<table>
<thead>
<tr>
<th>Title</th>
<th>Study on the Effect of Aggregation Structure of Segmented Polyurethanes on their Adhesion Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Kongpun, Teerin</td>
</tr>
<tr>
<td>Citation</td>
<td>Nagasaki University (長崎大学) 博士 (工学) (2009-03-19)</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2009-03-19</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10069/22086">http://hdl.handle.net/10069/22086</a></td>
</tr>
</tbody>
</table>

NAOSITE: Nagasaki University’s Academic Output SITE

http://naosite.lb.nagasaki-u.ac.jp
Study on the Effect of Aggregation Structure of Segmented Polyurethanes on their Adhesion Properties

December 2008

Graduate School of Science and Technology, Nagasaki University

TEERIN KONGPUN
## Chapter 1 Introduction

1.1 Polyurethane adhesives 1
1.2 Reactions of isocyanates 2
1.3 Various types of polyurethanes 5
1.4 Preparation of polyurethane 13
1.5 Preparation of polyurethane adhesives 14
1.6 Theories of adhesion 16
1.7 Conditions of joint formation and testing 22
1.8 Segmented polyurethanes in adhesive field 24
1.9 Literature review of polyurethane adhesives 27
1.10 Purpose of this study 29

References 32

## Chapter 2 Effect of Curing Agent Ratio of Diol to Triol on Microaggregation Structure and Adhesion Properties of Segmented Polyurethanes (Hot Melt Adhesive)

2.1 Introduction 36
2.2 Experimental 37
2.2.1 Materials 37
2.2.2 Polymer synthesis 38
2.2.3 Characterization 39
2.2.3.1 Swelling measurement 39
2.2.3.2 Macroscopic observation 40
2.2.3.3 Thermal analysis 40
2.2.3.4 Surface free energy measurement 40
2.2.3.5 T-peel strength 41
2.2.3.6 T-peel failure behavior 41
2.3 Results and Discussion 41
2.4 Conclusion 51

References 53
Chapter 3 Effect of Polymer Glycols on the Microphase-separated Structure and Adhesion Properties of Spherulite Size Graded Polyurethane Elastomers with Corona Treated Polypropylene Film (Reactive Adhesive)

3.1 Effect of Polymer Glycols on the Micro-aggregation Structure and Mechanical Properties of Segmented Polyurethanes

3.1.1 Introduction

3.1.2 Experimental

3.1.2.1 Materials

3.1.2.2 Polymer synthesis

3.1.2.3 Characterization

3.1.2.3.1 Preparation of thin film using a microtome

3.1.2.3.2 Density and swelling measurement

3.1.2.3.3 Macroscopic observation

3.1.2.3.4 Thermal analysis

3.1.2.3.5 Functional group analysis

3.1.2.3.6 Pulsed nuclear magnetic resonance measurement of molecular mobility

3.1.2.3.7 Hardness analysis

3.1.2.3.8 Tensile strength measurement

3.1.3 Results and Discussion

3.1.4 Conclusion

References

3.2 Effect of Polymer Glycols on the Micro-aggregation Structure and Adhesion Properties of Segmented Polyurethanes

3.2.1 Introduction

3.2.2 Experimental

3.2.2.1 Materials

3.2.2.2 Polymer Synthesis

3.2.2.3 Surface Modification of Polypropylene (PP)

3.2.2.4 Characterization

3.2.3 Results and Discussion

3.2.4 Conclusion

References
<table>
<thead>
<tr>
<th>Chapter 4 The Influence of Curing Temperature on Microaggregation Structure and Adhesion Properties of Segmented Polyurethanes (Reactive Adhesive)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Introduction</td>
</tr>
<tr>
<td>4.2 Experimental</td>
</tr>
<tr>
<td>4.2.1 Materials</td>
</tr>
<tr>
<td>4.2.2 Polymer synthesis</td>
</tr>
<tr>
<td>4.2.3 Characterization</td>
</tr>
<tr>
<td>4.3 Results and Discussion</td>
</tr>
<tr>
<td>4.4 Conclusion</td>
</tr>
<tr>
<td>References</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 5 Effect of Humidity on Microaggregation Structure and Adhesion Properties of Segmented Polyurethanes (Reactive Adhesive)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
</tr>
<tr>
<td>5.2 Experimental</td>
</tr>
<tr>
<td>5.2.1 Materials</td>
</tr>
<tr>
<td>5.2.2 Polymer synthesis</td>
</tr>
<tr>
<td>5.2.3 Characterization</td>
</tr>
<tr>
<td>5.3 Results and Discussion</td>
</tr>
<tr>
<td>5.4 Conclusion</td>
</tr>
<tr>
<td>References</td>
</tr>
</tbody>
</table>

| Chapter 6 Summary | 122 |

| Paper lists of thesis | 125 |

| Acknowledgement | 127 |
Chapter 1 Introduction

1.1 Polyurethane adhesives (PUAs)

PUAs are commonly prepared from polyurethane elastomers (PUEs). Thus, for clearly understanding in polyurethane adhesives, the principle of PUEs, method for preparing polyurethane adhesives and theory of adhesion are explained.

Polyurethane (PU) is a class of polar polymers containing the urethane links (1) in their backbones. PUs are commonly prepared by polyaddition polymerization. The most widely used preparation method is the reaction of di- or polyfunctional hydroxyl oligomers, e.g. hydroxyl-terminated polyethers or polyesters with di- or polyfunctional isocyanates.

\[
\begin{align*}
&\text{HO-R-OH} \quad \text{and} \quad \text{diisocyanate, OCN-R’-NCO, can be represented by the following general formula}^1: \\
&\begin{array}{c}
\text{O} \\
\text{R} \quad \| \\
\text{O} \\
\end{array} \\
&\begin{array}{c}
\text{N} \\
\text{C} \\
\text{O} \\
\end{array} \\
&\begin{array}{c}
\text{O} \\
\text{R’} \quad \| \\
\text{N} \\
\text{C} \\
\text{O} \\
\end{array}
\end{align*}
\]

In many cases, as PUs are formed, long chain and short chain diols alternate along the chain to form segments which are either soft or hard. On a microscope scale, the soft and hard segments coexist in a domain morphology characteristic of what are known as segmented polyurethanes (SPUs). The very good impact and fatigue resistance of SPUs are attributed to this phase-separated microstructure. The particular diol or polyol chosen will greatly influence the rubbery and impact resistance properties of the SPUs, while the isocyanate chosen will strongly influence the strength, modulus and hardness of the SPUs. The domain morphology of SPUs is most pronounced for systems containing no chemical crosslinking. In contrast to most adhesive systems, low levels of crosslinking tend to degrade the properties of PUAs because of disruption of the domain morphology.
PUAs have somewhat poorer thermooxidative and moisture resistance than acrylic and epoxy structural adhesives. This has historically limited their expansion into certain areas of use. On the other hand, SPU adhesives have high flexibility, usually strong peel strength, and generally good impact and fatigue resistance recommended their use when these characteristics are important. A variety of adhesives have been developed which incorporate SPUs into acrylic or epoxy structural adhesives\(^2\). With the diverse range of high performance properties, polyurethanes are essential to a multitude of end-use applications. Additionally, PUAs was used as one application of SPUs. A detailed breakdown of the SPUs industry by application is shown in figure 1.1. The versatility of SPUs is demonstrated by a summary of their applications in five important areas that are automotive, furniture, construction, thermal insulation and footwear. PUAs are widely used in footwear (i.e. shoe and slipper manufacture) glue, sealant and packaging \(^2\).

![Figure 1.1 World SPU market by industry \(^2\).](image)

---

2) Source: [SPU Industry Overview](https://example.com/spu-industry-overview)
1.2 Reactions of isocyanates

The isocyanates, containing the highly unsaturated –N=C=O group, are very reactive with active hydrogen, and may also react with themselves. Of the many reactions surveyed herein, only a few have been of sufficient importance to justify detailed kinetic studied such as catalyzed and uncatalyzed reactions. The electronic structure of the isocyanate group indicates that it should have the following resonance possibilities (2)\(^3\):

\[
\begin{align*}
R-\tilde{N}=\tilde{C}=\tilde{O} & \rightarrow R-\tilde{N}=\tilde{C}=\tilde{O} \\
& \rightarrow \tilde{R}=\tilde{N}=\tilde{C}=\tilde{O}
\end{align*}
\]

The normal reaction ultimately provides addition to the carbon-nitrogen-double bond. In most reactions, especially with active hydrogen compounds, the aromatic isocyanates are more reactive than aliphatic isocyanates. In addition, substitution of electronegative groups on the aromatic ring enhances the reactivity whereas electropositive groups reduce the reactivity of the isocyanate. For these reasons, isocyanates are often used as intermediate products in the organic chemistry. For the better understanding of polyurethane chemistry, basic reactions which are related to the synthesis of polyurethanes\(^4\) are represented as shown in figure. 1.2.
Figure. 1.2. Reaction of isocyanate with active hydrogen compounds.
1.3 Various types of polyurethanes

PUs are certainly the most versatile class of polymers because of the great variety of types (i.e. polycarbonate-, polyether- and polyester based PU), molecular weights, curing agent ratios and so on\(^5\). The end products of PUs can be applied to many categories such as elastomers, foams, plastics, fibers, coatings, films, binders, adhesives and so on.

a. Polyurethane elastomers (PUEs)

PUE is one of block copolymers with an [hard-soft\(_n\)]-type structure, which consists of a relatively flexible component called the soft segment and a relatively polar and stiff component known as the hard segment\(^6\). PUEs have excellent mechanical properties compared with general purpose elastomers. PUEs have attained a special importance in widely differing industrial applications because of their unique properties, their large versatility, and their various processing techniques\(^7\). The physical properties of typical elastomers\(^8\) can be found in table 1.1. PUEs usually have three-dimensional network structures which are obtained by permanently linking polymeric chains together as shown in figure 1.3. The crosslinks may be either chemical bonds (as is illustrated by tri- or multifunctional polyols as a soft segment, or through the hard segment, using tri- or higher functional chain extender) or physical aggregation as crystallites in partially crystalline polymers or glassy domains in a multi-phase block copolymer as shown in figure 1.4. PUEs presently exist in two basic groups, classified on the basis of their morphological structure as single phase network PU and multi phase SPU.
Table 1.1 Physical properties of typical elastomers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Pure-Gum Vulcanizates</th>
<th>Carbon-Black-Reinforced Vulcanizates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tensile Strength (MPa)</td>
<td>Elongation (%)</td>
</tr>
<tr>
<td>Natural rubber (NR)</td>
<td>20.68</td>
<td>700</td>
</tr>
<tr>
<td>Styrene-butadiene rubber (NR)</td>
<td>2.76</td>
<td>800</td>
</tr>
<tr>
<td>Acrylonitrile-butadiene rubber (NBR)</td>
<td>4.14</td>
<td>600</td>
</tr>
<tr>
<td>Polyacrylates (ABR)</td>
<td>2.07</td>
<td>300</td>
</tr>
<tr>
<td>Thiokol (ET)</td>
<td>24.13</td>
<td>800</td>
</tr>
<tr>
<td>Neoprene (CR)</td>
<td>20.68</td>
<td>1,000</td>
</tr>
<tr>
<td>Butyl rubber (IIR)</td>
<td>20.68</td>
<td>700</td>
</tr>
<tr>
<td>Polyisoprene (IR)</td>
<td>34.47</td>
<td>600</td>
</tr>
</tbody>
</table>

Figure 1.3 Three-dimensional network structures of polyurethane elastomer

---

Table 1.1 Physical properties of typical elastomers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Pure-Gum Vulcanizates</th>
<th>Carbon-Black-Reinforced Vulcanizates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tensile Strength (MPa)</td>
<td>Elongation (%)</td>
</tr>
<tr>
<td>Natural rubber (NR)</td>
<td>20.68</td>
<td>700</td>
</tr>
<tr>
<td>Styrene-butadiene rubber (NR)</td>
<td>2.76</td>
<td>800</td>
</tr>
<tr>
<td>Acrylonitrile-butadiene rubber (NBR)</td>
<td>4.14</td>
<td>600</td>
</tr>
<tr>
<td>Polyacrylates (ABR)</td>
<td>2.07</td>
<td>300</td>
</tr>
<tr>
<td>Thiokol (ET)</td>
<td>24.13</td>
<td>800</td>
</tr>
<tr>
<td>Neoprene (CR)</td>
<td>20.68</td>
<td>1,000</td>
</tr>
<tr>
<td>Butyl rubber (IIR)</td>
<td>20.68</td>
<td>700</td>
</tr>
<tr>
<td>Polyisoprene (IR)</td>
<td>34.47</td>
<td>600</td>
</tr>
</tbody>
</table>

Figure 1.3 Three-dimensional network structures of polyurethane elastomer

---

Table 1.1 Physical properties of typical elastomers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Pure-Gum Vulcanizates</th>
<th>Carbon-Black-Reinforced Vulcanizates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tensile Strength (MPa)</td>
<td>Elongation (%)</td>
</tr>
<tr>
<td>Natural rubber (NR)</td>
<td>20.68</td>
<td>700</td>
</tr>
<tr>
<td>Styrene-butadiene rubber (NR)</td>
<td>2.76</td>
<td>800</td>
</tr>
<tr>
<td>Acrylonitrile-butadiene rubber (NBR)</td>
<td>4.14</td>
<td>600</td>
</tr>
<tr>
<td>Polyacrylates (ABR)</td>
<td>2.07</td>
<td>300</td>
</tr>
<tr>
<td>Thiokol (ET)</td>
<td>24.13</td>
<td>800</td>
</tr>
<tr>
<td>Neoprene (CR)</td>
<td>20.68</td>
<td>1,000</td>
</tr>
<tr>
<td>Butyl rubber (IIR)</td>
<td>20.68</td>
<td>700</td>
</tr>
<tr>
<td>Polyisoprene (IR)</td>
<td>34.47</td>
<td>600</td>
</tr>
</tbody>
</table>

Figure 1.3 Three-dimensional network structures of polyurethane elastomer
Single phase network PUs are usually homogeneously amorphous polymeric networks having only one phase, e.g. one that may be prepared by a reaction of long chain, non-crystalline, unbranched, OH-functional polyethers or polyesters with stoichiometric amounts of diisocyanates. They may be formed by chemical crosslinking as perfect networks (without dangling chain and loops). The chains between two points of linking, called network chains, exhibit a distribution of molecular weights about an average. The network structures may be characterized by the average network chain length, junction point functionality and network chain length distribution, and so forth. Although hardness, strength and thermal stability of single phase network PUs are comparatively low, they are useful in applications where high tensile strength and thermal stability are not required. Furthermore, although a perfect network can never be obtained in reality, they exist as an imaginary ideal model for researches interested in studying relationships between chemical structure and physical properties. In recently, some well-defined model networks prepared by endlinking techniques\textsuperscript{10-12} rather than conventional crosslinking techniques\textsuperscript{13, 14}, have been used in investigation.

