practically insulated it, a physical property that is often used to insulate the hot runners in the mold. Because of this low temperature drop, all simulations were run without considering the convective cooling of the mold surface during the opening and closing phase.

A temperature increase of the melt due to the exothermic curing reaction, estimated by Equation 3.4 and by using elastomer compounds value of c_p between 1.65 kJ/(kg K) and 2.12 kJ/(kg K) and reaction enthalpies of 2.5 kJ/kg and 5.8 kJ/kg, given temperature increase less than 4 °C can be considered to be negligible [66 in 63].
Figure 3.4: Mold Opening Temperature Drop for $\lambda_1$ and $\lambda_2$
\[ \Delta \theta_R = \Delta h_R / c_p \]  

where:  
\( \Delta \theta_R \) = Exothermic temperature increase [\(^\circ\)C]  
\( \Delta h_R \) = Specific reaction enthalpy [kJ/kg]  
\( c_p \) = Specific heat capacity [kJ/(kg K)]  

3.6 Simulation Results

The difference in \( \lambda \) values can be seen in the mold heating time improvement. By changing the \( \lambda \) value from \( \lambda_1 = 30 \text{ W/(m K)} \) to \( \lambda_2 = 50 \text{ W/(m K)} \), allowing the heat to be transferred more quickly and more uniformly, the reduction of heating mold time from 600 to 400 seconds was apparent.

Figure 3.5 and Figure 3.6 illustrate the curing ratio and temperature developments in the elastomer part cross section at several time steps for Cases 1 and 2, respectively. The effect of having a thermoplastic insert can be seen to obstruct the heat flow from the mold to the elastomer material, causing the temperature increase delay for node C and in the end causing an uneven heating for the elastomer melt, which further led to an uneven curing of the elastomer part.

It can also be seen that changing the value of mold thermal conductivity \( \lambda \) improved the curing ratio of the elastomer at nodes C and D, where about 3\% increase in the final curing ratio was gained. Comparing both figures, it can also be seen that about 30-second saving per cycle can be achieved for Case 2 yet the curing percentage for Case 1 can still be maintained, yielding a more economic operation. Furthermore, not only has
Figure 3.5: Temperature and Curing Developments for Case 1
Figure 3.6: Temperature and Curing Developments for Case 2
the final curing percentage changed, but there is also a shift in the whole curing developments, resulting in a part with higher curing percentage inside.

Focusing the attention on the temperature developments on the thermoplastic cross section, node A, it was clear that only after a few seconds (about 6 seconds), the thermoplastic insert reaches near the mold temperature. This means that T/R processing needs a thermoplastic that can withstand the mold curing temperature for a relatively long time. Even by shortening the whole cycle time by speeding up the curing process (using Liquid Silicone Rubber - LSR, for example) will not help much in avoiding the heating of the thermoplastic. However, as has been mentioned in section 2.2, it will reduce the thermoplastic residence time in the hot mold and barrel.

Changing the elastomer melt temperature from 100 °C (Case 2, Figure 3.6) to 120 °C (Case 3, Figure 3.7) increased the curing ratio even more accompanied with the curing percentage shifting as mentioned above. In this case, a further cycle time reduction of about 30 seconds can also be accomplished.

Changing the insert temperature from 25 °C (Case 2) to 100 °C (Case 4, Figure 3.8) only brought a slight improvement in the curing ratio of the elastomer part and the overall curing percentage upshift was not very obvious. Naturally, when one increases the insert and the elastomer melt temperature simultaneously (Case 5, Figure 3.9), one obtains a more significant improvement in the curing ratio and the overall shifting in the curing percentage. However, it is apparent that elastomer melt temperature is an important process parameter in determining the process condition in the part making process.
Figure 3.7: Temperature and Curing Developments for Case 3
Figure 3.8: Temperature and Curing Developments for Case 4
Figure 3.9: Temperature and Curing Developments for Case 5
3.7 Thermal Insulation Study

In order to see the insulator effect on protecting the thermoplastic insert from high temperatures, a simulation was done by adding an insulator, with the material being the same with insulator plates, behind the thermoplastic part. The thickness was varied from 1.5, 2.5, and 3.5 mm. Upon running the simulation, it was concluded that due to difficulties in releasing heat, temperature buildup in the insulator was unavoidable. Since it also received a heat flow from the elastomer side, the insulator’s surface would reach mold temperature eventually (with 3.5 mm thickness, at the end of the second cycle) and render it useless to provide thermal insulation to the thermoplastic part.

Even if this method had been successful in prohibiting the heat from going through the thermoplastic part, one would have still had to consider the effect this would have brought to the elastomer curing, which then would have been depending thoroughly on the heat flow from one side only.

3.8 Additional Mold Geometry

To get a more thorough idea, as many as 5 more part geometries were investigated. The parts are illustrated in Figure 3.10 and listed in Table 3.4 along with their processing conditions. Although the relatively thick part thickness can allow heat flow from the third dimension, one can still expect a pretty good estimate due to the elastomer’s and thermoplastic’s insulating nature.
Figure 3.10: Additional Geometries Simulated
To simulate the real part production, the thermoplastic was set to be 25 °C, while the elastomer melt temperature was set at 120 °C, since (from Section 3.6) this was thought to be most favorable to the curing process of the parts. The determination of the initial and boundary conditions was the same as the previous simulation.

<table>
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<tr>
<th>Simulation</th>
<th>Geometry</th>
<th>$\lambda$ [W/(m K)]</th>
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<th>$\theta_{EPDM}^0$ [°C]</th>
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<tr>
<td>14</td>
<td>6</td>
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</table>

Table 3.4 Parameter Changes in Thermal Simulation

3.9 Results

Not surprising, from the simulation study previously done, one can directly conclude that these geometries have a drawback that the elastomer parts were “covered” by the thermoplastic preventing the direct contact to the mold surface.

For all geometry, most parts of the elastomer did not reach sufficient stability required for part ejection if the part is to be produced economically. The figures showed that when the surface curing ratio of the elastomer has already reached about 100%, most of the compound is still at about 8% curing ratio. In the case where heat does not
necessarily reach the elastomer due to the insulation by thermoplastic, the curing ratio even stays at 0% (Figure 3.11, Figure 3.12, Figure 3.13, and Figure 3.14).

With most of the part still about 8% cured, even an ejection at the thermoplastic part will risk part defect, not mentioning that the adhesion failure was due to the movements at the interface. For an economic operation, these types of geometry are then not recommended.

For another type of geometry, Case 10 (Figure 3.13) illustrates a good example of the importance of the heat supply for elastomer curing. Comparing Case 10 and Case 12 (Figure 3.14), one can see that for node B at both cases, the one at Case 10 reached a curing ratio of about 70%, while the other stayed at 0% for the same curing time. Covering this heat supply with a thermoplastic (Case 14, Figure 3.15), a considerable curing ratio decrease to about 10% was apparent for node B.

The heat supplied to the elastomer by the same steel insert (Case 10), however, was not enough to supply the heat necessary for node A. Looking at the temperature profile for node A, one can expect a relatively long time for it to reach a substantial amount of curing ratio.

3.10 Summary

Although the thermal simulation used is more suitable to simulate the thermal and curing developments in the cross section that is relatively thin to justify the 2-D assumption, it is nevertheless an important tool to help a designer in evaluating part...
Figure 3.12: Temperature and Curing Developments for Case 8
Figure 3.15: Temperature and Curing Developments for Case 14
designs with relatively thick sections such as those encountered in Geometry 2 - 6 since the thermoplastic and rubber possess poor thermal conductivity.

From the simulations performed above, it can be concluded that it is important to have heat transferred to most of the area of the elastomer. The thicker thermoplastic (1.5 mm for Case 2 and 5 mm for Case 8) delayed the heat transfer from the mold to the interface location, in addition to the fact that the thick rubber prohibits the heat from the other side of the mold to reach the interface location.

Since the exothermic reaction during the elastomer curing can be considered negligible in elastomer processing, heat supply from the outside becomes a necessity for curing, and it has to be supplied by the mold only. Furthermore, because the elastomer curing state depends directly upon the temperature developments in the part, the thicker elastomer shell will bring out the consequences of a longer cycle time. There will also be a greater risk of running across an overcured surface for the corresponding elastomer causing a reversion, which is typically encountered with natural rubber.

This means that optimally, the part for T/R processing has to have a shell-type geometry, a part geometry that can be found in many of the sealing elements where the heat can be supplied in two directions, or the part cover where most of the heat can only be supplied from one side of the part geometry. Care needs to be taken so that the heat can be supplied over a relatively large area so curing can be done economically. Some part geometry examples can be seen in Figure 3.16.

It was also observed that the curing percentage within the part can be changed more effectively and uniformly throughout the part by changing the elastomer melt
Processing Advantage:

Large area allowing effective heat transfer

Applications:
- Sealing Elements
- Damping Elements
- Surface Covering (e.g. against slippage)

Figure 3.16: Shell Type Geometries for T/R Parts
temperature rather than changing the insert temperature, as can be seen in Figure 3.8 and Figure 3.9, illustrating Case 4 (changing insert temperature from 25 °C to 100 °C while maintaining melt temperature at 100 °C) and Case 5 (changing melt temperature from 100 °C to 120 °C while maintaining insert temperature at 25 °C). It has to be noted that the elastomer melt temperature is not such that a premature curing occurs before the mold is completely filled.

From the simulations performed, it is clear that part form stability is important in the part forming process to produce the T/R product since the thermoplastic have to operate with the elastomer curing temperature. Judging from the relatively long time the typical elastomer has to cure, another possibility might come from the LSR cured in a shorter amount of curing time. The investigation on the adhesion mechanism between the thermoplastic and the LSR, however, needs to be done.
CHAPTER 4

RUBBER COMPOUND AND THERMOPLASTIC MATERIAL OVERVIEW

This chapter reviews the general description of the rubber compound, as well as its components and those of the thermoplastic material pertaining to the discussion before getting into a more detailed explanation of the materials used in the next chapter and taken mostly from [3, 9, 24 and 25].

4.1 Rubber Compound Overview

The properties of technical rubber compounds and their vulcanizates depend not only on the type of the rubber but also to a significant degree on other ingredients and their proportions. Generally, it can be said that the rubber compound consists of:

- **Inhibitor** preventing premature curing of the compound during storage and plastification.
- **Initiator** initiating the curing reaction of the compound in the form of sulfur or peroxides, among others. In the injection molding process, initiation is typically triggered by thermal activation from the hot mold.
• **Elastomer basis**, such as SBR, NBR, etc. serving as the matrix material for the compound. Blending of various elastomer basis is naturally possible.

• **Fillers**, such as carbon black, kaolin, zinc oxide, and talc.

• **Additives**, such as plasticizer and curing chemicals.

### 4.1.1 Chemical Effects of Compound

XNBR is a carboxylated NBR having a tendency to be easily cured due to the more functional carboxyl group (COOH-) reactants. In the processing, it is important to avoid humidity and also the more functional bonding (e.g. amine, metal oxide, etc.). The vulcanisate shows increasingly better swell resistance and abrasion durability with greater hardness in comparison to NBR.

When cured with peroxide, one obtains lower mechanical properties, especially lower resistance against tear propagation, unfavorable swell behavior and dynamic properties.

### 4.1.2 Fillers

In general, aside from economic reasons, fillers improve the product quality. They increase the strength, elasticity module, tear resistance, and decrease the elongation at rupture and the rebound elasticity.
Filler can be divided into an active, semi-active, and inactive one, all of which are determined by the filler size, geometrical form, and chemical arrangements. For each rubber basis, filler affects the vulcanisate properties differently. For the active filler especially, there exists a maximum or even a minimum effect due to its addition, while for the inactive one, a constant increase or decrease effect can be expected on the vulcanisate’s properties.

**Filler activity** is determined in various ways, among others are:

- **Size**

- **Specific surface specified through BET - Nitrogen adsorption method -** with 0 - 10, 10 - 60, 60 - 250 m²/g as inactive, semi-active, and active, respectively, or through DPG (Nitrogen Diphenylguanidin or Iod adsorption). However, the BET value shows the activity for each particle, even if they are in the agglomerate form. This value, hence, doesn’t have any value in the rubber processing since there is not a high enough shear rate produced to disperse the secondary structure in the operation. The values can only be used for quality control purposes.

- **Structure** (specified through oil adsorption: high adsorption means high structure) indicating the degree of interlinking or branching of the aggregates is formed from the fusion of primary carbon black particles. Extensive interlinking or branching is called “high structure“, while the less extensive interlinking or branching is called “low structure“ [5].

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Filler can further be divided into *carbon blacks* and *light fillers* (colloid silicic acid, calcium, aluminum silicate, clay, kaolin, silica, talc, chalk, or metal oxide (ZnO, metal carbonate)).

Carbon blacks can be divided into 3 categories: F (furnace blacks), C (channel blacks), and T (thermal blacks). Among the three, furnace blacks play the most important role.

Higher activity means higher reinforcing effect, while a high structure means high dispensability in the compound, high compound viscosity, lower waviness on the flat extrudate surface as well as in the vulcanisate with the higher module, high degree of hardness, and better abrasion resistance. Low structure carbon blacks means low thermal release at dynamic loading, high tensile strength, and crack propagation resistance, good bending tear resistance, and low tension value.

The most active light filler is pure silicic acid having a large specific surface but difficult to process due to the high viscosity and without the presence of filler activator. It is followed by the less active yet more processable calcium silicate giving a soft and elastic vulcanisate at a high content. Aluminum silicate is even a less active filler than calcium silicate and doesn’t reach all characteristics obtained by silicic acid or calcium silicate. All silicic acid and silicate filler are characterized through strong polarity at the surface.

With increasing content of silicic acid, it attracts not only water and accelerator, but also the rubber itself, causing an increase in viscosity. To avoid this further, the accelerator is added so the silicic acid attracts it instead, lessening the possibility of viscosity increase. Examples of such an accelerator are Vulkacit DPG or DOTG,
compounds containing hydroxyl groups (glycol, diethylene glycol, triethylene glycol), and compounds containing basic nitrogen such as triethanolamine, dibutylamine. These accelerators are also called filler activator since they promote better processing and lessen the accelerator's adsorption. Since they also have a function as a vulcanizing agent activator, these functions are hard to separate.

As with other fillers, the structure of the light filler can be divided into primary, secondary, and tertiary parts. For precipitated silicic acid, the primary part has a diameter less than 15 - 20 mm. A high surface energy causes the primary parts to build agglomerates, also called the secondary parts, and the secondary parts to build a tertiary structure in network or chain arrangements. These agglomerates need a high shear for better dispersion (homogenity) in the compound, which can be eased by adding plastificizer.

Inactive light filler serves mainly to make the product less expensive. Examples are chalk (ground, washed, precipitated) affecting the color, processability, injectionability and vulcanization. The difference between the above-mentioned chalk is not so distinct. Kaolin, silica, zinc oxide, and aluminum oxidhydrat are the examples of inactive light fillers.

4.1.3 Plasticizer

The purposes of the plasticizer addition into the compound are to cheapen the product, improve the flow (energy saving during processing), improve the dispersion in
the compound, the processing, and the compound tack, influence the physical property of
the vulcanisate (especially the extensibility and the elasticity at low temperature), lower
the glass temperature, increase the electrical conductivity, etc.

Interaction between rubber and plastisizer can be distinguished between the
primary plasticizer (to loosen the rubber thereby promoting the micro- and macro-
brownian movement of the chain, thereby affecting the viscosity of the melt) and the
secondary plasticizer (to lessen the distance between the rubber chain less or even not at
all).

Plasticizer can be divided into mineral oil (to cheapen the product), natural (fatty
acid, wool grease, vegetable oil, lime, gum, etc. to improve the processing, compound
tack and the dispersion of the filler), and the synthetic one (mostly being PVC plasticizer
too, improving low temperature flexibility and elasticity of the vulcanisate tack).

In regards to the peroxide curing agent, plasticizer from aromatic and ether
plasticizer can destroy the curing and should not be combined. Vulkanol is an example of
an ether plasticizer.

4.1.4 Vulcanization and Vulcanization Chemicals

Vulcanization is a process of building the curing bridges by means of sulfur,
peroxide, or a special curing agent. It changes the uncured state rubber (macrobrownian
movement, plastic - mechanically and thermodynamically irreversible flow) to an elastic
cured rubber, whose properties will depend on the rubber curing density itself (good vulcanisate properties need a high curing density).

Compared with the vulcanization process using sulfur, the peroxide-cured one has lower mechanical properties, a lower elasticity, unfavorable dynamic properties, a slightly lower swell resistance, more heat resistance (it causes heat stability achieved by NBR), and a good heat pressure deformation.

The degradation temperature of the peroxide (stability) is an essential criterion for the pre-vulcanisation temperature and speed. The curing temperature also affects the amount of radicals and hence the crosslinking density.

The peroxide curing agent can be divided into hydrogen peroxide (H-O-O-H), hydroperoxide (R-O-O-H) and peroxide (R-O-O-R). Hydroperoxide does not usually lead to curing, but it can destroy the curing effect of other peroxides and also the polymer chain, so it plays a small role in the rubber processing.

Organic peroxide with a tertiary carbon atom is the most used since it is more stable in comparison with primary or secondary carbon atoms (for storing and handling purposes).

Peroxide degradation can occur through heat, light, energy radiation, and reaction with the other substances. For the peroxidically cured rubber, homolytical split is a requirement. One can divide the peroxide further to the symmetric peroxide, where two radicals with same strength and effect can be released during the curing reaction, and the mixed peroxide consisting of two radicals with different reactivities.
Activation through metal oxide and stearic acid is not possible. The curing density depend on the type and amount of peroxide (radicals available) and reactivity of the rubber. The coactivator, depending on the type of the rubber, increases essentially the free radicals, influencing the vulcanisate.

4.2 Thermoplastic Material

As a brief description of the thermoplastic material used and its processing guidelines, this section gives the description necessary which is translated from the information given by the manufacturer [9].

4.2.1 Injection Molding of VESTAMID Parts

General

The modified VESTAMID parts for the T/R process can principally be processed with the typical screw injection molding machine. General processing hints for drying, machine setup, and mold layout can be referred in the Hüls brochure “Formmassen VESTAMID” (VESTAMID Parts) [9].

Injection Molding

The processing of VESTAMID parts should proceed within the barrel temperature zones explained as follow. The upper limit temperature (300 °C) should be set only in a
cycle running quickly and automatically. This is only possible at the two-step process. In the second graph, the barrel temperature for the one-step process is presented. At this processing temperature no material defect is encountered during the four-minute elastomer heating time. In this case, the measuring stroke should not less or equal than 50% of the maximum plastification stroke.

Entry problems frequently result from excessive temperatures at the entry zone. It should be tempered from 40 °C to 80 °C. If the problem exists, it can be eliminated by uniformly mixing the granulate with about 0.05% calcium stearat. In the two-step process, the mold temperature should be at 80 °C. In the one-step process, the mold temperature depends on the movement of the inserts inside the mold (see process description) and should be from 60°C to 120°C. When the rubber curing takes place in the same mold area, the mold temperature should be kept as cold as possible during injection. A well laid out ejection system should be noted. Nevertheless, should an ejection problem appear, in certain cases it is possible to add an inner releasing agent.