**Figure 1.4.** The model of chemical crosslink and physical crosslink in polyurethane elastomer chains.
Multi-phase segmented PUs are a class of polymers which include soft and hard segments, and exhibit phase separation. The soft segment (flexible long chains) is usually formed from a polyether or polyester macrodiol\textsuperscript{15,16} of molecular weight between 600 and 3,000. The hard segment (stiff short chains) is formed by extending an aromatic diisocyanate with low molecular weight diol (1,4-butanediol is commonly used)\textsuperscript{17,18}, as shown in figure 1.5. Typical SPUs such as thermoplastic PU (TPU) usually show a domain structure by virtue of their physical aggregation of chains as shown in figure 1.6.

Figure 1.5. Block structure of SPUs prepared from diisocyanate (\[\text{H}\]), chain extender (\[\text{O}\]) and polyol (\[\text{\textmu\textmu}\])\textsuperscript{17}. 
Microphase separation begins even during the reaction; this separation continues during cooling of the polymer (figure 1.6). Phase 1 consists of long chain polyols which may also have been extended by individual diisocyanate molecules. Phase 2 contains polyurethane blocks produced from diisocyanate and the chain extender. They form ordered domains which are held together by intermolecular forces in which hydrogen bonds play an important role. As a result of interaction between the two microphases which are linked by chemical bonds, the material assumes its rubber elastic properties. The moving element is formed by the long and flexible polyol chains with a glass temperature below room temperature. Phase 2 (consisting polyurethane blocks) provides the crosslinking domains which largely prevent the irreversible flow of the material when under mechanical stress. It has become customary to refer to the polyol blocks as soft segments and to the urethane blocks as hard segments. Hard

![Domain structure of SPUs](image-url)
segments domains act as physical crosslinks and reinforcement sites, significantly affecting mechanical properties, particularly modulus hardness and tear strength.

b. Polyurethane foams

Polyurethane foam was created during World War II for the insulation of refrigerators and airplanes because this polymer was cheaper, easier to shape, man-made and abundant, it possessed great potential to be used in many practical applications. So these polymers are used in many areas of our lives including: furniture cushions, shoe soles, insulating materials, adhesives, flotation devices, cellular scaffolding for bone regeneration, and acoustical vibration control. They are synthesized by the reaction of a polyester polyol, or polyether polyol and water with an aromatic or aliphatic isocyanate (figure 1.7).

Figure 1.7. Polyurethane foam reaction\(^ {18} \).

Polyurethane foam can be flexible or rigid depending on the type of crosslinking that exists between the molecules.
**Rigid Foam** is a highly crosslinked closed celled material of low density, and is widely used in the construction industry. The polyurethane foam properties can be modified within wide limits depending on the raw materials used. This is also true for rigid foams. The density, fluidity, strength, thermal stability and other properties can be adjusted by changing polyols and isocyanates to suit the unique requirements of an application.

**Flexible foams** have a limited resistance to an applied load. They have mainly open cells, formed by gas bubbles that have popped. Air can pass through the foam easily, resulting in a soft, resilient, flexible material. The material is thus harder and less resilient. Controlling the proportion of open cells to closed cells during the production process is one of the ways that the properties of foam can be manipulated, adding to the materials versatility\(^9\). The formation of PU flexible foams depends on two basic reactions, namely urea reaction and urethane reaction. The urea reaction was formed by the addition of water to isocyanate, while CO\(_2\) is generated. The urethane reaction was occurred by the addition of branched polyols containing OH-groups to isocyanate.

The simple fabricating techniques and attractive costs of flexible foams are the important factors which have led to the manifold uses. The major area of application are furniture cushioning, mattresses, transportation, textiles, packaging, household goods and miscellaneous applications.

c. **Polyurethane adhesives (PUAs)**

PUAs are actually coatings between two surfaces. The forces between the adhesive and the adherend may be small but, as in other intermolecular attractions related to macromolecules, those forces are additive. PUAs must be fluid at some stage during the application and must wet the surfaces of the adherend while in the fluid state. Adhesion is favored when the solubility parameter of the adhesive has a high numerical value. The adhesion is enhanced by the presence of polar groups.

PUAs are normally defined as the adhesives that contain a number of urethane groups in the molecular backbone or are formed during use, regardless of the chemical composition of the rest of the chain. Thus, a typical urethane adhesive may contain, in addition to urethane linkages, aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea and allophanate groups. An isocyanate group reacts with the hydroxyl groups of a polyol to form the repeating urethane linkage. Isocyanates will react with water to form a urea linkage and
carbon dioxide as a by-product. Linear thermoplastic PUs may be obtained by using compounds with two reactive groups such as diisocyanate and diols. Crosslinked PUs can be occurred either when polyols with three or more hydroxyl groups (i.e. a functionality of 3 or more) are reacted with an isocyanate or when isocyanates with three or more isocyanate groups are reacted with a polyl. The amount of crosslinking affects the stiffness of the polymer. Contrary to linear polymers, crosslinked polymer will not flow when heated. All structural adhesives are crosslinked because this eliminates creep, that is, deformation under constant load. In reaction systems, where there is an excess of isocyanate crosslinking reactions may occur. These reactions form linkages of allophanate and biuret.

**d. Other applications**

SPUs also have some potentially useful applications, for instance, plastics, coating, fibers, films, laminates, sealants and so on. Films is a continuous, homogeneous, dimensionally stable form of a polymer having a small thickness in relation to area\(^{20}\). The polyurethane films obtain their performance from their common chemical structure. This is characterized by hard and soft segments the former provides stiffness and the latter gives flexibility. During processing the hard parts can soften and thus allow the material to be shaped. But upon cooling they reform to yield the elastomeric behavior required. In the PU films, 4,4-diphenylmethane diisocyanate (MDI) is almost used as the hard segment, while the various polyols such as polyether or polyester polyols are used as the soft segment. PU film based on polyether polyl exhibited best hydrolysi, heat stability, weather stability and oil resistance. In addition, PU film based on polyester polyl showed the best tear, chemical resistance and good mechanical properties\(^{21}\). The third basic component is the chain extender which controls the molecular weight and chain length of the polymer and therefore the hardness or flexibility.

Fibers containing at least 85 weight % of SPU are called “Spandex”\(^{22}\). Spandex fibers are highly elastic and have replaced natural and synthetic rubber fibers for many textile purposes.

Urethane coatings have some outstanding properties, as for superior abrasion resistance, adhesion force, chemical resistance, flexibility, light and weather stability. PU surface coatings are applied as sealants to wood, concrete, and machine parts and as linings for tanks and pipes; moisture-curing PU resin is used as a general purpose waterproof glue. For PU coating, PU-based polymeric films applied on steels provide a very effective protection.
against corrosion as a result of the combination of excellent adhesion to metal substrates and barrier properties\(^{23}\).

1.4 Preparation of polyurethane

PUs can be prepared by various methods such as one-shot method and prepolymer method. Prepolymer and one-shot methods are commonly used in the preparation of flexible and rigid foams, cast elastomers, TPU and PUA.

a. One-shot method

The one-shot of PU is schematically represented in figure 1.8. The entire PU formation may be carried out by simultaneously mixing together polyol, diisocyanate and chain extender or crosslinker\(^ {24}\).

![Figure 1.8. Preparation of polyurethane by one-shot method.](image-url)
b. **Prepolymer method**

The prepolymer technique has two step for synthesized polyurethane. In the first step, prepolymer is obtained by the reaction of polyol and diisocyanate, and next, the prepolymer is teated with curing agent which is a potentially active hydrogen compound, and is altered into the final high molecular weight PU. This step is generally reffered to the chain extender or crosslinking stage (figure 1.9)\(^{25-27}\).

![Figure 1.9. Preparation of polyurethane by prepolymer method.](image)

**1.5 Preparation of polyurethane adhesives**

The preparation methods of PUAs are depending upon the application of use. There are many types of adhesives available today, each with unique characteristics. In general, adhesives can be classified into many types given below.
a. Water borne adhesive

These adhesives are high molecular weight polyurethanes dispersed in water (PUD). The water carrier is eliminated during use, leaving the precipitated and coalesced polymer to form the adhesive bond. The PUDs are not a direct plug-in for the solvent-based polyurethanes. The film forming mechanism of the PUDs is very different from that of the solvent-based resins. In order to realize their optimum properties, they have to be skillfully formulated. The composition of the polymer backbone as well as the formulating ingredients will have significant influence on film formation properties.

PUDs are small and discrete polymer particles ranging from 0.01-5.0 microns in a continuous water phase. They are free of isocyanate residues and have a zero or a very low volatile organic content (VOC)\textsuperscript{28}. They are safe to handle and are a good choice for compliant coatings. PUDs can be made to have 30-65% solid content and a wide range of film hardness.

One of the drawbacks of PUDs is their relatively higher cost. To compensate for the higher cost, the PUDs are blended with other low cost dispersions to improve adhesion to certain substrates. Acrylic emulsions are the most commonly used blending materials due to the familiarity of the formulators with their properties. Waterborne PUAs are an interesting alternative to the current solvent-based PUAs used in footwear industry\textsuperscript{29}, automobile, paint, furniture, and textile industries and also in biomass foam incorporated with renewable raw materials\textsuperscript{30}.

b. Solvent adhesive

Solvent PUAs consist of high molecular weight hydroxyl terminated PU dissolved in a solvent. PUs are obtained by reacting of a high molecular weight polyester diol with diisocyanate and dissolve in solution. The polymer solutions are applied to both surfaces to be bonded. Some time is allowed for the solvent to evaporate and the surfaces are then pressed together, at which point interdiffusion of the polymer chains will occur.

Solvent PUAs are suitable for a number of different industrial and construction applications. Solvent PUAs have good adhesion to rubber, leather, textiles, metal, paper, wood, and plastics. In addition, solvent PUAs are used for a wide variety of laminating applications\textsuperscript{31}. 

c. Hot melt adhesive

These adhesives are consisted of high polar group based SPU. Hot melt adhesives are most commonly applied as adhesive film in lamination type of applications, aerospace and aircraft structure assemblies, automotive and packaging industries. These adhesives are formed the adhesive bond by cooling from the molten state. The difference between hot melt adhesive and other liquid adhesives is that hot melt adhesive bond simply by cooling rather than by the evaporation of a solvent or by chemical curing which is done for other adhesives.

**Advantages of hot melt adhesives**

- Presence of high viscosity allows hot melt adhesive to be used on different non-porous and porous substrates without sacrificing the strength of bond.
- Since no chemical curing method is used, pollution problem is not created in hot melt adhesives.
- As it remains as a complete solid system, transportation and storage problems are reduced in hot melt adhesives.

**Disadvantages of hot melt adhesives**

- Hot melt cannot be used along with heat sensitive substrates.
- Hot melt adhesive bonds lose strength at high temperature.

1.6 Theories of adhesion

A general theory of adhesion must account for both the bonding process and the unbonding or fracture process. The theory should take into consideration both the adsorption and interdiffusion theories of adhesion and should include the aspects of cohesion and autohesion as a special case. In addition, mechanical adhesion is also important to the improvement of adhesive strength. The mechanical adhesion should be enhanced by greater contact with the irregularities or pores of the substrates; the viscosity and certain other properties of the adhesive will therefore be important on this basis. The term of adhesion refers to the coherence between two contiguous surfaces of materials of different nature, while the term autohesion refers to the ability of two contiguous surfaces of the same material to form a strong bond which prevents their separation at the site of contact. Two types of adhesion are often distinguished, namely the specific of inherent adhesion which involves the
binding force between adhesive and surface, and mechanical adhesion which refers to the penetration of the adhesive into pores and fissures of the surface, and retention of the solidified adhesive in these pores owing to mechanical wedging. The specific or inherent adhesion is accomplished via specific interaction between the adhesive and the substrate molecules, just as cohesion is regarded as a result of the action of forces of molecular attraction between similar molecules\textsuperscript{32}.

a. Mechanical interlocking theory

The mechanical interlocking theory of adhesion states that good adhesion occurs only when an adhesive penetrates into the pores, holes, crevices and other irregularities of the adhered surface of a substrate, and locks mechanically to the substrate (figure 1.10)\textsuperscript{33}. The adhesive must not wet the substrate, but also has the right rheological properties to penetrate pores and openings in a reasonable time. This theory explains a few examples adhesion such as ultra high modulus polyethylene (UHMPE) fiber and vinylester resin\textsuperscript{34} and the common practice to roughen a wood surface with glass paper\textsuperscript{35}. Since good adhesion can occur between smooth adherend surfaces in many studies suggests that the interlock may help promote adhesion, but is not really a generally applicable adhesion mechanism.