The plastification follows advantageously at specific back pressure of 50 to 100 bar. In order to avoid the long cycle time and the unnecessary long residual time of the melt in the screw front, especially in the one-step process, the plastification should follow as late as possible. The injection speed should be set up, that an average flow front speed is reached. The holding pressure value should be set up so that no over injection occurs in the part where a proper change from the injection speed to the holding pressure is required.
More processing information at the point of working interruption, ejection speed, and processing shrinkage can be referred in the above-mentioned Hüls brochure.

4.2.2 T/R Combination between VESTAMID and X-NBR

General

The VESTAMID rubber combination adhesion using X-NBR rubber compounds (NBR containing carboxyl groups), is based on an interface reaction of the functional groups from both combination partners.

What is to be considered during the production of the combination?

On the rubber side

- Peroxide curing systems must be used.
- With a very soft rubber compound (Shore A<45), an increased oil content can interfere the adhesion.
- High active filler or hydrophylic agents (e.g. polyethyleneglycole, glue, etc.) can damage the adhesion of the peroxide-cured systems.
- The rubber curing temperature should not go above 180°C.
- During the part production, it depends upon "intimate contact" during the rubber and the VESTAMID phase. A minimum pressure depending on the part geometry must be maintained. Under normal conditions, a contact pressure of about 50 bar is
sufficient.

**On the thermoplastic side**

- During the production of the VESTAMID part, the parameters should be chosen so that a smooth surface is obtained; mold temperatures up to 100°C, injection speed profile, etc. can be used. Lower part temperatures can lead to better adhesion results.

- In the two-step process, it has to be noted that the VESTAMID part surface is dry and free from grease and dirt. To clean the dirty surface, alcohol or soap solution can be used, which should be dried or cleaned before the combination production. A necessary storage should then proceed in a cool, dark, and dry place.

- During the production of the VESTAMID part, a releasing agent such as silicon or Teflon spray must never be used.

- The production of the VESTAMID insert part (prototypes) through surface machining should proceed so that no oil or grease containing coolant (drilling milk) is used. Surface overheating through tension or machining work must also be avoided.

- Color batch, such as from the PE base, as well as the processing helper from wax base, can lead to adhesion weakness.

**On the combination part production side**

- During the production of the combination part, it has to be noted that during the removal of the part in hot conditions there are no movements in transfers or longitude in the part interface.
During the cooling phase, the polymer and cured rubber should also not be split from each other.

What needs to be noted during the combination part usage?

- With tensional force, certain media can not only lead to tension cracks on the VESTAMID part, but also to the weakening and elimination of the adhesion. Under compression, however, the effect is frequently fully different: no combination damage and no stress cracking in the VESTAMID part.
CHAPTER 5

EXPERIMENT

On a collaboration with Franz Joseph Wolfgang & Co. (WoCo), Bad Soden-Salmünster - Germany, a two-step T/R processing experiment divided into two stages (preliminary and intermediate study) was done to investigate the effect of compound material on the adhesion strength between thermoplastic and rubber.

5.1 Material Used for the Experiments

5.1.1 Elastomer Compounds

In the first stage, the preliminary study, ten elastomer compounds were used in combination with one type of thermoplastic material (PA612). The basis elastomer, Compound 1, was a carboxylated NBR and the compound recipe was obtained from an example for X-NBR recipe for T/R combination [9], omitting the titan dioxide (TiO₂) and Opassin Blau 6900 while adding Carbon Black 1 (proprietary) (sample recipe can be seen in the Appendix).
The compounds’ serial numbers were 50 DL 173/#, where # was the number from 1 to 10 for the ten compounds produced. To determine each component’s effect on the adhesion strength, the experiments were run using the same processing conditions.

From the results of the preliminary study, Compound 8 had the highest adhesion strength, so the mold temperature was changed once to see its effect on the adhesion strength (Compound 8**). Also studied was compound reproducibility for Compound 8 (through Compound 8*) and for Compound 1 (through Compound 1*), and four new compounds, Compound 11 - 14.

Table 5.1 shows the compositions of each compound, and the components for Compound 1 were explained further in the following section. Due to the proprietary nature of the recipes, the amount and trademark of each component were omitted, prohibiting a more detailed review on them.

As the compound change direction was not given, section 5.1.1.2 describes the direction determination based on the viscosities change observation by using some general properties known from the literature about the filler and its effect on the compound viscosity.
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<tr>
<td>Processing Helper 1</td>
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<td>Processing Helper 3</td>
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<td>Processing Helper 4</td>
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</tbody>
</table>

X: Used  —: Not Used  D: Content Changed

Table 5.1: Rubber Compounds used in the Study
5.1.1.1 Overview of the Compounds’ Components

Rubber 1 - XNBR from Bayer

NBR rubber containing carboxyl groups from Bayer AG, Leverkusen - Germany with applications in industrial drive belts, footwear, hose, O-rings, packing, seals, pump linings, roll covers, oil well specialties, etc.

Most compounds based on XNBR exhibit excellent mold flow by virtue of the thermoplastic nature of it. At comparable hardness levels, XNBR compounds have lower viscosities than the regular NBR compounds. Consequently it is possible to transfer or injection mold the products in the 80 - 90 hardness range with much more ease than with the NBR compounds.

Explained through polarisation theory (see section 2.3.3), the addition of carboxyl groups to or by increasing the hydroxyl, OH-, amount in the polymer has been known to increase the polarity of the polymer, typically followed by better adhesion in the adhesion strength (through dipole, induction, or hydrogen force) although it was also plausible that OH- and COOH- groups forms chemical reaction, such as in the case of glass/epoxy and aluminum/polyvinylformal combination [72].

XNBR has a tendency to be easily cured due to more functional carboxyl group reactants. In the processing, it is important to avoid humidity and also the more functional bondings (e.g. amine, metal oxide, etc.). The vulcanisate shows increasingly better swell resistance and abrasion durability with higher hardness in comparison to NBR.
When cured by peroxide, however, one obtains lower mechanical properties, especially lower resistance against tear propagation, and unfavorable swell behavior and dynamic properties.

Light Filler 1 - Vulkasil C

A light-colored, semi-reinforcing (semi-active) precipitated silica with low calcium silicate content, about 30 - 40 nm in size, having DBP (dibutyl phthalate) absorption values of about 155 ml/100 g filler from Bayer AG, Leverkusen - Germany.

It is also characterized by high surface polarity (activity), coming predominantly from the hydroxyl (silanol) groups attached to the silicon atoms, measured in terms of the BET value of 60 m²/g by determining the adsorption of nitrogen gas. As mentioned in the previous section, this value, however, serves mainly as one of the production quality control values, not about the activity of the filler itself.

The adsorptive filler surface is able to adsorb not only moisture and other compounds containing hydroxyl groups, but also other basic substances.

Light Filler 2 - Polestar 200 R

This is calcined china clay having a BET value of 8.5 m²/g and 55% of SiO₂ and 41% of Al₂O₃ from the ECC International company, St. Austell, Cornwall - Great Britain [7].
Plasticizer - Stearic Acid and Vulkanol 88 (possibly)

- **Stearic Acid**

  Although it has an activator function needed as the completion for the usage of accelerator by increasing the vulcanization considerably by only adding small amount, in this case, it has a function as a lubricant, since it doesn’t do its job effectively when combined with peroxide vulcanizing agents.

  As lubricant it also acts as the mill release agent, preventing the sticking of the compound. It also plays a role as a retarder to avoid scorch (early curing), albeit without a high level of effectiveness, which is similar to other retarders when combined with XNBR.

- **Vulkanol 88 [3]**

  Consists of esters with thioether groups (dibutyl methylene bis-thioglycolate) and known as a synthetic plasticizer with low viscosity used almost exclusively in the rubber industry such as for NBR or NBR/PVC blends and also for CR, EVM and other rubbers.

  Generally, it works as a processing aid by being able to reduce the compound’s viscosity (plasticizing effect), enhancing the green tack of the compounds (tackifying effect), extenders (reducing compound cost), and active ingredients capable of imparting special properties to vulcanizates.

  The use of Vulkanol 88 for NBR has a function to give a swelling action, increasing the molecular distance thereby increasing the elasticity. It also has a lubricating effect, aiding processing (possibly by exerting a dispersing effect on other ingredients of the compound, facilitating the incorporation of fillers).
The vulcanization behaviour may be affected as Vulkanol 88 shortens both the scorch time and the cure time.

On the vulcanizates, the effect of the Vulkanol 88 addition can be seen in the loss of Shore hardness normally accompanied by a loss of strength, rebound resilience improvement, and low temperature flexibility.

**Aktivator 1 - BDMA**

Buthandiol 1,4 dimethylacrylate from Degussa, Hanau - Germany [4] is an activator that has a function to accelerate the work of the peroxide by acting as radical donors.

**Peroxid 1 - Perkadox BC 40**

Peroxide (dicumyl peroxide) from Akzo-Chemie, Netherlands, is a monofunctional peroxide used for the crosslinking of natural and synthetic rubbers [8].

According to Hofmann [25], dicumyl peroxide is an example of a peroxide without a carboxylic acid group, containing aromatics. Generally, it is also stated that the peroxides without the carboxylic group also show:

- marked sensitivity to acids, aliphatic substitution being preferable to aromatic,
- higher decomposition temperatures, and
- less sensitivity to oxygen than peroxides with a carboxylic acid group.
At this point, the fact that the combination of Vulkanol with the peroxide (mentioned to destroy the curing in section 5.1.3) worked was probably caused by the different rubber systems used.

**Carbon Black 1 - proprietary**

Carbon black is normally used in high performance vulcanizates [38], typically giving them a high degree of toughness, which often makes trimming difficult and expensive (can be eliminated with almost flash-free injection molding process). Bonding of rubber to metal usually involves highly reinforced compounds containing carbon black, identified by particle size and ‘structure’ (agglomeration behavior).

### 5.1.1.2 Change Direction Determination based on Observations of Compounds’ Viscosities

In analyzing the direction change of the compounds, some assumptions were made:

- The filler/additive amount (for one type or one category) was kept constant when it was replaced, otherwise mentioned, e.g. for Compound 2, the amount of Carbon Black 1 added is equal to the amount of Carbon Black 1 and Light Filler 1 & 2 combined (1 category), or for Compound 7, the amount of Peroxide 2 is equal to the amount of Peroxide 1 substituted (1 type).
- At the end of the vulcanization reaction, the crosslinking density for each
compound is similar, except when noted (for example a possible crosslinking density increase due to the effect of activator).

The existence of the carbon black alone in the compound results in a viscosity increase which can be seen for Compounds 2, 9, and 10 in Figure 5.1.

Assuming that the filler amount, both the light one and the carbon black one, is constant in the compound (see assumption above), eliminating the light filler caused the higher viscosity for Compound 2 to imply the increase of the carbon black content from the original amount in Compound 1. By using this assumption also and looking at Compounds 9 and 10, one can see that the injection time was higher, indicating higher viscosity typically caused by using carbon black with higher specific surface area (decreasing particle size) [5] for the same content of carbon black.

From the observation above, it could be then established that the order of the carbon black activity, measured by its size, specific surface, and structure (see section 4.1.2), can be represented in Equation 5.1:

\[ \text{Activity: Carbon Black 2 > Carbon Black 3 > Carbon Black 1} \] (5.1)

Changing the content of the light filler alone (Compound 3) decreased the viscosity of the compound slightly. This change, probably by decreasing the content, can be caused by the reinforcing nature of the filler which tends to attract the rubber molecules. A lower amount of light filler means fewer molecules are attracted, resulting in lower viscosity.
Figure 5.1: Effect of Component on the Elastomer Melt Viscosities
Comparing Compounds 1 (Activator 1) and 4 (Activator 2), one can observe that Compound 4’s viscosity is lower than that of Compound 1.

Rubber types seemed to affect the viscosity in a more subtle way compared with the carbon black. The viscosity’s decrease in the order of Compound 4 (Rubber 1), 5 (Rubber 2), and 6 (Rubber 3), can not be explained in more detail other than the fact that different types of rubber interact differently with the fillers added.

The peroxide’s effect on the compound’s viscosity can be seen by comparing Compound 1 (Peroxide 1) and Compound 7 (Peroxide 2). This lower viscosity, however, can not be explained at this moment, since ideally, peroxide doesn’t exert its influence before the crosslinking process begins. It is added on the relatively small amount, and the viscosity should have remained constant for Compound 7.

Adding processing helper (Processing Helper 1 & 2) effect can be directly seen in Compound 8, where the injection time was reduced dramatically.

Comparing Compound 8 and Compound 11, it can be seen that the content of the light filler was increased because the compound’s viscosity was observed to increase. The incorporation of the Processing Helper 1 & 2 could not counter the viscosity increase due to the addition of light filler.

If we look at Compounds 1, 3, and 11, it can be established that the amounts of light filler added to the compounds were in the order depicted by Equation 5.2.

**Light filler amount:** Compound 11 > Compound 3 > Compound 1 \hspace{1cm} (5.2)
The plasticizer amount was increased in Compound 12. This could be concluded because compared to Compound 8, the viscosity of Compound 12 is slightly lower.

In analyzing Compound 13, two comparisons can be made. By comparing it with Compound 11, one can draw a conclusion that the amount of the plasticizer was increased a lot in Compound 13, assuming the increase of light filler is the same with Compound 11.

Comparing Compound 13 with Compound 12, assuming the plasticizer amount of Compound 13 was the same as Compound 12, one can draw the conclusion that the amount of light filler was decreased, resulting in lower viscosity for Compound 13. Among these two possibilities, one can look into the adhesion strengths obtained and compare them analogically to see which one is more feasible. The trends observed, however, were similar, so the change of direction of the light filler for Compound 13 could not be established. Increasing the amount of light filler was observed to give a similar (Compound 8 vs Compound 11) or a higher (Compound 8* vs Compound 11) adhesion strength. Increasing the plasticizer content was observed to give a lower (Compound 8 or 8* vs Compound 12) adhesion strength.

If one takes the position of comparing Compounds 11 and 13, as mentioned above, one will conclude that the plasticizer amount was increased, resulting in a lower adhesion strength, a trend that can be observed in the figure. However, by comparing Compounds 12 and 13, the trend observed by decreasing the light filler content in the compound can also be observed in the figure.
Comparing Compound 1, Compound 8, and Compound 14, the incorporation of Processing Helper 3 & 4 in Compound 14 was proven to be more effective in lowering the compound’s viscosity compared with Processing Helper 1 & 2 in Compound 8.

Table 5.2 summarizes the change possibility.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Change made</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 1</td>
<td>Original Compound</td>
</tr>
<tr>
<td>Compound 2</td>
<td>Light Filler 1 &amp; 2: omitted, Carbon black 1: increased</td>
</tr>
<tr>
<td>Compound 3</td>
<td>Light Filler 1 &amp; 2: decreased</td>
</tr>
<tr>
<td>Compound 4</td>
<td>Activator 1: omitted, Activator 2: added</td>
</tr>
<tr>
<td>Compound 5</td>
<td>Rubber 1: omitted, Rubber 2: added</td>
</tr>
<tr>
<td>Compound 6</td>
<td>Rubber 1: omitted, Rubber 3: added</td>
</tr>
<tr>
<td>Compound 7</td>
<td>Peroxide 1: omitted, Peroxide 2: added</td>
</tr>
<tr>
<td>Compound 8</td>
<td>Processing Helper 1 &amp; 2: added</td>
</tr>
<tr>
<td>Compound 9</td>
<td>Light Filler 1 &amp; 2: omitted, Carbon Black 2: added</td>
</tr>
<tr>
<td>Compound 10</td>
<td>Light Filler 1 &amp; 2: omitted, Carbon Black 3: added</td>
</tr>
<tr>
<td>Compound 11</td>
<td>Light Filler 1 &amp; 2: increased, Processing Helper 1 &amp; 2: added</td>
</tr>
<tr>
<td>Compound 12</td>
<td>Plasticizer: increased, Processing Helper 1 &amp; 2: added</td>
</tr>
<tr>
<td>Compound 13</td>
<td>Light Filler 1 &amp; 2: undetermined, Plasticizer: increased</td>
</tr>
<tr>
<td></td>
<td>Processing Helper 1 &amp; 2: added</td>
</tr>
<tr>
<td>Compound 14</td>
<td>Processing Helper 3 &amp; 4: added</td>
</tr>
</tbody>
</table>

Table 5.2: Possibility of the Changes made in the Compounds

As mentioned in section 1.2, the batch to batch variations usually occur in the elastomer processing industry. This can be observed also in Figure 6.1. At the least, the repeatability of the viscosity for Compound 1 was not so good, while it is repeatable for Compound 8.
It has to be noted that the decrease in Compound 8** was caused by a mold temperature increase.

5.1.2 Thermoplastic used in the Experiment

The thermoplastic material used was VESTAMID X7099, a development product from Hüls AG, Marl - Germany. It is a heat-stabilized, 20% wt glass fiber-reinforced, semi-crystalline polyamide 612 material that has been designated for the T/R processing.

The inserts for adhesion tests were injection molded in one of the CAMPUS molds designating to produce standardized test parts, consisting of two fan-gated plates each 80 mm x 80 mm x 2 mm. On an 80-ton Boy horizontal hydraulic injection molding machine (2065 bar maximum injection pressure), the mold temperatures were set to be 70 °C, and the polymer melt temperature was set to be 280 °C. The plates were then cut down from their original sizes to 60 mm x 25 mm x 2 mm using a circular blade saw cooled with water to fit the groove in the mold.

To test the effect of heating on the inserts, 0.0 mm x 25.1 mm x 1.95 mm inserts were put in the oven at 100 °C and were measured to be 60.1 mm x 25.15 mm x 2.05 mm, which can be considered negligible.

The cut inserts were then deburred and degreased using alcohol (99% ethanol) since aromatic hydrocarbon or chlorohydric acid was mentioned to be unsuitable [7], allowed to dry before the experiment, and covered to protect them from dusts.
The earlier literature on the T/R processing experiment between PA612 and rubber can be found in the available patents [33] and [31]. Although they contain the descriptions of the T/R processing using polyamide materials and rubber, due to the nature of the literature, the analysis of the adhesion process and the mechanism were not adequately discussed.

5.2 Experiment Setup

The mold used for the experiment is the mold designed by Klaas [47] originally used to investigate the adhesion between metal and rubber. It was preheated to processing temperature before the thermoplastic inserts were put in the available grooves. The elastomer melt injection then proceeded on an Arburg Allrounder 750-210 320D, a hydraulic, vertical rubber injection molding machine.

The elastomer stock barrel and the mold temperatures were set to be 70°C and 180°C (measured to be 160°C), respectively, and the heating time was set to be 180 seconds. The injection speed, showed in the terms of injection time, was controlled by utilizing maximum injection pressure and varied from compound to compound due to different viscosities imposed on the machine by each compound, which is also showed in Table 5.1

The parts were then cut for testing and further analysis.
5.3 Sample Preparation and Testing

To quantify the adhesion strength of the thermoplastic/elastomer combination, a roll peel test was done. This test is similar to the DIN (Deutsche Industrie Normen - German Industry Standards) 53 289 and DIN 53 350, and the reading of the chart was done similar to DIN 53 539 Process B.