![Figure 1.10. The schematic model of mechanical interlock.](image)

Pretreatment methods applied on surfaces enhance adhesion. These pretreatments (especially plastic surface treatments) result in micro-roughness on the adherend surface, which can improve bond strength and durability by providing mechanical interlocking. Beyond mechanical interlocking, the enhancement of the adhesive joint strength due to the
roughing of the adherend surface may also result from other factors such as formation of a larger surface, improved kinetics of wetting and increased plastic deformation of the adhesive.

b. Adsorption theory

The adhesive macromolecules are adsorbed onto the substrate surface and held there by various forces of attraction. The adsorption is usually classified into primary forces and secondary molecular forces, sometimes called “Chemical bonding force” and “Van der Waals force”, respectively. This theory assumes a definite interface between the adhesive and adherend. The primary bonds are the strongest energies in the range of 100-1000 kJ/mol as compared with 20-40 kJ/mol of secondary forces. In case of urethane adhesives bonded to active hydrogen containing substrates, a primary bond is believed to exist as explained in figure 1.11.

![Figure 1.11. Schematic representations for covalent bonding of urethane adhesive with polar surface](image)

In addition, this theory is involving interactions between dipoles of various types but they fall into three groups:
(i) **Dipole/dipole interactions-Keesom forces**: This first group arises from the interaction and attraction of pairs of molecules which both have permanent dipoles.

(ii) **Dipole/induced dipole interactions-Debye forces**: The second group arises when a molecule with a permanent dipole approaches a molecule with no dipole and induces a temporary dipole in the neutral molecule and then an attraction arises.

(iii) **Molecule-molecule interactions-London Dispersion forces**: The third group is universal, causing attraction between energy pair of nonpolar particles which approach each other sufficiently closely, irrespective of any recognizable dipoles. They arise from the instantaneous quantum mechanical asymmetry of the electron clouds and hence transitory dipoles which interact.

c. **Diffusion theory**

The adhesive macromolecules diffuse into the substrate thereby eliminating the interface. The diffusion of segments and chain ends of polymers was suggested as a mechanism for the adhesion of similar elastomers above their $T_g$\(^3\)\(^3\). This is now generally accepted at least as the adhesion of two pieces of the same materials are contacted; their boning is termed “autohesion or self-bonding”, although not for the adhesion of different polymers even if they are reasonably similar. The consideration for quantitative development was derived from theories of mixing of liquids and being from Fick’s laws of diffusion\(^3\)\(^9\).

Fick’s first law relates the quantity of material diffusing (in the $x$-direction) across a plane normal to the concentration gradient:

$$dw = -D_f dt \frac{dc}{dx}$$

where $w$ is the quantity of material, $D_f$ the diffusion coefficient, $t$ the time, and $dc/dx$ the concentration gradient.

For deduced the various functions for the dependence of $D_f$ on other factors including concentration and nature of the diffusing molecule, and derived a theoretical peel energy, assuming that this depended on the depth of penetration and the number of chains crossing the phase boundary.

$$P = k_d(2Np/M)^{2/3}D_d^{1/2}c_1^{1/4}$$
Where $P$ is the peeling energy, $M$ the Avogadro’s number, $k_d$ a constant, $D_d$ is a constant which characterizes the mobility, of the macromolecules and is related to $D_f$, $N$ the number of chains crossing the boundary, $p$ the density, and $t_c$ the time of contact.

**d. Electrostatic theory**

The electrostatic theory describes that an electrical double layer is produced at any interface and the consequence coulombic attraction largely accounts for adhesion and resistance to separation. The theory can be viewed as treating the adhesives/substrate system as a capacitor that is charged due to contact of the two different materials. The Deryaguin’s theory as shown below can be used to represent the electrostatic theory,

$$A_c = \left( \frac{d_c \Sigma d}{8 \pi} \right) \left( dV_c/dh_c \right)^2$$

where $V_c$ is the discharge potential at the discharge gap, $h_c$ and $\Sigma d$ are the dielectric constant. A common example often described by the electrostatic theory is the adhesion of a plastic film on a layer of paper or another film of plastic.

**e. Weak boundary layers**

Two real materials, say A and B, that are composed of molecular components $a_i$ and $b_i$, respectively as shown in figure 1.12. These are located in the bulk ($a_{ib}, b_{ib}$), at the surface ($a_{is}, b_{is}$), and/or with in the near surface region ($a_{in}, b_{in}$). Upon contacting A and B under ambient conditions, the interface, defined as the locus of interactions between the two materials, initially involves the surface species on each and any entrapped air. In general, the interface will not be continuous at first. Entrapped air and surface rougosity prevent immediate, full molecular contact, although applied pressure can speed interface formation. With time, depending on the particular system, the region between the two bulk materials, the so-called interphase, changes. For example, the interface may thicken by interdiffusion and chemical reaction may occur. If the interface contains a mechanically weak boundary layer, it may be the site of fracture when the adhesive joint is loaded. Weak boundary layers (WBLs) may originate on or near the surface of materials before they are contacted, or they may develop in situ during the dynamic conditions of contact.
The provide a strong joint, the structural components, for instance, those responsible for the cohesive strengths of A and B, must interact well at the final interface, and a WBL must not be present. WBLs may be removed prior to bonding or be disrupted by diffusion during bonding.

After an adhesive contacts a solid substrate, it is normally necessary to convert it to a hardened state (setting) so that the joint will be capable of supporting stress. However, since setting severely reduces the molecular mobility required to achieve true contact and good bond formation, it should not take place too quickly. Many weak adhesive joints can be traced to rapid setting before sufficient interface formation. Setting of adhesive can occur by physical or chemical means. In order to minimize internal stresses in a joint, there should not be large change in volume of the adhesive during solidification, and the thermal expansion coefficients of the adhesive and adherends should be similar. This is especially important when the solid adhesive has a high modulus. Furthermore, joints with plane interfaces have been suggested to be more sensitive to adhesive shrinkage than are joints made with complex, high surface area adherends. Solvent based adhesive experience the most shrinkage during setting compared to those which harden by cooling (hot melt) or by chemical reaction (usually thermosets). The facts that epoxy resins shrink only about 3% upon setting is one reaction compared to many other condensation polymerizations that is no small molecules such as water which can interface with bonding, are created during setting. PU reactions are

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.12.png}
\caption{Two hypothetical real materials A and B; (a) prior to contact and (b) after contact.}
\end{figure}
also favorable in this regard. Some inorganic substances adhere exceptionally well because they expand on freezing. For example, ice will adhere to almost any surface, even those not wetted well by water. When water freezes in a depression in a solid surface, expansion causes it to lock against the sides of the depression and form a strong joint.

1.7 Conditions of joint formation and testing

In addition to the condition of the substrate surface, the conditions of joint formation and testing will affect the strength of an adhesive joint. In forming joint, increasing the temperature will lower the viscosity of the adhesive and this will generally, within certain limits, lead to higher bond strengths. Increasing the time at a particular temperature and increasing the pressure will also lead to improved wetting. The time lapse between forming and testing an adhesive joint is also important. Testing conditions that may have an important effect on the bond strength include (1) strain rate\(^46\), (2) temperature\(^47\), (3) humidity\(^48\) and (4) thickness of the adhesive layer\(^49\). In general, the bond strength increases with increasing strain rate. Increasing the temperature may either increase or decrease the bond strength. If stress concentrations are reduced, then higher values are achieved and this effect is perhaps most marked in peeling tests. However, in shear and direct tension tests, if the cohesive strength of the adhesive is greatly reduced by increased temperature, then large reductions in bond strength may result. Adhesive joints tend to be adversely affected by conditions of high humidity. It has frequently been shown, in direct tension and shear tests, that the strength of an adhesive joint decreases with increasing glue-line thickness. The precise reason for this is not clear, although one popular view is that thin layers of adhesive tend to minimize stress concentrations. Peeling tests are more important when flexible substrates such as films are involved, whereas shear and direct tension tests are more important with rigid substrates, such as molded plastic parts. To conclude, the strength of an adhesive joint depends on many factors some of which are associated with the formation and others with the breaking of the joint. It is clearly desirable that published bond strength should be accompanied by details of all the experimental conditions\(^50\).

The mechanical performance of the adhesive bond can be measured in a variety of methods. Many common tests are used to measure the mechanical properties of an adhesive bond such as peel test, wedge test, lap shear test and so on. The peel test is the method to access the bond energy for such a joint in which one of the adhering test is either much stiffer than the other or is firmly attached to a rigid support. Figure 1.13 describes the three
commonly used peel test configurations, i.e. 90°-peel test\textsuperscript{51}, 180°-peel test\textsuperscript{51} and T-peel test\textsuperscript{52}. Usually the peel angle ($\theta$) is kept constant during the test.

![Figure 1.13](image1.png)

**Figure 1.13.** Several typical peel test configurations: (a) 90° peel test, (b) 180° peel test and (c) T-peel test.

The use of lap shear test is convenient because the test geometry is simple and representative of commonly used joint designs in industry. A wide variety of joint configurations are possible when bonding structures. The single-lap and double-lap configurations are the most commonly found in practice and are applicable for joining relatively thin adherents. On the other hand, the more advanced stepped lap and scarf configurations are used to transfer high loads in joint with thicker adherents. Figure 1.14 represents two commonly used methods of lap shear test that is single lap shear test\textsuperscript{53} and double-lap shear test\textsuperscript{54}.

![Figure 1.14](image2.png)

**Figure 1.14.** Several typical lap shear test configurations: (a) single lap shear test and (b) double lap shear test.

Both tests were used to measure the SPU/aluminum and SPU/polypropylene joint strength in the present work.
1.8 Segmented polyurethanes in adhesive field

SPUs are linear polymers that have a molecular backbone containing urethane groups. These groups are produced through a reaction between a diisocyanate and a polyol. SPUs formulations cover an extremely wide range of stiffness, hardness and densities. Chemically these products are located between the two prototypes of two-component PUs. From a polymer physics point of view, however, it is a new class of elastomeric products which are characterized by segmented structure (block copolymer structure) of the primary chain. The secondary and tertiary structures, consequently, the morphology of these SPUs are dependent on the chemical composition and the length of the segment (blocks). The reason for the high property level of these products is due to the two- or polyphase structure. These polymers are used in building insulation, surface coating, solid plastic and adhesive. The crosslinked SPUs are important polymer although the linear SPUs are widely used in many applications because the crosslinked SPUs have more excellent mechanical properties than that in the linear one. The crosslinked SPUs have the general structure (A-B), where the soft segment (B) is usually formed from a polyether or polyester macroglycol. In addition, the hard segment (A) is formed by extending an aromatic diisocyanate with a low molecular weight diol, for instance 1,4-butaindiol. The SPUs can be separated into two microphases due to the structural difference of soft and hard segments. Hard domains play the role of physical crosslinks and act as a higher modulus filler in the low modulus soft matrix, whereas the soft phase gives extensibility to the polymer. Moreover, the incorporation of low molecular weight triol molecules into the SPU structure results in the formation of chemical crosslinks. Thus, the mechanical properties of SPUs are predominantly the result not only of two-phase morphology but also of the chemical crosslinker concentration\textsuperscript{55, 56}.

During the last seventy years, the scope of adhesive applications has grown from the familiar aspects of furniture and container manufacture to include such previously unexpected problems of producing plywood suitable for aircraft production, bonding rubber to metal, and preparing metal to metal joints more durable than riveted assemblies. Some of the major problems which were encountered and which have been only partially solved include the preparation of uniformly strong, vibration resistant and temperature resistant rubber to metal, plastic to metal, and metal to metal bonds and the adhesion of both natural and synthetic rubber to synthetic fibers. The adhesives based on isocyanates have shown promise for bonding metals, plastic, glass and wood but further development is required to clearly evaluate their merits for these purposes. One advantage of the isocyanate adhesives is
that of curing at room temperature. In a chemical sense the great majority of the isocyanate adhesive formulation may be divided into three classes: (1) polyisocyanates, which may be used alone or in mixtures with rubber (2) reaction products (prepolymer) of an excess of a polyisocyanate with an organic compound containing two or more active hydrogen groups such as polyesters and glycols (3) polymeric compounds containing active hydrogen groups which have been modified by reaction with a polyisocyanate. As in most classifications the line of demarcation between groups is sometimes obscure, but the classification is useful when considering the chemistry of curing the adhesive\textsuperscript{57, 58}.

a) Polyisocyanate adhesives

The first group of isocyanate adhesives is made up of the polyisocyanates which are used alone or more often in conjunction with polymers normally considered as unreactive such as rubber. Adhesives of this group are especially valuable for bonding unvulcanized rubber to fabrics and metals. In the bonding of rubber to fiber, the reaction of isocyanate groups with active groups in the fibers is also important, for instance, the common cellulose. The reaction occurred with water in the cellulose, rather than with the hydroxyl groups. Such a reaction with water would lead to the formation of polymeric ureas, which might contribute significantly to the good adhesion because of the mode of application. It is likely that reaction with atmosphere moisture plays an important part in the curing of adhesives of this group. The important factor, that is, the period of time might be enough for the solvent to evaporate and for the isocyanate to absorb moisture. Furthermore, the self life of adhesives is also affected by moisture. Moisture which is absorbed from the atmosphere will convert the polyisocyanate to polymeric, insoluble ureas. All isocyanate solutions or adhesives containing free isocyanate groups exhibit this sensitivity toward water. The self life may also be influenced by polymerization of the isocyanate by the dimerization of trimerization of NCO groups.