The tests were performed on the Zwick tensile test machine, with a testing temperature of 24°C. The peeling speed was set to be 100 mm/min, and with the part geometry used, a roller diameter of 15 mm and the distance between them of 20 mm, the pull angles formed a range from 81.1° (rubber compressed to 3 mm) to 75.5° (rubber uncompressed). Since the polymer is viscoelastic, it can be expected that the change in the pull speed will change the adhesion strength value and might lead to a different type of failure.

From the tests, Force vs Time diagrams were obtained and the force needed to peel the rubber from the thermoplastic can be calculated. Peel force, defined as the force divided by 25 mm (the width of the thermoplastic plate), can then also be calculated.

To read the peeling test result chart, one needs to eliminate the increasing slope at the beginning of the test. As illustrated in Figure 5.2. The evaluation zone was then limited to the point where the starting slope ends, and the end of the test when the force reaches zero. The test evaluation area was taken within 10% from the ignored test beginning and ending. If the end of the graph has a slow increase in force resulting from the end peeling and a sudden jump at the end of the graph caused by the sudden release of the
Figure 5.2: Roll Peeling Test Evaluation and Experimental Setup
sample from the roller, this area was ignored also. When peaks were recorded, the force values were taken and the average value was reported as the adhesion strength for that particular sample. From each compound combination, only three samples were tested due to the limited compound amounts.

From the test part length of 60 mm, the elastomer must be manually peeled off until about 30 mm so that the elastomer can be clamped down properly, leaving only about 30 mm of peeling distance. Care was also taken so that the rubber attached to the sides of the thermoplastic didn’t influence the result by cutting them first.

5.4 Surface Analysis

To identify the surface of thermoplastic inserts, two methods were used. First, morphological analysis using a light microscope was done and the photographs were taken, and second, to confirm the light microscope analysis, the surface of the polyamide was analyzed for rubber compound elements by using an ESCA (Electron Spectroscope for Chemical Analysis, illustrated in Figure 5.3), M-Probe Surface Spectrometer manufactured by Surface Science Instruments.

The ESCA analysis is based on examination of the reflected photoelectrons energy intensity, measured as a function of kinetic energy upon contact with the surface, which gives the information enabling the elemental identification and chemical bonding as well [74]. More detailed information about ESCA can be seen in [6].

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Figure 5.3: ESCA Schematic Diagram
To prepare the sample, a section from the PA plate with the size of 5 mm x 5 mm was cut and inspected in the vacuum, covering an area of 200 x 750 µm². With the beaming angle of 55°, the depth covered was about 100 Å (10 nm), which depends also on the density of the sample, among others. The power of the X-ray tube was set to be 100 Watts.

The analysis in the cross section direction to detect the width of the interface was not done due to the possible technical difficulties. These include the presence of rubber if the sample is to be metallographically polished, and the presence of glass fibers in the PA when the sample is to be cut in cold temperature [41]. This test could have been used as one of the ways to identify if the interdiffusion process took place, a technique that Voyutskii [70] used to describe the interdiffusion mechanism between PMMA and PVC.

5.5 Interfacial Surface Tension Measurements

The importance of wetting has been mentioned to be essential in having optimal adhesion strength. The first criteria that can be used to define whether the rubber will adhere to the thermoplastic is by evaluating whether the rubber melt will wet the thermoplastic adherend by comparing the rubber melt's surface tension to the thermoplastic surface tension. However, since the rubber melt already has a tackifying effect to it, it was assumed that it adhered to the thermoplastic to some degree. Moreover, due to the relatively high viscosity of rubber melt and its curing characteristics, it is
possible that it is very difficult to measure its surface tension. Brinkmann [12] encountered this difficulty when a PA melt failed to form a drop necessary for the measurement.

As mentioned in section 2.4.4.2, there is a relation between interfacial surface tension and the joint strength. In order to see if this relationship also exists for the T/R combination, surface tension measurements were done on the thermoplastic and the rubber failure surface.

Surface tension was tested by using a microscope and measuring the tangent of the liquid dropped on the solid surface (sessile drop method) directly using a telescope fitted with a goniometer eyepiece. The liquid, measured using a micrometer to ensure a consistent liquid drop size, was dropped using a syringe with a bent extension. For the relatively viscous glycerol, the small extension orifice made it difficult to use the micrometer as the measurement method, so it was not used.

Two liquids (distilled water and 99+% glycerol) with both components of their surface tension known, the polar and the dispersion part, allowed the calculation of both components of the surface energy of a solid. For the distilled water and the glycerol used, both components are $\gamma_{lv}^d = 18.7$ mN/m, $\gamma_{lv}^p = 53.6$ mN/m, and $\gamma_{lv}^d = 28.3$ mN/m, $\gamma_{lv}^p = 36.9$ mN/m, respectively. Wu [79] presented a derivation of the calculation needed and it can be seen in the Appendix.

Although it has been mentioned [15] that the contact angle formed exhibited hysteresis, the advancing being greater than the receding one, the equipment used didn’t enable the evaluation of receding contact angles. From each material combination, three
contact angle measurements, also measured from the left and the right, were done on each of the two samples used.
CHAPTER 6

ANALYSIS, RESULTS, AND DISCUSSIONS

6.1 Peeling Test Investigation

Manually peeling of the elastomer from the thermoplastic parts revealed that in the course of an adhesion failure, the surface of the thermoplastic appeared to be relatively clean from rubber components although a very small amount of rubber particles can be traced. Moreover, during the roll peeling test it was observed that although the part failed cohesively when it was peeled manually, this type of failure changed to an adhesive one. From the roll peeling graph, this was indicated also by a decreasing peeling force.

From the relatively clean surface it can be directly hypothesized that there is no chemical reaction between the rubber and the thermoplastic for most of the part surface since the chemical and interdiffusion mechanism would be likely to give an adhesive failure at the rubber. Table 6.1 summarizes the inspections of the failure occurrences for the parts for both preliminary and intermediate study, where the failure type was given to the area within the testing length.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Peel Force [N/mm]</th>
<th>Type of Failure</th>
<th>Microscopic Visualisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.6</td>
<td>Adhesive Failure¹, Incomplete peeling² Combination failure at the end³</td>
<td>Clean PA surface</td>
</tr>
<tr>
<td>1*</td>
<td>6.5</td>
<td>Adhesive failure, Incomplete peeling</td>
<td>Clean PA surface</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>Adhesive failure, Complete peeling</td>
<td>Clean PA surface</td>
</tr>
<tr>
<td>3</td>
<td>8.3</td>
<td>Adhesive failure, Incomplete peeling Combination failure at the end</td>
<td>Clean PA surface</td>
</tr>
<tr>
<td>4</td>
<td>9.2</td>
<td>Combination failure, Incomplete peeling Combination failure at the end</td>
<td>Elastomer traces</td>
</tr>
<tr>
<td>5</td>
<td>6.5</td>
<td>Adhesive failure, Complete peeling</td>
<td>Clean PA surface</td>
</tr>
<tr>
<td>6</td>
<td>5.7</td>
<td>Adhesive failure, Incomplete peeling Combination failure at the end</td>
<td>Elastomer traces</td>
</tr>
<tr>
<td>7</td>
<td>6.4</td>
<td>Adhesive failure, Complete peeling</td>
<td>Elastomer traces</td>
</tr>
<tr>
<td>8</td>
<td>9.2</td>
<td>Adhesive failure, Incomplete peeling</td>
<td>Elastomer traces</td>
</tr>
<tr>
<td>8*</td>
<td>7.4</td>
<td>Adhesive failure, Incomplete peeling</td>
<td>Clean PA surface</td>
</tr>
<tr>
<td>8**</td>
<td>7.9</td>
<td>Combination failure, Incomplete peeling</td>
<td>Clean PA surface</td>
</tr>
<tr>
<td>9</td>
<td>1.4</td>
<td>Adhesive failure, Completely peeled</td>
<td>Clean PA surface</td>
</tr>
<tr>
<td>10</td>
<td>1.7</td>
<td>Adhesive failure, Completely peeled</td>
<td>Clean PA surface</td>
</tr>
<tr>
<td>11</td>
<td>9.2</td>
<td>Mixture failure, Incomplete peeling</td>
<td>Elastomer traces</td>
</tr>
<tr>
<td>12</td>
<td>6.4</td>
<td>Adhesive failure, Incomplete peeling</td>
<td>Elastomer traces</td>
</tr>
<tr>
<td>13</td>
<td>5.5</td>
<td>Adhesive failure, Incomplete peeling</td>
<td>Clean PA surface</td>
</tr>
<tr>
<td>14</td>
<td>6.2</td>
<td>Adhesive failure, Incomplete peeling</td>
<td>Clean PA surface</td>
</tr>
</tbody>
</table>

Table 6.1: Failure Inspections for Preliminary Study Compounds

¹ Adhesive failure: Failure at interface, visually clean. Mixture failure: at the same part, some portion fails adhesively, some portion cohesively at the rubber side.
² Incomplete peeling denotes that the rubber still sticks to the end of the part with the width of about 1-2 mm.
³ In the occurrence of cohesive failure, incomplete peeling is accompanied by combination failure, rubber traces appeared on the thermoplastic surface only near the location of where the rubber still adheres to the thermoplastic.
Using the same processing conditions, and assuming that the contact area and surface roughness were similar for all the thermoplastic inserts, it can be induced that the differences in peel test results come from the component in the compounds.

It was also noted that the evaluation of the graph was difficult due to the relatively short testing distance (in certain cases one can read one peak only (presumably due to the slip stick effect)) to characterize the graph. The final result, along with the corresponding viscosities, are illustrated in Figure 6.1. The peeling test result values obtained are within the ranges that Kriesten [52] found (see Section 2.2.5.1).

During the peeling test, one can readily see the effect of the peeling rate and peeling angle on the failure mechanism. At the end of peeling, especially with the rubber that shows pretty strong adhesion to the thermoplastic, incomplete peeling was observed as the peeling angle was getting bigger towards the end of peeling. The parts were sometimes held by the roller while it was kept pulled down, resulting in the force peak at the end of the graph, as also indicated in Figure 4.2.

In the following sections, the correlation between the component and the adhesion strength will be done based on the change interpretation made in section 5.1.1.2.

6.1.1 Viscosity’s Effect on Adhesion

To see the relationship between the viscosity of the compound and the peeling force, they are also illustrated simultaneously in Figure 6.1.
Figure 6.1: Effect of Components on the Elastomer Melt Viscosities and the Adhesion Strength
Although one can see that for certain compounds the peel force follows the trend imposed by viscosities (the lower the viscosity, the higher the adhesion, as shown by comparing Compound 1 with Compounds 3, 4, 8, 9, and 10), the other compounds did not follow this trend, so a direct relationship can not be concluded.

The high viscosity can affect the adhesion in a manner that the elastomer has already lightly cured upon contact with the thermoplastic, and furthermore, high viscosity can also prevent an effective pressure transfer along the flow length, causing non-uniform adhesion strength or worse, an incomplete contact of the melt to the thermoplastic adherend.

6.1.2 Component’s Effect on Adhesion

From Figure 6.1, one can see that by removing the light filler and relying on Carbon Black 1 (Compound 2), 2 (Compound 9), or 3 (Compound 10) alone reduced the peeling force drastically from Compound 1’s original adhesion strength of 7.6 N/mm to about 2 N/mm, signifying the importance of the light filler as filler materials compared with carbon blacks.

For the carbon blacks themselves, based on the activity used (see Equation 1 on section 5.1.1.2), one can see in Figure 6.2 that the increasing activity, in this case, decreases the adhesion strength between the XNBR and the PA612, which may be caused by the stronger attraction of the carbon black with higher reactivity to the other chemicals in the rubber compound.
Figure 6.2: Component Effect on the Adhesion Strength
The trend observed, however, is different from the results obtained in the patent literature [31] using VESTAMID X4887 (PA12 from Hüls AG, Marl - Germany, with NH₂- to COOH- ratio of 5:1) and Chemigum NX 775 (XNBR from Goodyear Fire & Rubber, Akron, Ohio - USA), whose mixtures were represented in Table 6.2.

<table>
<thead>
<tr>
<th>Components</th>
<th>Units</th>
<th>3.4&lt;sup&gt;4&lt;/sup&gt;</th>
<th>3.5</th>
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<td>Chemigum NX 75</td>
<td>phr</td>
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<td>100</td>
</tr>
<tr>
<td>Corax N 550</td>
<td>phr</td>
<td>40</td>
<td>0.5</td>
</tr>
<tr>
<td>Vulkasil C</td>
<td>phr</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>phr</td>
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<td>EDMA</td>
<td>phr</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Perkadox BC 40</td>
<td>phr</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

**Table 6.2: Compound Recipes used with PA12 [31]**

For Compounds 3.4 (with carbon black) and 3.5 (with light filler - Vulkasil C), the peel forces (DIN 53 531: 90° peeling angle, 50 mm/min pulling speed) was reported to be 16.1 N/mm and 16.2 N/mm, respectively, with rubber cohesive failure in both cases.

By increasing the amount of the light filler in Compound 3, one can see the increasing adhesion strength. Increasing it further in Compound 11 (see Equation 5.2 on section 5.1.1.2) results in a further increase in the adhesion strength, which can be seen more clearly in Figure 6.2. However, this increase in peeling strength for Compound 11
can not be contributed to the light filler amount alone, as the addition of Processing Helper 1 & 2 (Compound 8) also increases the adhesion strength.

Nevertheless, although one needs to proceed with caution, it can be said that Light Fillers 1 & 2 have an important role in giving the rubber compound its adhesion strength behavior. To know just how far the trend will show the corresponding relationship one needs to investigate it further. At this point it is worth mentioning that it has also been stated that the presence of Vulkasil C (section 2.4.5.3), among others, is important in the RFK mixture. In this case, the applicability or the knowledge transfer from the mentioned study to the T/R system will be another interesting topic to pursue.

Changing Activator 1 with Activator 2 (Compound 4) results in an increase in peeling force. The cause might be that one of the activator functions was controlling the amount of radicals, and hence the elastomer curing density.

It has been mentioned that the curing degree in the rubber affects properties such as hardness, elongation failure, etc. However, as the trend observed shows a maximum (e.g. tensile strength), a minimum (e.g. remaining deformation), and even a constant decrease or increase as the curing degree increase, the type of Activator 2 could not be determined.

It has been known that a small addition of activators can lead to a considerable increase in the degree of vulcanization [24], and it was even mentioned that in many cases, practically no vulcanization takes place in the absence of an activator. In our case, it can be said that the right activator can improve the adhesion strength further.

\[\text{4 Numbered according to the original}\]
Changing the rubber basis (Compound 4, 5, and 6) was observed to lower the adhesion strength. Unfortunately, an exact cause cannot be determined without knowing what they are because each rubber reacts differently with the corresponding filler, additives, etc.

For Compound 7, the effect of peroxide can be seen to decrease the adhesion strength, which was probably caused by the curing density in the rubber determined by the peroxide.

Since an external type of plasticizer should have lowered the adhesion value due to an adhesion barrier effect, it is quite possible that Processing Helpers 1 & 2 are some type of internal plasticizers used to reduce the viscosity of the melt, easing the processing for Compound 8.

Comparing Compound 8* and Compound 11, the effect of adding the Light Filler content can be seen to increase the adhesion strength despite the simultaneous increase in the compound's viscosity. In this case, one can consider whether the additional strength obtained is worth the time increase. In this case, an optimization of the mixture content can be done to find the optimal solution.

To see the effect of increasing amount of the plasticizer, one can compare Compound 8 or 8* with Compound 12. They were observed to decrease the adhesion strength despite the fact that plasticizer can improve the compound tack (see section 4.1.3). One reason that can cause this is that during the testing, softer material caused by adding plasticizer can yield lower adhesion strength.
Since the change direction could not be determined, the correlation between the adhesion strength and the compound's component could not be carried out.

Addition of Processing Helpers 3 & 4 (Compound 14) was observed to decrease the adhesion strength, showing that Processing Helpers 3 & 4 were not as compatible with the rubber as the Processing Helpers 1 & 2 in giving the high adhesion strength.

6.1.3 Conclusion

From the observations made during the preliminary and intermediate studies, the following can be concluded:

- From the relatively clean failed surface, it can be hypothesized that the adhesion mechanism between XNBR and the PA 612 comes from intermolecular interaction (van der Waal’s force) at the interface. The exact mechanism of the interaction as well as the link between curing density and the adhesion strength (Compounds 4 and 7), however, can not be determined without further investigation.

It can be hypothesized that the adhesion mechanism is due to be a polar interaction by considering the NBR is a polar rubber, added to COOH-groups, and the presence of light filler (Vulkasil C and Polestar 200R) and Carbon Black 1.

- Despite the role of viscosity in the wetting mechanism and its implication on the adhesion strength, the results did not show a consistent trend that the
higher the viscosity is, the harder it is to wet the adherend, and hence the lower the adhesion strength is. For a more economical operation, to drive viscosity lower, melt temperature should increase through mold temperature, and a barrel temperature increase can be done. However, this also increases the risk of early vulcanization, especially for highly reactive compounds, as discussed by Krehwinkel and Schneider [51].

- Light Fillers 1 & 2 affect the adhesion strongly, and although the relation between the content and the adhesion strength is not linear, the trend shows that with an increasing amount of light filler, the adhesion strength increases.

- Peroxide (Compound 7), and rubber (Compounds 5, 6) types seemed to affect the adhesion strength less than the light filler did.

- Activator (Compound 4) was observed to have an important effect in determining adhesion strength.

- It can be established that in the experiment performed, when used alone, the carbon black filler tends to give a poor adhesion strength. This is more apparent with the more active carbon black.

- Processing Helper can help increasing the adhesion strength only if the right combination of high adhesion strength has been obtained (Compound 1 vs Compound 8), while the Plasticizer tends to decrease it (Compound 8 vs Compound 12). It has to be noted though, that the correct choice of a processing helper is crucial in determining if better or worse adhesion will be obtained (Compound 8 vs Compound 14).
From the conclusions drawn above, one has to keep in mind that the chemical nature of the rubber compound is complex and interaction between the various components is always possible.

6.2 Microscopic Investigation

By using a light microscope, it can be revealed that:

- With 32 times magnification, it can be seen that the visually smooth thermoplastic surface consists of pits inherently present in the molding of the glass fiber-reinforced thermoplastic material. These pits, which can act as an addition to the adhesion area thereby increasing the strength, were replicated very well by the elastomer.

- Adhesively failed surfaces, clean from the elastomer traces, were typically observed.

- The elastomer traces present on the PA surfaces were observed to be sparsely distributed, and with the naked eyes, some elastomer traces which were present at some clean PA surface (Compounds 6, 7, and 8) could hardly be seen.

- The thermoplastic insert became so soft that the mold surface contours and finish were imprinted at the back of the thermoplastic inserts due to the high temperature and the pressure exerted by the elastomer during the part manufacturing process, which signifies the importance of polymer form
stability in the heat. In fact, molded with a mold temperature of 160 °C, which is significantly lower than the Vicat softening temperature of 215 °C for Process A and 205 °C for Process B (see section 3.3), under the pressure of the elastomer melt, the thermoplastic inserts were also observed to soften such that they conformed to the small circular dent contour present in the mold cavity.