b.) Prepolymer adhesives

The second group of isocyanate adhesives includes polymers of low to moderate molecular weight which contain free isocyanate groups. These may prepared by reacting a polyfunctional active hydrogen compound with more than enough polyisocyanate to react with all of the active hydrogen groups. The prepolymer, which obtained from the reaction
between OH groups of polyol and NCO groups of diisocyanate is a high molecular weight isocyanate and will undergo reactions typical of isocyanates. It may be further cured by reaction with atmospheric moisture, as indicated below using more simplified formulas:

\[
R\text{NCO} + \text{H}_2\text{O} \rightarrow R\text{NH}_2 + \text{CO}_2
\]

Such a reaction with water will lead to chain lengthening if a difunctional active hydrogen compound was used initially or to chain lengthening and crosslinking if a polyfunctional active hydrogen compound was used. Crosslinking may also occur by reaction of isocyanate groups with the active hydrogen of urea and urethane groups in the adhesive itself:

\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
\text{NCO} & \quad \text{NCO} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R}
\end{align*}
\]

The polyhydroxy compound used in preparing these prepolymers may be a polyether, polyester, castor oil, a simple glycol, or related materials. Adhesive in this second group may be applied in one or both of two different techniques. First, in the case of low curing temperature, a solution of the adhesive is applied to the surface to be bonded. This coating exposed to the air for 10 to 15 minutes to permit the solvent to evaporate and for atmospheric moisture to initiate the cure. The surfaces are then joined under moderate pressure and held unit the cure is complete. The curing time varies from several hours to a day at room temperature, to a few minutes at 150 to 200 °C., and may be shortened by the proper choice
Curing agents other than water, e.g. diamines\textsuperscript{60)} or glycols\textsuperscript{61)} may also be mixed into the prepolymer just before applications. The second method of application is similar, except the adhesive film is first cured to a nontacky stat, which is stable indefinitely. The surface to be bonded are then joined and heated under pressure and fuse the adhesive film. One to five minutes may be required at 175 to 200 °C. After cooling, full or nearly full bond strength is obtained. This method is appropriate for materials which are not sensitive hydrogen groups. The good results from this second type of curing demonstrate that free isocyanate groups are not required for adhesion to metal or glass, but that a polymer of suitable molecular weight, degree of crosslinking and other physical properties, and containing urea and urethane links are adequate. In contrary, the reaction of isocyanate groups with the reactive groups of the polymers bonded may play an important role in establishing adhesion. The shelf life of these adhesives may be affected by polymerization of the isocyanate or reaction with atmospheric moisture or with active groups in the adhesive. Catalysts should not be included in the prepolymer during storage if maximum shelf life is desired.

c) Isocyanate-modified polymers

This group of isocyanate adhesives includes those active hydrogen containing polymers which are combined with disiocyanates or polyisocyanates. The polymers in this class include polyesters, polyethers, castor oil, hydroxyl-terminated urethane elastomers, and polyvinyl alcohol. The isocyanate is normally used in an amount of nearly equivalent to the hydroxyl groups in the polymer, so that the molecular weight of the polymer is greatly increased and crosslinking is normally introduced.

In this work, SPU adhesive was prepared by prepolymer technique due to the good application of this method, namely prepare in the moderate pressure and the adhesive can be cured in several temperatures.

1.9 Literature review of polyurethane adhesives

During the past 41 years, the use of adhesives has greatly increased as a result of the availability of improved adhesives based on synthetic polymers. PUs forms a particularly versatile class of adhesive polymers. It is well known that PUAs are widely used in the field of footwear, packaging and lamination. Adhesives are not replacing screws, rivets and nails
but are becoming a preferred alternative to spot welding, soldering and brazing. Use of adhesive can produce joints of higher strength, allow the assembly of components without the need to drill or perforate them, and avoids the heat distortion resulting from high temperature jointing processes. Surface modification for non-polar substrate is important for adhesive strength of PUA. In case of polar substrate, the surface modification is not necessary to use in the adhesive field.

Cui et al.\textsuperscript{62}) prepared isocyanate reactive hot melt adhesive from polyester or polyether glycols and diisocyanates. They found that the crystal of isocyanate prepolymer consisted in spherulites and sample with higher crystal content showed better green strength but slower adhesion development as a result of hindrance to moisture diffusion by the crystalline structure. Crystalline structure was suppressed by the penetration of crosslinking reactions. Heat of crystallization and onset crystallization temperature in cooling traces of cured sample melty was reduced by interruption of crosslinked bonding. Park et al.\textsuperscript{63}) studied the hot melt adhesive properties of a series of ethylene vinyl acetate copolymer (EVA)/aromatic hydrocarbon resin blend. The peak of loss modulus increased with increasing softening point of the aromatic hydrocarbon resin. The melt viscosity of the blends decreased with increasing temperature. In addition, the melt viscosity increased with increasing softening point, but decreased with increasing aromatic hydrocarbon resin and vinyl acetate content. In case of the same blend ratio, the increasing of softening point of the aromatic hydrocarbon resins increased the crystallinity whereas the addition of aromatic hydrocarbon resin decreased the crystallinity. Moreover, the lap shear strength increased with increasing softening point of the aromatic hydrocarbon resin. Somani et al.\textsuperscript{64}) synthesized PU adhesive from various polyols, obtained by reacting a castor oil derivative and diols (glycols) with diisocyanate adducts, where different NCO/OH ratios were used to give various compositions. They studied the effect of NCO/OH ratios, types of isocyanate adducts and chain length of glycols by determined wood-to-wood adhesion strength. They found that PU adhesives synthesized from ethylene glycol and aromatic isocyanate adduct show good adhesion strength and chemical resistance as there is no ether linkages in the networks whereas ether linkages in diethylene glycol and triethylene glycol is some what responsible for lower adhesion strength value and chemical resistance. O'Hare et al.\textsuperscript{65}) investigated the physicochemistry of the surface of untreated and corona discharge treated biaxially oriented polypropylene (BOPP) film using contact angle analysis, x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The surface energy was increased with increasing energy of corona. The functional groups incorporated onto the surface have been identified as hydroxyl, peroxy, carbonyl,
ester, carboxylic acid and carbonate. These groups are present in varying relative concentration, depending on the energy of the corona utilized. The morphology of the film changed after corona discharge treatment. Initially, a fibrillar crystalline structure was observed. On the other hand, after corona discharge treatment, a globular morphology became apparent. These globular features were attributed to low molecular weight oxidized material (LMWOM) created by corona discharge treatment. The roughness of the film was not found to increase under the corona conditions employed. Formation of LMWOM was found to be independent of treatment energy. However, two mechanisms have been suggested for its formation and these mechanisms dependent on the energy of treatment. Xu et al.\textsuperscript{66} prepared surface modification of polyester fabric by corona discharge irradiation at different voltages. The treated fabric showed increased wicking and hydrophilic properties and the properties can be preserved for a long time. Surface affinity between the treated fabric surfaces with modified starch sizing was also confirmed to be increased. Dyeing of the treated fabric showed that dyeing speed and the dye-uptake were improved. All the results are supposed due to the improved hydrophilic properties produced by the corona discharge treatment. Kwon et al.\textsuperscript{67} studied surface characteristics of polypropylene (PP) film treated by an atmospheric pressure plasma. They measured the contact angle of the surface by using polar solvent (water) and nonpolar solvent (methylene iodide) after the atmospheric pressure plasma treatment of PP film surface. And they also calculated surface free energy with respect to the conditions of atmospheric pressure treatment. The change of surface morphology and roughness before and after plasma treatment was observed by AFM analysis. The surface roughness of PP film showed the highest value when the plasma treatment time was 90 second. Finally, they analyzed the change of chemical compositions on the PP film surface through XPS. They found that polar functional groups, such as -CO, \text{-C=O} and -COO were introduced on the PP film surface after atmospheric pressure plasma treatment.

1.10 Purpose of this study

SPUs, consisting of soft segments and hard segments, are well known to separate into two microphases\textsuperscript{68}. Hard domains play a role of physical crosslink and acts as higher modulus filler in the low modulus soft matrix, whereas the soft phase gives extensibility to the SPU. SPU is one type of thermoplastics because physical crosslinks disappear above their melting points and are restored upon cooling\textsuperscript{69}. Their microphase separated structure reveals excellent mechanical properties in the bulk properties. SPUs are now widely utilized as
engineering materials in various industries such as automotive\textsuperscript{70}, medical equipment\textsuperscript{71}, adhesive products\textsuperscript{72} and so forth.

The process that allows the adhesive to transfer a load from the adherend to the adhesive joint is known as the adhesion. In general the adhesive can be intimately interacted either through chemical or physical forces to the adherend surface. The chemical interactions result from atomic scale attractions between specific functional groups of the adhesive and the adherend surface. During the curing process, the viscous adhesive material will flow to enable contact with the adherend and penetration of the surface asperities. As curing proceeds, the viscous product becomes rigid solid as the compounds react and cohesively link the adhesive, often referred to as crosslinking. This process enables strength to be established between the joined adherends.

Polyurethane adhesives are normally defined as those adhesives that contain a number of urethane groups in the molecular backbone, regardless of the chemical composition of the rest of the chain. Thus a typical urethane adhesive may contain urethane linkages, aliphatic and aromatic hydrocarbons, esters, ethers, amides, ureas and allophanate groups. An isocyanate group reacts with the hydroxyl groups of polyol to form the repeating urethane linkage. Isocyanate reacts with water to form a urea linkage and a carbon dioxide as a byproduct. Urethane adhesive have some advantages due to the following reasons:

1. They readily form hydrogen bonds to the substrates
2. They form covalent bonds with substrates that have active hydrogen
3. They effectively wet the surface of most substrates
4. Small molecular size allows them to permeate porous substrates

One of the primary mechanisms of bonding by urethane adhesive is believe to be through isocyanate (-NCO) to the active hydrogen containing surfaces and the through polar group (-NH and C=O). These polar groups are capable of forming strong chemical or physical interactions with the polar surfaces owning to the functional group having active hydrogen. Acceptance of polyurethane adhesive in a wide variety of different industrial uses (i.e. sealant\textsuperscript{73, 74}, automotive\textsuperscript{75}, glue, etc.) can be attributed to the versatility of the urethane polymer. This enables it to fulfill a number of important functions, such as providing comfort, safety and structural strength to the various industrial parts as needed.

The purpose of this study is the investigation about the effect of the aggregation structure of segmented polyurethane on adhesion properties. The segmented polyurethane were synthesized by a prepolymer method\textsuperscript{76-78} and the adhesive joint between polyurethane adhesive and substrate was made by hot melt adhesive\textsuperscript{79-82} and reactive hot melt adhesive\textsuperscript{83-85}.
method. An attempt to control the morphology and adhesion between adhesive and adherend was done by performing the different chemical crosslink density that is incorporated trifunctional agent (1,1,1-trimethylol propane) into segmented polyurethane structure through curing in different temperature, in different environmental (e.g. different relative humidity) and transferring into different mold temperature. In addition, polyurethane adhesive was performed with two types of substrates (aluminum and polypropylene) to examine the adhesive strength and fracture behavior. Moreover, the surface roughness of aluminum and corona treatment of polypropylene was controlled as follows:

- Aluminum substrate was immersed in 5% w/v hydrochloric acid for 60 min.
- Polypropylene film was treated by AC corona discharge under ambient conditions for treatment time of 10 sec. The corona treatment using a high frequency corona treater with an output voltage of about 10 kV. The distance between the grounded sample and the stationary tip of the corona needle was 1 cm.

Thus, this study hopefully might develop the new application for diisocyanate-terminated polyurethanes which have good adhesion properties without enormously loosing its mechanical properties.
References


Segmented polyurethane elastomers (SPUs) are composed of hard segment domain and soft segment matrix which separate into two microphases\(^1\). Hard segment domains play a role of physical crosslinks in a soft segment matrix. The soft segment phase gives extensibility to the polyurethane. The microphase-separated structure causes excellent mechanical properties in bulk of the SPUs. Thus, the SPUs are used in various applications such as daily life materials, industrial parts, elastomers and adhesives\(^2, 3\). In order to attain excellent properties, many studies have been directed toward understanding the microphase separation and its effect on the bulk properties\(^4-8\).

The distribution of polar hard segment domains at the surface as well as the microphase-separated structure is quite important when polyurethane is used as coating materials, adhesives and so on. Okazaki et. al\(^9\) reported the effects of blend ratio of BD/TMP on friction and abrasion properties of polyurethanes. When the content of BD is increased, phase separation proceeds and spherulites are observed. SPU with higher BD blend ratio exhibited lower friction coefficient. If the crosslinking agent such as TMP is incorporated into SPUs, it would affect the interfacial structure. When polyurethane is used as an adhesive, the degree of microphase separation and its distribution at the polyurethane adherend interface is more important because they strongly affect interaction at the interface. Duffy et. al\(^10\) reported the model of polyurethane based reactive hot melt adhesive using a ternary blend of polyether, polyester and an acrylic. The incorporation of urethane groups tends to improve ternary blend miscibility when increasing the molecular weight of polyether and polyesters. On the other hand, an increase in the molecular weight of the prepolymer destabilizes the ternary blends. However, the relationship between the aggregation of hard segment domains at the interface and the adhesion properties of SPUs has not been well understood.

In this study, the chemically crosslinked SPUs was produced by different blend ratios of BD/TMP and investigated the effect of the blend ratio on the microaggregation structure and adhesion properties of SPUs.
2.2 Experimental

2.2.1 Materials

Poly(oxytetramethylene) glycol (PTMG) with the average molecular weight ($M_n$) of 2018 and 4,4’-diphenylmethane diisocyanate (MDI) were supplied from Nippon Polyurethane Industry, Co., Ltd, Japan. 1,4-Butanediol (BD) and 1,1,1-trimethylol propane (TMP) (Wako Chemical, Co., Ltd., Japan) were used as a curing agent. PTMG was dried with dried nitrogen under reduced pressure. To remove water, BD was distilled prior to use in polymerization. Toluene (Wako Chemical, Co., Ltd., Japan) was also distilled prior to use in swelling test. Methylene iodide used in contact angle measurement was supplied from Wako Chemical, Co., Ltd., Japan. Ultra pure water for contact angle measurement was prepared with a Millipore Simpli Lab-UV (Nippon Millipore, Japan). Figure 2.1 shows chemical structure of materials for synthesis SPUs.

![Chemical structures of materials for synthesis SPUs](image)

**Figure 2.1.** Chemical structures of all materials for synthesis SPUs.
2.2.2 Polymer synthesis

SPUs were synthesized using a prepolymer method. Synthetic scheme of the SPUs is shown in Figure 2.2. The prepolymer was prepared from PTMG and MDI with a ratio of \([\text{NCO}]/[\text{OH}] = 3.30\) at 70 °C for 6 h under a nitrogen atmosphere. The curing agents was added to the prepolymer with NCO INDEX = \([\text{NCO}]_{\text{pre}}/[\text{OH}] = 1.05\) and stirred for 5 min, where \([\text{NCO}]_{\text{pre}}\) is the concentration of NCO groups in a prepolymer. The viscous product was then poured into a mold constructed by a spacer of 0.5 mm thickness. The two aluminum plates were heated at 130 °C prior to use. The sample was cured for 24 h at 100 °C under an air atmosphere. SPUs with various blend ratios of BD/TMP were denoted as SPU-100/0, SPU-90/10, SPU-75/25 and SPU-50/50.

![Synthetic scheme of SPUs with different blend ratio of BD/TMP.](image)

**Figure 2.2.** Synthetic scheme of SPUs with different blend ratio of BD/TMP.
2.2.3 Characterization

2.2.3.1 Swelling measurement

Gel fraction ($g$) of the SPU was determined from the original weight and the weight of dried sample after swollen to the equilibrium state in toluene at 60 °C as follows: $g = W_b/W$, where $W_b$ and $W$ are the weight at which a sample is swollen and dried, and the original weight, respectively. The degree of swelling of the SPUs was determined from the weight before and after equilibrium swelling with toluene. The degree of swelling ($q$) was calculated by equation (1) and (2).

$$q = 1 + Q$$

$$Q = \left[ \frac{(W_a - W_b)/d_s}{W_b/d_p} \right]$$

where $Q$, $W_a$, $d_s$, and $d_p$ are the volume ratio of solvent in the swollen state to gel in the unswollen state, the weight of a sample swollen to the equilibrium state, the density of solvent and the density of a sample, respectively.

Crosslink density and molecular weight between crosslinking points were calculated from the Flory-Rehner equation$^{11-13}$.

$$\nu_c = \frac{-1}{V_s} \left[ \frac{V_p + \chi V_p^2 + \ln(1 - V_p)}{d_p \left( V_p^{1/3} - V_p / 2 \right)} \right] = \frac{1}{M_c}$$

where $\nu_c$ is the crosslink density; $V_s$ is the molar volume of the solvent (toluene: $1.068 \times 10^2$ cm$^3$/mol); $V_p$ is the volume fraction of polyurethane in the swollen state, which is equal to $V_p = 1/(1+Q)$; $\chi$ is the solvent interaction parameter (In this case, $\chi = 0.5353$); $d_p$ is the density of the polyurethane; and $M_c$ is the molecular weight between crosslinking points.
2.2.3.2 Macroscopic observation

Macroscopic structures were observed by polarized optical microscopy (POM; Optiphotp2-Pol, Nikon Corporation, Japan) at room temperature. A sensitive color plate with a wavelength of 530 nm was used for birefringence analysis.

2.2.3.3 Thermal analysis

Differential scanning calorimetry (DSC) measurements were performed to investigate the thermal properties of the SPUs. Thermograms of the SPUs were recorded with DSC (DSC8230, Rigaku Denki, Co., Ltd., Japan) at a heating rate of 10 °C/min from -140 to 250 °C under a nitrogen atmosphere.

2.2.3.4 Surface free energy measurements

Surface free energy were investigated using contact angle (θ) measurements with water and methylene iodide\textsuperscript{14, 15}. Water and methylene iodide were used as probe liquid because it did not interact with polyurethane. The contact angle of these liquids on the surface of SPUs was measured with a Dropmaster 300 (Kyowa Interface Science Co., Ltd., Japan) using a sessile drop method. The averaged contact angle was determined from at least ten different locations for each SPUs. The surface free energy of the SPUs was calculated, according to the extended Fowkes equation\textsuperscript{16-18}. The surface free energy (\(\gamma_S\)) can be expressed as follows;

\[
\gamma_S = \gamma_S^d + \gamma_S^p
\]  

(4)

where \(\gamma_S^d\) is from the dispersion (nonpolar) component and \(\gamma_S^p\) represents the polar one.

During the equilibrium contact angle measurements for a liquid drop on an ideally smooth and homogeneous solid surfaces, Owens and Wendt\textsuperscript{19}, and Wu extended the Young’s equation using geometric means\textsuperscript{20}, as follow;

\[
1 + \cos \theta = 2\sqrt{\gamma_S^d \left(\frac{\gamma_L^d}{\gamma_{LV}}\right)} + 2\sqrt{\gamma_S^p \left(\frac{\gamma_L^p}{\gamma_{LV}}\right)}
\]  

(5)
where subscripts $L$ and $S$ are the liquid and solid states, respectively. The superscripts $d$ and $p$ refer to the dispersion force and polar force components, respectively.

### 2.2.3.5 T-peel strength

Testing specimens were prepared as follows; the aluminum plates were washed with acetone and put in 5% w/v hydrochloric acid solution for 90 min at room temperature. They were then washed with distilled water and dried at 40 °C for 2 hours. The press condition were selected at 250 °C corresponding above melting temperature of the hard segment domains under 0.5 MPa for 10 min, followed by slow cooling, and then kept for overnight with the relative humidity of 40%. The adhesion joint of SPUs and two aluminum plates were obtained by pressing in the dimension of 114×25 mm$^2$ and the SPUs thickness was 0.5 mm. T-peel strength of SPUs was measured using a tensile tester (RTE-1210, A&D Co., Ltd., Japan). The sample was peeled at a crosshead speed of 20 mm/min at room temperature. The peel strength was obtained from the mean of three experiments.

### 2.2.3.6 T-peel failure behavior

To investigate the failure behavior of the SPU adhesive, the surface of the aluminum plates were observed after T-peel testing with optical microscopy (OPTIPHPT2-POL, Nikon Corporation, Japan).

### 2.3 Results and discussion

Table 2.1 shows structural parameter and properties of SPUs. The degree of swelling increased with decreasing TMP content. Total crosslink density was calculated using Flory-Rehner’s equation. Chemical crosslink density was determined stoichiometrically. The total crosslink density and chemical crosslink density increased whereas physical crosslink density decreased with an increase in TMP content. This result indicates that the formation of physical crosslinking in SPUs was suppressed by the network structure in SPU chains.
Table 2.1 Structural parameters and properties of SPU with various blend ratio of BD/TMP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Curing agent (wt%)</th>
<th>Degree of swelling in Toluene</th>
<th>Total crosslink density (mol/cm³)×10⁻³</th>
<th>Physical crosslink density (mol/cm³)×10⁻³</th>
<th>Chemical crosslink density</th>
<th>Molecular weight between crosslinks (g/mol)×10³</th>
<th>T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPU-100/0</td>
<td>100 0</td>
<td>2.56</td>
<td>0.37</td>
<td>0.37</td>
<td>0.00</td>
<td>2.67</td>
<td>-65.9</td>
</tr>
<tr>
<td>SPU-90/10</td>
<td>90 10</td>
<td>2.44</td>
<td>0.41</td>
<td>0.31</td>
<td>0.10</td>
<td>2.44</td>
<td>-64.1</td>
</tr>
<tr>
<td>SPU-75/25</td>
<td>75 25</td>
<td>2.38</td>
<td>0.48</td>
<td>0.24</td>
<td>0.24</td>
<td>2.09</td>
<td>-52.5</td>
</tr>
<tr>
<td>SPU-50/50</td>
<td>50 50</td>
<td>2.14</td>
<td>0.71</td>
<td>0.22</td>
<td>0.49</td>
<td>1.40</td>
<td>-49.1</td>
</tr>
</tbody>
</table>

Figure 2.3 shows DSC thermograms of the SPU with various blend ratios of BD/TMP. Glass transition temperature of the soft segment chains (T_g) elevated from –66.0 to –56.3 °C with an increase in TMP content. Melting temperature of hard segment domains (T_m,H) of SPU-100/0 was observed at 188.4 and 209.0 °C. T_m of SPU-90/10 and SPU-75/25 were observed at 210.8 and 208.0 °C, respectively. It is noteworthy that no T_m was observed for SPU-50/50. It is well known that increasing T_g of soft segment in SPU means an increase in miscibility of two components on account of the molecular interaction between soft and hard segments. The change of microaggregation structure with different TMP content can be explained as follows. For the lower TMP content, the hard segment possesses a linear urethane chain, resulting in high crystallizability. On the other hand, for higher TMP content, the content of linear hard segment chains was reduced and chemical crosslinking points increased. Thus, crystallizability of the hard segment is quite low. Therefore, the degree of microphase separation of the SPU became weaker with increasing TMP content.
Figure 2.3. DSC thermograms of the various SPUs measured at a heating rate of 10 °C min⁻¹.
Figure 2.4 shows polarized optical micrographs of SPU with different blend ratios of BD/TMP. The spherulite size of SPU-100/0, SPU-90/10, SPU-75/25 and SPU-50/50 were 25-35, 20-25, 10-20 and 8-10 μm, respectively. When the TMP blend ratio decreased, the spherulite size increased. These spherulites are found to be negative spherulites; that is, polymer chains oriented perpendicular to the radial direction. It is known that the spherulites were composed of a small soft segment component and a lot of hard segment component.\(^9\) SPU with low chemical crosslinking had small negative spherulites with well-defined Maltese cross. However, the structure of spherulites of SPU with high chemical crosslinking turn into loose spherulites, so-called sheaf-like.\(^4, 21\) Thus, it seems reasonable to consider that the chemical crosslinking points interrupt the aggregation of hard segments to form spherulites.

![Figure 2.4](image_url)  
**Figure 2.4.** Polarizing optical microscopic images of SPUs with various blend ratio of BD/TMP; (a) SPU-50/50, (b) SPU-75/25 (c) SPU-90/10 and (d) SPU-100/0.
The relationships between contact angle and TMP content is shown in Figure 2.5. The contact angles of water and methylene iodide of all SPUs was found from 87.8 to 107.7° and 65.9 to 74.1°, respectively. SPU-100/0 had the highest wettability by water, i.e. smallest contact angle, indicating the highest surface free energy. These results suggest that the excellent intermolecular interaction between SPUs surface and water that is the high hydrophilic component (polar component) on the surface of SPUs.

**Figure 2.5.** Relationships between contact angle and TMP content for SPUs.
The value of total surface free energy ($\gamma_S$), dispersion component ($\gamma_S^d$) and polar component ($\gamma_S^p$) of the SPUs are summarized in Table 2.2. These values were calculated by eq.(4) and (5). Figure 2.6 shows $\gamma_S$, $\gamma_S^d$ and $\gamma_S^p$ of the SPUs with various blend ratios of BD/TMP. The $\gamma_S$ of SPU-100/0, SPU-90/10, SPU-75/25 and SPU-50/50 were 39.8, 33.3, 32.3 and 27.3 mJ/m$^2$, respectively. With increasing content of TMP, the value of $\gamma_S$ for the SPUs decreased. $\gamma_S^p$ exhibited same trend as well. On the other hand, the value of $\gamma_S^d$ increased with increasing TMP content. The reason that the $\gamma_S^p$ of SPU-100/0 is the highest in the four SPUs are attributed to strong segregation of the hard segment chains at the surface. For SPU-50/50, segregation of the hard segment chains was suppressed and many soft segments were segregated at the surface because of existence of TMP molecules.

Table 2.2 The value of $\gamma_S$ and its components for SPUs with various blend ratios of BD/TMP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\gamma_S^d$ (mJm$^{-2}$)</th>
<th>$\gamma_S^p$ (mJm$^{-2}$)</th>
<th>$\gamma_S$ (mJm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPU-100/0</td>
<td>20.7</td>
<td>19.2</td>
<td>39.8</td>
</tr>
<tr>
<td>SPU-90/10</td>
<td>23.1</td>
<td>10.2</td>
<td>33.4</td>
</tr>
<tr>
<td>SPU-75/25</td>
<td>24.7</td>
<td>7.7</td>
<td>32.4</td>
</tr>
<tr>
<td>SPU-50/50</td>
<td>25.8</td>
<td>1.6</td>
<td>27.4</td>
</tr>
</tbody>
</table>
Figure 2.6. Effect of BD/TMP blend ratio on surface free energy (in mJm$^{-2}$) of SPUs.

$\gamma_{s}^d$; surface free energy of the dispersion component.