6.3 Surface Analysis Investigation with ESCA

In the preliminary stage, ESCA was proposed as a method to see if in the relatively clean failure surface of PA (confirmed with light microscope), there still exist traces of elastomer on a very small scale.

To be able to compare ESCA results, a scan was done on an original sample. A test was done at two different locations to see if scanning at different places yields different results. Since the results were identical, other experiments were carried out at one location only.

Figure 6.3 shows the overall spectrum from the samples scanned with the atom percentage for each compound while Figure 6.4 shows the amount of each element detected on the surface. As can be seen for the overall spectrum, ESCA was able to identify the overall bonding energy characterising molecule with certain atoms at its center (531.7 eV for O, 496.7 for Sn, 399.5 eV for N, 284.6 eV for C, and 102.0 eV for Si).
Figure 6.3: Detected Overall Atom Percentage at the Surface: Spectrum
**Figure 6.4**: Detected overall Atom %age at the Surface: Amount
As seen in Equation 6.1, for PA612, the atom percentage from the surface composition should theoretically consist of 81.81% of C atom bonding (18 atoms from 22 atoms) and 9.09% for each N (2 atoms from 22 atoms) and O (2 atoms from 22 atoms) atom bonding.

\[
\begin{array}{c}
\text{H} \\
\text{N} \text{-(CH}_{2}\text{)}_{5} \text{N} \text{C-(CH}_{2}\text{)}_{10} \text{C} \\
\end{array}
\]

(6.1)

The amounts detected by ESCA for the original compound, as also indicated in Figure 6.4, however, are 80.69% for C, 7.29% for N, and 12.02% for O. By taking into account the presence of the water molecules present at the surface, one can explain how the discrepancy occurred. From 23 atoms (with water molecules added to the composition), one will get 78.26% for C, 8.69% for N, and 13.04% for O, which is pretty close to the results obtained considering 1% error from the ESCA.

However, by using ESCA, a more detailed analysis on the surface to detect the elastomer residues that might not be able to be seen using a microscope was not possible. Only for Compounds 3 and 6 some peculiarities were found, which were the presence of Sn, and Sn and Si, respectively. Therefore, for parts detected with a light microscope as having elastomer traces (Compounds 4, 6, 7, and 8), only the part with Compound 6 was detected with “foreign” particles, which might come from the rubber’s filler or from dust particles. The presence of Si might be from the light filler present in the rubber since elastomer traces were also present in the PA surface. This indication, however, was not
always observed for a PA surface with elastomer traces on it, possibly due to the very low
distribution of the elastomer traces themselves, while for Compound 3, viewed through a
microscope with no elastomer traces, the appearance of Sn might come from the dust.
Except for Compounds 3 and 6, one can pretty much consider that the surface
composition of the thermoplastic plates are identical.

The difficulties in analyzing ESCA results for the samples, as it turned out,
originated from the way ESCA works [20]. As has been explained in the previous chapter,
ESCA measures the reflected photoelectron’s energy intensity after it hits the molecules.
For the C-H, C-C, C=C, and C≡C bonding, the bonding energy measured will show up to
be 276.06 eV, as can be seen more clearly in Figure 6.5. For the bonding between C and
other atoms, one can see in more detail how the central peak experiences a shift, the so-
called chemical shift, when the photoelectrons emitted by the X-ray source hits C atom
connecting to the other atom, such as C-O (1.6 eV), C=O (2.8 eV), and O-C=O (4.1 eV).
Through these shiftings, one then can identify the bonding presence in more detail. One
can then, theoretically, determine the excess of bonding that presents by comparing the
bonding amount, for example see Figure 6.6 in this case, in the adherend chemical
composition and with what ESCA gives.

Since ESCA didn’t give more significant improvement in the analysis, it wasn’t
used in the intermediate study.
Figure 6.6: Specific Elements Identifications using ESCA: Amount
6.4 Interfacial Surface Tension Relationship with Adhesion Strength

Using water and glycerin dropped at the adhesively failed surface, the surface tension from PA and rubber was measured to obtain the interfacial surface tension and it’s correlation with the system’s adhesive strength.

The angle formed by water or glycerin on both the PA and rubber surfaces, however, didn’t show a good repeatability. The angle’s standard deviations ranged from 2° to 8°, listed in the Appendix, and might be caused by the irregular roughness at the failure surfaces and the relatively inconstant amount of the glycerin.

Despite having similar roughness with the PA counterpart, the rubber failure interface had more irregularities than previously thought. At the various locations, it has been observed that when the PA surface was free from elastomer traces, and especially for the one with elastomer traces, the rubber interface didn’t fail into a smooth surface, but it was observed that at certain locations, the surface is pulled out. Since the wetting angle is very closely related to the condition of the surface, these irregularities can cause the inconsistencies mentioned.

As a result, the surface tension components obtained for the rubber fluctuated more compared with their PA counterparts. In some cases, the number obtained for the rubber was not making any sense (negative). Since the data was unreliable, the correlation between $\gamma_{12}$ and adhesion strength from the surface tension was not found.
CHAPTER 7

FUTURE STUDY RECOMMENDATIONS

From the trends observed recently in the Multi-Component Injection Molding area, there is a bright future in this special injection molding process niche. Along with the multi-color, multi-material, T/TPE combination, it can not be denied that the T/R combination as a new player in the field also offers its own advantages through the special characteristics possessed by the rubber and the part production cost savings, among others.

In this report, it was demonstrated that the mechanism governing the adhesion between XNBR and PA612 was found to be an intermolecular phenomena in nature. While some important aspects, such as the mold concept for the T/R processing, part design recommendation, T/R adhesion mechanism, and the possibility to use LSR in the process have been addressed, further understanding is needed so the technology can reach its maturity before being fully accepted by the industry.

As has been shown in the previous chapter, some trends have been found correlating to the component’s effect to the adhesion strength.
For example, in the systems investigated, the amount of increase in light filler (Vulkasil C and Polestar 200R) has a positive effect on the adhesion strength, while when used as the only filler in the compound, the carbon black with higher activity tends to lower the adhesion strength.

Unfortunately, in the experiment performed in this report, the proprietary nature of the material components investigated in the compounds made it difficult to carry out a detailed analysis on the exact cause of the adhesion, a know-how that is very important in the material combination pairs possibility development, and in assisting the processors obtaining the best results within a relatively short time. This can be set as a long-term goal of the project, while in the meantime, the knowledge of what works and what doesn't can be formed through research.

It was also found that various compounds' components such as a rubber basis, plasticizer, activator, peroxide, and processing helper influence the adhesion strength by various degrees.

In this respect, further research in this area can progress by combining the chemical investigation, in terms of a compound's components effect on adhesion, and the processing study. At least two methods can be mentioned to approach this. One can proceed either by carrying out some type of a trend study, costly in time and effort but important to see how a component change affects the adhesion property, or by a factorial design study where the time invested in experimentation can be cut down significantly and the correlation between the processing conditions can be investigated. The important processing parameters can then be established.
As can be realized, the study will be an immense task to perform. Along with some difficulties commonly encountered in the rubber processing (batch to batch variations, among others), the chemical nature of the components in the compound along with their interactions possibilities demand attention also.

Some of the topics that can be further investigated are:

- Effect of the thermoplastic on the adhesion strength.
- Effect of various compound components (filler, additives, rubber basis, etc.) on the adhesion strength. In this respect, the application possibility of LSR can also be further investigated.
- Effect of processing parameters on the adhesion strength.
- The T/R adhesion characteristics in the dynamic loading mode, as rubber is known for its excellent properties in vibration damping elements in various automotive applications.
- Mold design guidelines for T/R processing.
- Part design guidelines for T/R processing.

Naturally, the usage of computer simulations, be it for thermal, rheological, or part design purposes, can be done simultaneously to achieve a well-rounded knowledge of the process.
## ABBREVIATIONS AND SYMBOLS

### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>BDMA</td>
<td>Butadiol 1, 4 dimethylacrylate</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett, and Teller</td>
</tr>
<tr>
<td>BR</td>
<td>Polybutadiene, butadiene rubber</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>CR</td>
<td>Polychloroprene, chlorbutadien rubber</td>
</tr>
<tr>
<td>DBP</td>
<td>Dibutyl phtalate</td>
</tr>
<tr>
<td>DIN</td>
<td><em>Deutshe Industrie Normen</em>, German Industry Standards</td>
</tr>
<tr>
<td>DPG</td>
<td>Diphenylguanidin</td>
</tr>
<tr>
<td>EPDM</td>
<td>Ethylene propylene dien rubber</td>
</tr>
<tr>
<td>EPM</td>
<td>Ethylene propylene rubber</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electrons Spectroscope for Chemical Analysis</td>
</tr>
<tr>
<td>EVA</td>
<td>Ethylene vinyl acetate</td>
</tr>
<tr>
<td>IIR</td>
<td>Isobutylene isoprene copolymer, butyl rubber</td>
</tr>
<tr>
<td>IR</td>
<td>Synthetic polyisoprene</td>
</tr>
<tr>
<td>ISO</td>
<td>International Standard Organization</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low density polyethylene</td>
</tr>
<tr>
<td>LSR</td>
<td>Liquid Silicone Rubber</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>NR</td>
<td>Natural Rubber</td>
</tr>
<tr>
<td>O</td>
<td>Oxygen</td>
</tr>
<tr>
<td>PA</td>
<td>Polamide</td>
</tr>
<tr>
<td>PBT</td>
<td>Polybutadiene terephthalate</td>
</tr>
<tr>
<td>phr</td>
<td>parts per hundred</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethylmethacrylate</td>
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<tr>
<td>PNR</td>
<td>Polynorbonen rubber</td>
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<td>POM</td>
<td>Poloxymethylene</td>
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<td>PP</td>
<td>Polypropylene</td>
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<td>PPE</td>
<td>Polynphenylene ether</td>
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<td>PVC</td>
<td>Polyvinylchloride</td>
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<tr>
<td>RFK</td>
<td>Resorcin Formaldehyd Kieselsäure, Resorcinol formaldehyde Silicic Acid</td>
</tr>
<tr>
<td>RFL</td>
<td>Resorcinol Formaldehyde Latex</td>
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SBR : Styrol butadien rubber
Si : Silicium
T/R : Thermoplastic/Rubber
T/TPE : Thermoplastic/Thermoplastic elastomer
TPE : Thermoplastic elastomer
XNBR : Carboxilated NBR