$\gamma_{s}^p$; surface free energy of the polar component.
Figure 2.7 shows T-peel strength of SPUs with different blend ratios of BD/TMP. To understand the aggregated hard segment affect adhesive strength in SPUs in Figure 2.7, the schematic model of the aggregated hard segment components at the SPUs/aluminum interface was drawn in Figure 2.8. T-peel strength of SPUs decreased as the content of TMP increased, namely decreased from 10.36 MPa of SPU-100/0 to 2.03 MPa of SPU-50/50. In other words, the adhesive strength decreased with an increase in crosslink density. Since SPU-100/0 and SPU-90/10 were pressed with aluminum substrates above melting temperature of hard segment, the SPUs melt was spreaded properly on the surface of substrates and they can adhere to aluminum surface after cooling. In this cooling process, high surface free energy component, hard segment chains in a linear molecular structure, segregates at the adhesive/aluminum interface to minimize the interfacial free energy. Thus, the strong interaction between SPUs and aluminum surface can be attained. On the other hand, opposite phenomena happened to SPU-50/50. For SPU-50/50, TMP suppresses the formation of the well-ordered and crystallized hard segment domains and causes phase mixing trend between soft and hard segment components. It seems that these phenomena occurs even at the surface region of SPUs. Furthermore, there is no hard segment domain, which can be melted by heating. Thus, peel strength of SPU-50/50 was the lowest of the all SPUs. It seems reasonable to conclude from surface free energy that polar hard segment component exists at the top surface of SPU with low TMP content, in contrast, both disordered hard segment chains and soft segment component exist with high TMP content.

Figure 2.7. T-peel strength of SPUs with different blend ratios of BD/TMP.
To investigate directly the surface failure of the SPUs, we made optical microscopy observations for the aluminum plate surface. Figure 2.9 shows optical microscopic images of aluminum surface after T-peel testing for (a) SPU-100/0, (b) SPU-90/10, (c) SPU-75/25 and (d) SPU-50/50. Three different failure modes were observed after T-peel test. First, the cohesive failure was observed for SPU-100/0 and SPU-90/10. The high residue of SPU adhesive was found in all aluminum surface area as shown in Figure 2.9(a) and (b). These results clearly imply the strong interaction between SPU and aluminum plate surface, which is caused from the lower chemical crosslink density and segregation of higher surface free energy component. Second, the interfacial failure was observed for SPU-50/50. No residue of SPU adhesive was almost observed on the aluminum substrate as shown in Figure 2.9(d). These results indicate that the strong network structure in SPU chains was formed by chemical crosslinking and the SPU does not interact with the aluminum surface due to a phase mixing trend of soft and hard segment chains. That is, this fracture is attributed to poor adhesion between SPU-50/50 and aluminum substrate. Finally, the cohesive-interfacial failure was observed for SPU-75/25. The residue of SPU adhesive was found in almost area of aluminum substrate and the surface of substrate cannot see clear as shown in Figure 2.9(c). It can be suggested that the cohesive and interfacial failures were occurred simultaneously when the moderate crosslink density contained in the SPU structure.

Figure 2.8. Schematic model of the aggregated hard segment components at the SPUs/aluminum interface.
To understand the failure behavior of SPUs in Figure 2.9, the schematic model of T-peel fracture behavior of SPUs was drawn in Figure 2.10. Cohesive failure is fracture occurring within the adhesive layer that is when the specimen was peeled, the adhesive was deformed and the fracture was arisen within the adhesive layer. A typical fracture surface model of cohesive failure is shown in Figure 2.9(a). Interfacial failure as represented in Figure 2.9(c) is explained that when a specimen was peeled, the adhesive detached from the substrate and no residue adhesive or very low residue adhesive on the aluminum substrate. Moreover, cohesive failure and interfacial failure occurred simultaneously that is when a specimen was peeled, some adhesive layer was fractured and there was a residue of partial adhesive on the aluminum substrate. This is called cohesive-interfacial failure (Figure 2.9(b)).

![Figure 2.9. Optical microscopic images of aluminium surface after T-peel testing for SPUs; (a) SPU-100/0, (b) SPU-90/10, (c) SPU-75/25 and (d) SPU-50/50.](image-url)
2.4 Conclusion

Four kinds of PTMG-MDI-based SPUs were prepared by different blend ratios of BD/TMP (BD/TMP = 100/0, 90/10, 75/25 and 50/50). In this study, it can be concluded as followed:

1. The total crosslink density and chemical crosslink density increased whereas the physical crosslink density decreased with increasing blend ratio of TMP.

2. When increasing TMP blend ratio, the chemical crosslinking point interrupted the aggregation of hard segments to form spherulites and the degree of microphase separation of the SPUs became weaker.

3. The surface free energy, the water wettability and T-peel strength of the SPUs decreased because of the polar hard segment component cannot segregate at the top surface of SPUs with increasing TMP.

**Figure 2.10.** Schematic model of T-peel fracture behavior of SPUs; (a) cohesive failure (b) cohesive-interfacial failure (c) interfacial failure.
4. Three failure modes were observed after T-peel testing. That is, the cohesive failure, the cohesive-interfacial failure and the interfacial failure observed for the SPU with low, moderate and high TMP blend ratio, respectively. These were explained by the strong network structure, which is formed by chemical crosslinking and the SPU does not interact with aluminum surface due to a phase mixing trend of soft and hard segment chains, thus this fracture led to the interfacial failure and the strong interaction between SPU and aluminum plate surface led to the cohesive failure.
References

Chapter 3 Study of the Effect of Polymer Glycols on Mechanical and Adhesion Properties of Polyurethanes.

3.1 Effect of Polymer Glycols on the Micro-aggregation Structure and Mechanical Properties of Segmented Polyurethanes

3.1.1 Introduction

Polyurethane elastomers (PUEs) have excellent mechanical properties compared with general-purpose elastomers. These characteristics are utilized in many kinds of industrial products such as industrial parts, building materials, sport goods, medical fields and daily life products. These properties are strongly dependent on chemical structures and super-structures of PUEs. The super-structures of PUEs are varied with raw materials, recipes, preparation conditions, molding condition, and so on. Therefore, control of morphology of PUEs is required to obtain high performance PUEs\(^{1-4}\).

In recent years, investigation of multi-component polymers with graded micro-domain structures has been conducted. Okinaka et al.\(^ {5-6}\) studied binary polymer mixtures undergoing phase separation induced by a temperature gradient. Liu et al.\(^{7}\) designed the epoxy resin (EP)/polyurethane (PU) functionally graded material by microwave irradiation and reported that the temperature and thermal stress distribution decreased along the graded direction of these functionally graded materials. Okazaki et al.\(^ {8-10}\) designed polyether based PUE with graded microdomain structures by using of mold with different temperatures. They found that the mechanical properties were changed continuously with variation of micro-domain structure at mold temperature of 130 °C. Furukawa et al.\(^{11}\) found that the higher BD content and molecular weight of polymer glycol exhibited stronger phase separation on the temperature gradient of FGPUEs. However, structures and mechanical properties of functionally graded polyurethane elastomers have not been studied in spite of important research to develop novel functional materials.

In this study, PUEs with graded micro-domain structures were prepared from various polymer glycols using a mold with temperature gradient. The effect of polyether and polyester glycols on the micro-aggregation structure and mechanical properties of the PUEs were studied by DSC, polarizing optical microscopy, pulse NMR, micro-hardness test and tensile test.
3.1.2 Polymer preparation

3.1.2.1 Materials

Poly(oxytetramethylene)glycol (PTMG: $M_n = 2000$, Nippon Polyurethane Ind., Co., Ltd., Japan), poly(ethylene adipate)glycol (PEA: $M_n = 2000$, Mitsui Takeda Chemical, Co., Ltd., Japan), and poly(hexamethylene adipate)glycol (PHA: $M_n = 2000$, Nippon Polyurethane Ind., Co., Ltd., Japan) were used as a polymer glycol. The polymer glycols were dried by bubbling dried nitrogen gas under reduced pressure at 80 °C before preparing polyurethanes. 4,4-Diphenylmethane diisocyanate (MDI, Nippon Polyurethane Ind., Co., Ltd., Japan) was used as received after the determination of isocyanate content. 1,4-Butanediol (BD, Wako Chemical, Co., Ltd., Japan) and 1,1,1-trimethylol propane (TMP, Wako Pure Chemical, Co., Ltd., Japan) as a curing agent were used by purification with vacuum distillation and recrystallization, respectively.

3.1.2.2 Polymer synthesis

The PUEs were prepared from each polymer glycol, MDI and a mixture of BD and TMP as a curing agent by a prepolymer method. The blend ratio of curing agent (BD/TMP) was weight ratio of 75/25. Synthetic scheme of the spherulite size graded polyurethane elastomers is shown in Figure 3.1. The prepolymer was prepared from each polymer glycol and MDI with a ratio of $[\text{NCO}]/[\text{OH}] = 3.30$ at 70 °C for 6 h under a nitrogen atmosphere. The curing agents were added to the prepolymer with NCO INDEX = $[\text{NCO}]_{\text{pre}}/[\text{OH}] = 1.05$ and stirred for 3 min, where $[\text{NCO}]_{\text{pre}}$ is the concentration of NCO groups in the prepolymer. The viscous product was then poured into a mold constructed with a spacer 2 mm thick. Two aluminum plates were heated at 30 and 150 °C prior to use, respectively. When the casting was initiated, the temperatures of low and high temperature mold plates transformed to 60 and 130 °C, respectively. The sample was cured for 1.5 hours at 130 °C. Then, a sheet of 2 mm thickness was demolded, and the sheet was post-cured at 110 °C for 24 hours under an air atmosphere. PTMG based PUE, PEA based PUE and PHA based PUE were denoted as PTMG-PUE, PEA-PUE and PHA-PUE, respectively.
Figure 3.1. Synthetic scheme of polyurethane elastomers with spherulite size graded structure.
3.1.3 Characterization

3.1.3.1 Preparation of thin film using a microtome

The PUEs of 2 mm thickness was sliced up to five pieces (about 0.4 mm thickness) by a microtome (Yamato Koki Co., Ltd., ROM-380 model, Japan). These obtained sheets are used for following tests.

3.1.3.2 Density and swelling measurement

Density was measured by the weight of polyurethane in air and the weight of polyurethane in water.

The gel fraction (g) of the PUEs was determined from the original weight and the weight of the dried polyurethane after swelling to an equilibrium state in toluene and N,N-dimethyl acetamide (DMA) at 60°C, using the following formula:  
\[ g = \frac{W_b}{W} \]

where \( W_b \) is the weight of the sample that was dried after equilibrium swelling, and \( W \) is the original weight. The degree of swelling of the PUEs was determined from the weights before and after equilibrium swelling with toluene and DMA. The degree of swelling (\( q \)) was calculated by equations (1) and (2).

\[
q = 1 + Q
\]

\[
Q = \left[ \frac{(W_a - W_b) / d_s}{W_b / d_p} \right]
\]

where \( Q \), \( W_a \), \( d_s \) and \( d_p \) are the volume ratio of solvent in the swollen state to gel in the unswollen state, the weight of a sample swollen to the equilibrium state, the density of the solvent and the density of sample, respectively.

3.1.3.3 Macroscopic observation

The spherulite structures were observed by polarized optical microscopy (POM, Optiphoto2-Pol, Nikon, Co., Ltd., Japan). A sensitive color plate with wavelength of 530 nm was used for birefringence analysis.
3.1.3.4 Thermal analysis

Differential scanning calorimetry (DSC) measurement was performed to determine the thermal behavior of PUEs. Thermograms of PUEs were recorded with DSC (DSC8230HT, Rigaku Denki, Co., Ltd., Japan) at heating rate of 10°C/min from -140 °C to 250 °C under a nitrogen atmosphere.

3.1.3.5 Functional group analysis

Fourier transfer infrared (FT-IR) spectra of PUEs were recorded by FI-IR spectrometer (Bio-Rad FTS 3000, Nippon Bio-Rad Laboratories, Inc., Japan) in the ATR mode at the wavelength range between 4000 and 500 cm\(^{-1}\). The sensitivity, the resolution and the number of scanning were 1, 4 cm\(^{-1}\) and 32 times, respectively.

3.1.3.6 Pulsed nuclear magnetic resonance measurement of molecular mobility

Pulsed Nuclear magnetic resonance spectrometer (NMR; JNM-MU25AH model, JEOL, Co., Ltd., Japan) in the solid echo mode at 25 °C was used to determine the mobility of hard segment or soft segment chains. Samples were cut into small pieces and densely added into the sample glass tube.

3.1.3.7 Hardness analysis

The changes of micro-hardness due to the temperature gradient were measured by micro-hardness test. This test was performed for each 100 µm of cross section from one surface to the other surface by using micro-durometer (Asker, MD-1 model, Japan) based on JIS K 6253. The micro-hardness was determined as the International Rubber Hardness (IRHD).

3.1.3.8 Tensile strength measurement

Tensile test was performed by means of the Instron type tensile tester (RTE-1210, A&D Co., Ltd., Japan) at ambient temperature. Specimen size was 60.0 mm × 5.0 mm × 0.4 mm. The initial length and elongation rate were set to be 30 mm and 10 mm/min, respectively.
3.1.4 Results and discussion

Table 3.1 shows the density, gel fraction and degree of swelling for the lower, higher temperature side and the middle part of PTMG-, PEA- and PHA-PUEs. The samples obtaining from the lower, middle, and higher temperature sides of all PUEs were abbreviated as LTS, Middlle and HTS, respectively. Density of each position of PTMG-, PEA- and PHA-PUEs was quite similar about 1.05×10^3 kg/m^3, 1.21×10^3 kg/m^3 and 1.15×10^3 kg/m^3, respectively. These results clearly suggest that the density of each series of the PUEs was dependent on soft segment structure but independent on molding temperature. The gel fractions in both solvents of all three PUEs were over 97 %. The gel fraction of the all UEs at low temperature side (LTS) was smaller than that at high temperature side (HTS). The degree of swelling in toluene and DMA differed with structure of the polymer glycols, and that of all PUEs slightly increased from LT to HT. The results suggest that the morphology at each position of each PUEs are different and the morphology of PUEs with the different polymer glycols are also different.
Table 3.1 The density, gel fraction and degree of swelling for the lower and higher temperature side and the middle part of PTMG-, PEA- and PHA-PUEs.

<table>
<thead>
<tr>
<th>PUE</th>
<th>Position</th>
<th>Density (kg/m³)×10³</th>
<th>Gel Fraction (%)</th>
<th>Degree of Swelling Toluene</th>
<th>DMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMG-PUE</td>
<td>Middle</td>
<td>1.06</td>
<td>98.3</td>
<td>97.7</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>LTS</td>
<td>1.05</td>
<td>98.5</td>
<td>97.9</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>HTS</td>
<td>1.05</td>
<td>98.3</td>
<td>98.8</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td>LTS</td>
<td>1.20</td>
<td>97.2</td>
<td>98.6</td>
<td>1.32</td>
</tr>
<tr>
<td>PEA-PUE</td>
<td>Middle</td>
<td>1.21</td>
<td>98.0</td>
<td>98.9</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>HTS</td>
<td>1.21</td>
<td>98.5</td>
<td>99.2</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td>LTS</td>
<td>1.15</td>
<td>98.3</td>
<td>95.3</td>
<td>1.81</td>
</tr>
<tr>
<td>PHA-PUE</td>
<td>Middle</td>
<td>1.15</td>
<td>98.1</td>
<td>96.2</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td>HTS</td>
<td>1.15</td>
<td>98.9</td>
<td>97.6</td>
<td>1.84</td>
</tr>
</tbody>
</table>
Figure 3.2 shows polarizing micrographs taken at each part in PTMG-, PEA- and PHA-PUEs. The PUEs in contact at low temperature mold plate had many small pherulites. On the other hand, the opposite phenomena occurred with PUEs in contact at high temperature mold plate. Additionally, the spherulite size of PTMG-PUE was higher than that of PEA- and PHA-PUEs. These spherulites were the negative spherulites; that is, the molecule oriented perpendicular to the radial direction. It is known that the spherulites are composed of a small amount of soft segment component and a lot of hard segment component\(^9\). Thus, it can be suggested that the carbonyl group in polyester polyol interrupt the aggregation of the hard segments to form spherulites.

![Figure 3.2](image_url)  

**Figure 3.2.** Polarized optical microscopic images at each part in (a) PTMG-PUE, (b) PEA-PUE and (c) PHA-PUE.
The effects of molding temperature on the spherulite diameter and the number of spherulite were shown in Figure 3.3 and 3.4, respectively. All PUEs in contact with lower temperature mold had large number of spherulites. These spherulites grew to 12.6 ~ 16.3 µm diameter in PTMG-PUE, to 8.4 ~ 15.6 µm diameter in PEA-PUE and to 10.4 ~ 16.0 µm diameter in PHA-PUEs from the LTS toward the HTS. The number of spherulites decreased and the size increased gradually toward the HTS. The spherulite size of PEA- and PHA-based PUEs (polyester based PUEs) was smaller than those of PTMG based PUE (polyether based PUE) at each position. The continuous changes of spherulite size depending on the temperature gradient and type of polymer glycols were explained as follows. The spherulites grew outwards from the nucleation points but could not grow out radially in all direction either contacted at low temperature or when the spherulites met each other. Generally, the growth rate is extremely temperature sensitive and control by the nucleation. The nucleus growth in the HTS was very slow, resulting in the formation of larger spherulite. The growth of spherulite in the polyester based PUE was lower than polyether based PUE because the spherulites of polyester based PUE composed of a lot of hard segment components and a small amount of soft segment components. Moreover, the effect of carbonyl in ester group of polyester based PUEs can be induced the hydrogen bonding between hard and hard segments and also hard and soft segments of other chain. In contrast, the hydrogen bonding of polyether based PUE are mainly formed between hard and hard segments, but slightly formed between hard and soft segments. It is conceivable that the polyester chains had higher molecular interaction than that of in polyether chains. Thus, the hard segments domain components for spherulite growth in the polyester based PUEs was less than that in polyether based PUEs.
Figure 3.3. Relationship between diameter of spherulite and molding temperature of PTMG-, PEA- and PHA-PUEs.

○ PTMG-PUE, △ PEA-PUE, ▲ PHA-PUE
Figure 3.4. Relationship between number of spherulites and molding temperature of PTMG-, PEA- and PHA-PUEs.

- PTMG-PUE
- PEA-PUE
- PHA-PUE
Figure 3.5 shows DSC thermograms of each part of PTMG-, PEA- and PHA-PUEs. The glass transition temperature ($T_g$) of PTMG-, PHA- and PEA-PUEs increased from -55.3 °C, -33.8 °C and -19.0 °C at the LTS to -48.6 °C, -32.8 °C and -17.8 °C at the HTS, respectively. The endothermic peaks due to the melting of hard segment domains ($T_{m,H}$) of all samples were about 169-195 °C. The trend of $T_g$ of all PUEs increased and melting point of hard domains decreased from the LTS to the HTS. The results can be concluded that the microphase separation became weaker toward the HTS. In addition, the crystallization due to the rearrangement and melting of the crystals of soft segments were not observed in these PUEs. $T_g$ of soft segment of PTMG-PUE was the lowest and those of PEA-PUE was the highest at the same positions. $T_{m,H}$ of PTMG-PUE exhibited higher than that of PEA- and PHA-PUEs at every positions, resulting in high crystallizability in PTMG-PUE. On the other hand, in PEA- and PHA-PUEs, the intermolecular interaction was very strong. Thus, crystallizability of the hard segment is quite low. Therefore, the degree of microphase separation of polyester based PUE was weaker than that of polyether based PUE. In case of polyester based PUEs, the ester group along the chain of polyester induced force to hold the chains. Hence, the PHA-PUE with long methylene chain showed the greater microphase separation than the PEA-PUE with short methylene chain.
Figure 3.5. DSC thermograms at each position of (a) PTMG-PUE, (b) PHA-PUE and (c) PEA-PUE.
Figure 3.6 shows FT-IR spectra at the LTS, HTS and the middle part of PTMG-, PEA- and PHA-PUEs. In the PTMG-PUE, the peaks of $\nu\text{C}=\text{O}_{\text{free}}$ and $\nu\text{C}=\text{O}_{\text{bond}}$ of urethane group occurred at 1731 cm$^{-1}$ and 1703 cm$^{-1}$, respectively. The peak of $\nu\text{N-H}_{\text{bond}}$ shifted to low wave number from LTS to HTS. The $\nu\text{C}=\text{O}_{\text{bond}}$ intensity was higher than that of $\nu\text{C}=\text{O}_{\text{free}}$ at LTS and the middle part, but the trend of intensity peaks at the HTS was opposite with the LTS. These results demonstrate that the hydrogen bonding mainly occurred between the NH-group and carbonyl group of urethane linkages at the LTS and the middle part. This bonding exhibited strong cohesive force and tended to agglomerate between hard segments in the structure of PUEs. The microphase mixing was progressed at the HTS of the PUE. In case of polyester based PUEs, the intensity of $\nu\text{C}=\text{O}_{\text{free}}$ showed at 1730 cm$^{-1}$ for the PEA-PUE and at 1728 cm$^{-1}$ for the PHA-PUE. The $\nu\text{C}=\text{O}_{\text{bond}}$ peak of PEA- and PHA-PUEs showed at 1708 cm$^{-1}$ and 1704 cm$^{-1}$, respectively. It seems that the hydrogen bonding is occurred both between both carbonyl group of urethane and ester groups and NH-groups.
Figure 3.6. FT-IR spectra at each part of (a) PTMG-PUE, (b) PEA-PUE and (c) PHA-PUE.
Stress-strain curves of the PUEs with different positions exhibited similar curves for each polymer glycols series in Figure 3.7. Table 3.2 shows Young’s modulus, tensile strength and strain at break of all PUEs series at the LTS were higher than that of the HTS. These tendency was rapidly increased in polyester based PUE. Therefore, the polyester based PUE exhibited almost similar tendency at every position. This result indicates that the crystallization was occurred in the polyester series when the strain was increased but not found in the polyether series.

Table 3.2. The Young’s modulus, tensile strength and strain at break of PTMG-, PEA- and PHA-PUEs at the lower temperature side (LTS) and the higher temperature side (HTS).

<table>
<thead>
<tr>
<th>PUE</th>
<th>Position</th>
<th>Young’s modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Strain at Break</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMG-PUE</td>
<td>LTS</td>
<td>1.11</td>
<td>8.32</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>HTS</td>
<td>1.03</td>
<td>6.89</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>LTS</td>
<td>1.15</td>
<td>18.46</td>
<td>5.19</td>
</tr>
<tr>
<td></td>
<td>HTS</td>
<td>1.13</td>
<td>17.99</td>
<td>3.68</td>
</tr>
<tr>
<td>PEA-PUE</td>
<td>LTS</td>
<td>1.28</td>
<td>32.03</td>
<td>4.04</td>
</tr>
<tr>
<td></td>
<td>HTS</td>
<td>1.00</td>
<td>23.28</td>
<td>3.32</td>
</tr>
</tbody>
</table>

69
Figure 3.7. Stress-strain curves at each part of (a) PTMG-PUE, (b) PEA-PUE and (c) PHA-PUE.
Microhardness at every 100 µm depth of specimens of 2 mm thick of PTMG-, PEA- and PHA-PUEs are shown in Figure 3.8. Microhardness of the PTMG-PUE significantly increased from 74 at the LTS to 94 at the HTS. Interestingly, the microhardness of PEA-PUE slightly increased from the LTS toward the HTS. In addition, PHA-PUE was also exhibited in the same trend with PEA-PUE. Difference of microhardness between the LTS and the HTS was respectively 7 in PEA-PUE and 9 in PHA-PUE. The temperature gradient dependence of micro-hardness for PHA-PUE had identical tendency as PEA-PUEs. The microhardness of polyether based PUE and polyester based PUE exhibited dissimilar tendency, that is, the microhardness of polyether based PUE had a big different between the LTS and the HTS. On the other hand, polyester based PUEs was slightly different between the LTS and the HTS. These results can be suggested that the temperature gradient can be strongly affected on the microhardness of PTMG-PUE because the viscosity in polyether based PUE was very low compared with PEA- and PHA-PUEs.

Figure 3.8. Temperature gradient dependence of micro-hardness for PTMG-, PEA- and PHA-PUEs from the LTS to the HTS.

○ PTMG-PUE. ▲ PHA-PUE. △ PEA-PUE
The spin-spin relaxation times ($T_2$) and fraction of each segment at each positions of PTMG-, PEA- and PHA-PUEs are shown in Table 3.3. Every spin was slightly different field due to the same measurement temperature, that is, room temperature. The spin-spin relaxation times of soft segment matrix ($T_{2L}$) exhibited from 312 to 314 $\mu$S in PTMG-PUE, from 150 to 156 $\mu$S in PEA-PUE and from 157 to 170 $\mu$S in PHA-PUE. In addition, the spin-spin relaxation times of hard segment domains ($T_{2S}$) of PTMG-, PEA- and PHA-PUEs exhibited from 36-38 $\mu$S, 34-36 $\mu$S and 26-29 $\mu$S, respectively. $T_{2L}$ and $T_{2S}$ of all three PUEs similarly decreased with increasing mold temperature. The segment of PUEs in contact low temperature mold plate showed easy relaxation by the phase separation. In the case of PUEs in contact high temperature mold plate, the strong intermolecular interaction can be found resulting in microphase mixing. Thus, the mobility of PUEs chain in contact high temperature mold plate was more difficult than that of PUEs in contact low temperature mold plate. These results mean that the relaxation time was dependent on molding temperature. The spin-spin relaxation time ($T_2$) of PTMG-PUE showed the highest one while $T_2$ of PHA- and PEA-PUEs were the lower and lowest, respectively. This result indicates that the strong intermolecular interaction due to the carbonyl group of polyester polyol was suppressed the chain mobility of polyester based PUEs. Moreover, the chain mobility of PEA-PUE was more difficult than that of PHA-PUE because the short methylene chain length in PEA can be induced the strong intermolecular interaction in PUE compared to long methylene chain length in PHA.
3.1.5 Conclusion

Spherulite size graded polyurethane elastomers were successfully prepared by using mold with different temperature of each plate. In this study, it can be concluded as followed;

1. Microphase separation and the large number of spherulites were observed in the LTS of spherulite size graded PUEs. The number and diameter of spherulites decreased and gradually increased toward the HTS. The number of spherulite and the spherulite sizes of polyester based PUE higher and smaller than that of polyether based PUE.

<table>
<thead>
<tr>
<th>PUE</th>
<th>Position</th>
<th>Soft segment $T_{2L}$ (µS)*1</th>
<th>Hard segment $T_{2S}$ (µS)*2</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMG-PUE</td>
<td>Middle</td>
<td>314</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>HTS</td>
<td>312</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>LTS</td>
<td>157</td>
<td>36</td>
</tr>
<tr>
<td>PEA-PUE</td>
<td>Middle</td>
<td>156</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>HTS</td>
<td>150</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>LTS</td>
<td>170</td>
<td>28</td>
</tr>
<tr>
<td>PHA-PUE</td>
<td>Middle</td>
<td>164</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>HTS</td>
<td>157</td>
<td>26</td>
</tr>
</tbody>
</table>

*1$T_{2L}$: Long $T_2$ *2$T_{2S}$: Short $T_2$

**Table 3.3** The spin-spin relaxation times ($T_2$) and hydrogen fraction of each segment at the lower temperature side (LTS), higher temperature side (HTS) and the middle part of PTMG-, PEA- and PHA-PUEs.
2. Polyether based PUE exhibited stronger microphase separation than that of polyester based PUE. Microphase separation of long methylene chain length polyester based PUE was stronger than that of short methylene chain length polyester based PUE.