Formula Symbols and Letters

c_p : Specific heat capacity
ΔG_{mix} : Gibbs free energy of mixing
Δh_R : Specific reaction enthalpy
Δμ_A : Chemical potential of Component A
Δp : Pressure difference
Δθ, Δθ_R : Temperature increase, temperature increase due to a reaction
ΔS_{mix} : Entropy of mixing
E_a : Activation energy
ε_b : Failure elongation
ϕ_B : Volume part of B
γ : Surface tension
K_0 : Temperature independent reaction speed constant
λ : Heat conductivity
n : Reaction order
Π : Spreading pressure
Θ : Wetting angle
θ : Temperature
ρ : Density
σ_f : Failure strength
S_i : Scorch index
t : Time
t_0 : Time constant
T_0 : Temperature constant
T_1, T_2, T_c : Temperature of mold 1, 2, and for curing
W_a : Work of adhesion

Indices

c : curing
d : dispersion
l : liquid
mix : mixture
p : polar

143
<table>
<thead>
<tr>
<th>s</th>
<th>solid</th>
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<tbody>
<tr>
<td>T</td>
<td>Thermoplastic</td>
</tr>
<tr>
<td>TPE</td>
<td>Thermoplastic elastomer</td>
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<tr>
<td>v</td>
<td>vapor</td>
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</table>
REFERENCES


Rubbers consisting Carboxyl Groups and the Polymer Manufactured according to this Process). European Patent. EP 0 375 867 A2.


[67] Stoeckhert, K. (1979). Werkzeugbau für die Kunststoffverarbeitung (Mold Engi-
neering for Polymer Processing). Munich: Carl Hanser Verlag.


APPENDIX

A.1 Appendix for Chapter 2

| TP Material | $\gamma$ [mN/m] | Adhesive I | | Adhesive II | | Adhesive III | | Adhesive IV |
|-------------|-----------------|-----------|---|-----------|---|-----------|---|
| PTFE        | 19              | 1.95      | 2.48 | 0         | 3.5 | 0         | 5.46 |
| PIP         | 27              | 0.79      | 1.25 | 0.38      | 1.25 | 0.85      | 1  |
| PE          | 28              | 0.05      | 15   | 0.16      | 5   | 0.51      | 4.5 |
| PVC Red     | 34              | 0.18      | 77   | 0.06      | 73  | 0         | 1.5 |
| PVC Green   | 36              | 0.54      | 73   | 0.3       | 61.5 | 0.06      | 42 |
| PMA         | 39              | 1.21      | 51   | 6.84      | 36  | 0.38      | 42.3 |
| PEA         | 41              | 1.8       | 15   | 1.36      | 9   | 0.74      | 33 |
| PA 6        | 42              | 2.15      | 6    | 1.66      | 21  | 0.97      | 30 |

Adhesive I : PVC-PVA Paint  Adhesive III : Alkyl-Phenol Paint  $p = 9.80665 \times 10^{-3}$ N
Adhesive II : Alkyd resin Paint Adhesive IV : Polyurethane Paint

Table A.1 The Adhesion Strength of the Adhesive on different Thermoplastics [18]
A.2 Appendix for Chapter 5

<table>
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**Mixing Data**

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<tr>
<td>$t_{10}$ minute</td>
<td>1.4</td>
</tr>
<tr>
<td>$t_{90}$ minute</td>
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**Vulcanization (8 Minutes at 180°C)**

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<th>MPa</th>
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<td>Elongation at Failure</td>
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<td>Vulcanisate hardness at 22°C</td>
<td>Shore A</td>
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<tr>
<td>Rückprallelastizität at 22°C</td>
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<tr>
<td>Tear Resistance according to Pohle</td>
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<table>
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Table A.2: Example of X-NBR Rubber Compounds & VESTAMID Pair
<table>
<thead>
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<th>Properties</th>
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<th>Standard National</th>
<th>Unit</th>
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<td>ISO 1183</td>
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<td>Elasticity Module</td>
<td>Tensile Test</td>
<td>ISO 527</td>
<td>DIN 53 475</td>
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<td>Elasticity Module</td>
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<td>DIN 53 475-B3</td>
<td>kJ/m²</td>
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Table A.3: VESTAMID X7099 Material Data Sheet

155
Determining Surface Tension Components of Polymeric Solids from 2 Contact Angle Measurements [79]

\[ \gamma_{1s} = \gamma_i + \gamma_s - 4 \left( \frac{\gamma_i^d \gamma_s^d}{\gamma_i^d + \gamma_s^d} + \frac{\gamma_i^p \gamma_s^p}{\gamma_i^p + \gamma_s^p} \right) \]

\[ \gamma_s = \gamma_{1s} + \gamma_s \cos \theta \]

Combining both equations:

\[ \gamma_s = \gamma_i + \gamma_s - 4 \left( \frac{\gamma_i^d \gamma_s^d}{\gamma_i^d + \gamma_s^d} + \frac{\gamma_i^p \gamma_s^p}{\gamma_i^p + \gamma_s^p} \right) + \gamma_s \cos \theta \]

\[ \gamma_i(1 + \cos \theta) = 4 \left( \frac{\gamma_i^d \gamma_s^d}{\gamma_i^d + \gamma_s^d} + \frac{\gamma_i^p \gamma_s^p}{\gamma_i^p + \gamma_s^p} \right) \]

Let \( \gamma_{i1} = \gamma_i \) and \( \gamma_{i2} = \gamma_2 \), where \( \gamma_{ix} \) denotes the known surface tension of the liquid \( x \).

\[ \gamma_i(1 + \cos \theta_i) = 4 \left( \frac{\gamma_i^d \gamma_s^d}{\gamma_i^d + \gamma_s^d} + \frac{\gamma_i^p \gamma_s^p}{\gamma_i^p + \gamma_s^p} \right) \]

\[ \gamma_2(1 + \cos \theta_2) = 4 \left( \frac{\gamma_2^d \gamma_s^d}{\gamma_2^d + \gamma_s^d} + \frac{\gamma_2^p \gamma_s^p}{\gamma_2^p + \gamma_s^p} \right) \]

Setting \( x \) as \( \gamma_s^d \) and \( y \) as \( \gamma_s^p \), and

\[ Q_j = \frac{1}{4}(1 + \cos \theta_j) \gamma_j, \quad D_j = \gamma_j^d, \quad P_j = \gamma_j^p \]

we have:

\[ Q_i = \frac{D_i x}{D_i + x} + \frac{P_i y}{P_i + y} \]

\[ Q_i D_i + Q_i x - D_i x = \frac{P_i y}{P_i + y} \]

\[ (Q_i D_i + Q_i x - D_i x)(P_i + y) = P_i y(D_i + x) \]

\[ Q_i D_i P_i + y(Q_i D_i - P_i D_i) + x(Q_i - D_i) P_i + xy(Q_i - D_i - P_i) = 0 \]

156
\[ Q_i D_i P_i = (D_i + P_i - Q_i)xy + (D_i - Q_i)P_ix + (P_i D_i - Q_i D_i)y \]

let \( V_i = Q_i D_i P_i \), \( R_i = (D_i + P_i - Q_i) \), \( R_i = (D_i - Q_i)P_i \), \( U_i = (P_i D_i - Q_i D_i) \)

if two liquids are used, we will have:

\[ V_1 = S_1xy + R_1x + U_1y \]
\[ V_2 = S_2xy + R_2x + U_2y \]

for liquid 1:

\[ V_1 = (S_1x + U_1)y + R_1x \]
\[ \frac{V_1}{S_1x + U_1} = y + \frac{R_1x}{S_1x + U_1} \]

doing the same for liquid 2:

\[ \frac{V_2}{S_2x + U_2} = y + \frac{R_2x}{S_2x + U_2} \]

subtracting equation 1 from 2:

\[ \frac{V_1}{S_1x + U_1} - \frac{V_2}{S_2x + U_2} = \frac{R_1x}{S_1x + U_1} + \frac{R_2x}{S_2x + U_2} \]

rearranging the equation:

\[ (R_1S_2 - R_2S_1)x^2 + (R_1U_2 - R_2U_1 - V_1S_2 + V_2S_1)x + (V_2U_1 - V_1U_2) = 0 \]

solving the quadratic equation will give \( x \) and \( y \).
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### Table A.5: Contact Angle Measurements on PA using Water

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O: Original  - : Not Available  Units in °

### Table A.6: Contact Angle Measurements on Rubber using Water

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- Not Available  Units in °

Table A.7: Contact Angle Measurements on PA using Glycerin

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- Not Available  Units in °

Table A.8: Contact Angle Measurements on Rubber using Glycerin

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O: Original  x: Erroneous Result  -: Not Available  Units in mN/m

**Table A.9: Surface Tension Measurement Results**