3. The spherulite size graded polyether based PUE had large graded mechanical properties from LTS to HTS, while the polyester based PUE had slight graded mechanical properties.

4. The important knowledge was found to develop novel functionally graded polyurethane elastomers in this study.
References


Segmented polyurethanes (SPUs) are widely used in the field of coating and adhesives due to their high reactivity, high flexibility in formulation and application technologies, mechanical and adhesion properties. The super-structures of SPUs are varied with raw materials, recipes, preparation conditions, molding condition, and so on. Therefore, control of morphology of SPUs is required to obtain high performance SPUs\(^1\text{–}^4\). Moreover, for adhesive field, the problem owning to the low surface energy of plastic substrates such as polypropylene (PP) is encountered in industrial applications where adhesion to plastic substrate is required. Generally, the presence of polar groups and the morphology of the film surface play a very important role for obtaining a good adhesion\(^5\). However, PP substrates have limitations to their adhesion properties due to their non-polar nature and low surface tension. One of the techniques used to modify surface is the treatment of corona discharge of the polymer surface. The corona discharge is an electric discharge between two electrodes obtained under atmospheric pressure from a high voltage molecule (air) and dissociates some of them. These charged active species may react with polymer molecules that are also activated and may occur breaking of molecular bonds on the surface and addition of polar oxygen atoms. The functional groups incorporated onto the surface have been identified as hydroxyl [-C-OH], peroxy [-C-O-O-\(\cdot\)], carbonyl [-C=O], ester [-C(C=O)-O\(-\)], carboxylic acid [-C(\(\cdot\)C=O)-OH] and carbonate [-O(C=O)-O\(-\)]\(^6\). It is commonly assumed that surface oxidation during corona treatment is via a free radical process and the following reactions are proposed to account the PP surface oxidation (scheme 3.1)\(^7\). Therefore, the corona discharge is used frequently to treat polymers prior to adhesive bonding, and is the most widely used method for pre-treating polypropylene\(^7\) and polyethylene substrate\(^8\).
In recent years, the development of polyurethane adhesive with various substrates has been conducted. Xu et al.\textsuperscript{9} improved the hydrophilic properties of polyester fabric by corona discharge irradiation at different voltages and reported that dye-uptake ratio and dyeing speed was improved after the treatment. Castell et al.\textsuperscript{10} improved adhesion and wettability of PP using photografted method. Different benzophenone-type photoinitiators were photografted onto PP. They reported that the surface energy of the grafted surfaces of samples increased depending on the type of acrylate used. Malucelli et al.\textsuperscript{11} studied the surface properties of cure PU resin and of the different substrates such as PP, aluminum and blend of polyphenylene oxide with polyamide 6.

In this study, the effect of polyether- and polyester polyols on microphase-separated structure and on adhesion properties of SPU pressed with corona treated PP substrate was evaluated using swelling, differential scanning calorimetry (DSC), polarized optical microscopy (POM), T-peel testing, single lap shear testing, contact angle measurement and optical microscopy.

\textbf{Scheme 3.1} Surface oxidation during corona treatment of polypropylene (PP)\textsuperscript{7}.

\[
\begin{align*}
  \text{CH}_2\text{CH} \quad \overset{\text{hv}}{\longrightarrow} \quad \text{CH}_2\text{C} \\
  \text{CH}_3 \\
  \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
  \text{CH}_2\text{CH} \quad \overset{\text{H}}{\longrightarrow} \quad \text{CH}_2\text{COOH} \\
  \text{CH}_3 \\
  \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
  \text{CH}_2\text{C} \quad \overset{\text{R}}{\longrightarrow} \quad \text{CH}_2\text{C} \\
  \text{OO} \quad \text{OOR} \\
  \text{CH}_3 \\
\end{align*}
\]
3.2.2 Experimental

3.2.2.1 Materials

Poly(oxytetramethylene) glycol (PTMG: $M_n = 2018$) as a polyether polyol and poly(butylene adipate) glycol (PBA: $M_n = 1975$) as a polyester polyol and 4,4’-diphenylmethane diisocyanate (MDI) were supplied from Nippon Polyurethane Industry, Co., Ltd, Japan. 1,4-butanediol (BD) (Wako Chemical, Co., Ltd., Japan) was used as a chain extender. PTMG and PBA were dried with dried nitrogen under reduced pressure. To remove water, BD was distilled prior to use in polymerization. Toluene (Wako Chemical, Co., Ltd., Japan) was also distilled prior to use in swelling test. Methylene iodide used in contact angle measurement was supplied from Wako Chemical, Co., Ltd., Japan. Ultra pure water for contact angle measurement was prepared with a Millipore Simpli Lab-UV (Nippon Millipore, Japan). Figure 3.9 shows chemical structure of materials for SPUs.

![Chemical structure of materials for SPU.](image)

**Polymer glycol**

\[
\text{Poly(oxytetramethylene) glycol (PTMG: } M_n = 2018) \quad \text{Poly(butylene adipate) glycol (PBA: } M_n = 1975)
\]

**Diisocyanate**

\[
\text{4,4’-Diphenylmethane diisocyanate (MDI)}
\]

**Chain extender**

\[
\text{1,4-Butanediol (BD)}
\]
3.2.2.2 SPUs synthesis and adhesion of PP

Fig. 3.10 shows the synthetic scheme of segmented polyurethanes (SPUs). The SPUs was prepared from polymer glycol, 4,4-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BD) as a chain extender by a prepolymer method. Polymer glycols used were poly(oxytetramethylene) glycol (PTMG: $M_n = 2018$) and poly(butylenes adipate) glycol (PBA: $M_n = 1975$). Prepolymer was prepared at 70 °C for 6-8 hours under a nitrogen atmosphere ($K = 3.30$). The prepolymer and chain extender were well mixed for 3 min. Then the viscous product was poured onto treated PP. After that the viscous product was cured at 100 °C for 24 hours under air atmosphere.

![Synthetic scheme of SPU with various polymer glycols (PTMG and PBA).](image)

**Figure 3.10.** Synthetic scheme of SPU with various polymer glycols (PTMG and PBA).
3.2.2.3 Surface modification of polypropylene (PP)

In many plastic industries, the problems of low surface free energy of plastic films often are encountered in industrial applications where adhesion to plastic films is required. Corona discharge treatment (CDT) is a surface modification technique. CDT is used frequently to treat polymers prior to adhesive bonding, lamination to other films and other coating applications. CDT is the most commonly used method for pre-treating PP\(^6\). It consists of atmospheric plasma in air, obtained by a dielectric barrier discharge between high voltage electrodes and the surface of the film to be treated. CDT is based on an electrical discharge in air which activates nitrogen and oxygen producing electrons, metal stable species, ions, radicals, photons and ozone. As a result, the film surface is activated by ions and photons to give carbon radicals. These radicals react with the surrounded gaseous species, leading to the formation of mainly oxygen based functional groups, such as alcohol, ether, ketone, acid or ester (figure 3.11). In this result, one can observe the increase of surface energy due to the grafting of these polar groups and, to some extent, an improvement of the adhesion characteristics of the treated surface\(^12\).

In this study, PP films were treated by corona discharge (Kasuga Denki Co., Ltd., PS-601c model). The PP samples were cut into 100×25 mm\(^2\) and 152×25 mm\(^2\) for single lap shear test and T-peel test, respectively. The samples were exposed to AC corona discharge under ambient conditions for treatment times of 10 seconds and output voltage of 10kV.

![Figure 3.11. Corona discharge for polypropylene (PP) film.](image-url)
3.2.2.4 Characterization

Swelling measurement, macroscopic observation, thermal analysis, surface free energy measurement, T-peel strength and T-peel fracture behavior were used as the same conditions, equations and methods with chapter 2. Single lap shear strength was performed as below;

The adhesion properties analysis were done using Instron tensile tester (RTE-1210, A&D Co., Ltd., Japan). The adhesive joint between SPU and two PP sheets were obtained by pressing in the dimension of 12.5×25 mm\(^2\). The sample was tested at a crosshead speed of 5 mm/min at room temperature. The single lap shear strength was obtained from the average of three experiments.

3.2.3 Results and discussion

Table 3.4 shows properties of PTMG-SPU and PBA-SPU. Density of PTMG- and PBA-SPUs was 1.07 and 1.18 g/cm\(^3\), respectively. These results clearly suggest that density of SPU was dependent on soft segment structure. Gel fraction in toluene exhibited more than 99% in both SPUs. It seems that polymerization reaction was quantitatively proceeded. Crosslink density was calculated using Flory-Rehner’s equation and determined stoichiometrically. In case of PTMG-SPU, the crosslink density was largely low whereas the degree of swelling was high. On the other hand, the crosslink density and degree of swelling of PBA-SPU exhibited high and low, respectively. This result indicates that the crosslinking can be induced by carbonyl group in PBA polyl better than that ether group in PTMG polyl.
Figure 3.12 shows DSC thermograms of PBA-SPU and PTMG-SPU. The glass transition temperature ($T_g$) of PBA- and PTMG-SPUs exhibited at -39.6 °C and -69.7 °C, respectively. The melting temperature of soft segment ($T_{m,S}$) was observed at 48.1 °C of PBA-SPU and -3.9 °C of PTMG-SPU. The melting temperature of hard segment ($T_{m,H}$) of PBA-SPU and PTMG-SPU exhibited 191.0 °C and 175.8 °C, respectively. $T_g$, $T_{m,S}$ and $T_{m,H}$ of PBA-SPU was higher than that of PTMG-SPU. This result indicates that the microphase separation of the polyether based SPU (PTMG-SPU) was stronger than that of polyester based SPU (PBA-SPU).

**Table 3.4** Properties of PTMG-SPU and PBA-SPU.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density $d_p$ (g/cm$^3$)</th>
<th>Gel fraction (%)</th>
<th>Degree of swelling in Toluene</th>
<th>Crosslink density (mol/cm$^3$)$\times 10^{-3}$</th>
<th>Molecular weight between crosslinks (g/mol)$\times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMG-SPU</td>
<td>1.07</td>
<td>99.5</td>
<td>1.89</td>
<td>1.18</td>
<td>8.47</td>
</tr>
<tr>
<td>PBA-SPU</td>
<td>1.18</td>
<td>99.1</td>
<td>1.33</td>
<td>5.03</td>
<td>1.99</td>
</tr>
</tbody>
</table>

**82**
Figure 3.12. DSC thermograms of various polymer glycols based SPUs.
Figure 3.13 shows polarizing micrographs of SPUs. PBA-SPU had many smaller spherulite than that of PTMG-SPU. The spherulites were composed of a lot of hard segment components and a small amount of soft segment components. For polyester based SPU (PBA-SPU), the hydrogen bonding was not only occurred between hard segment components but also occurred from carbonyl group (C=O) of soft segment components. In case of polyether based SPU (PTMG-SPU), the hydrogen bond was mostly occurred between hard segment components (hydrogen bond between N-H group and C=O group of urethane linkages) and slightly formed from ether groups of soft segment components. These results indicate that the C=O groups in polyester soft segments was suppressed the hydrogen bond in urethane linkages. The spherulite growth in PBA-SPU was lower than that of PTMG-SPU. Thus, the small spherulite was found in PBA-SPU compared with PTMG-SPU.

![Polarized optical microscopic images of different polymer glycols based SPUs.](image)
Figure 3.14 shows the relationships between contact angle and polymer glycols. The value of total surface free energy ($\gamma_S$) and its components for SPUs with various polymer glycols, in addition the surface free energy of untreated PP substrate and corona treated PP substrate were shown in Table 3.5. The contact angle of water exhibited 84 degree in PBA-SPU and 91.9 degree in PTMG-SPU. The contact angle of water of PBA-SPU was lower than that of PTMG-SPU, indicates the good wetting was occurred in PBA-SPU compared to PTMG-SPU. Additionally, the contact angle of methylene iodide exhibited 65 degree in PBA-SPU and 76.8 degree in PTMG-SPU. It can also be seen that the values for the contact angle of methylene iodide obtained for interfacial SPU surfaces fall in polyester based SPU, that is, polyester based SPU (PBA-SPU) > polyether based SPU (PTMG-SPU). These results can be suggested that in the case of polyester based SPU, the strong intermolecular interaction between SPUs surface and water, namely the high hydrophilic component on the surface of SPU. The increasing of hydrophilic component (polar component) in SPU might be due to the diffusion of hard segment and the carbonyl group in polyester polyol on the surface of this SPU. In the case of polyether based SPU (PTMG-SPU), the amount of polar component on the top surface of SPU was decreased. It is noteworthy that the change of polymer glycols are primarily improved the wettability and adhesion properties of SPU. The surface free energy was also calculated by using the measured values of contact angles, according to an extended equation (4) and (5). The $\gamma_S$ of PP film showed the extremely high value when the corona discharge treatment time was used, namely the $\gamma_S$ of corona treated PP and untreated PP exhibited 101.1 and 28.6 mJ/m$^2$, respectively. These results mean that the corona discharge treatment can be improved the hydrophilic component in PP. The $\gamma_S$ of PBA-SPU and PTMG-SPU has been determined to be in the value of 46.5 and 35.3 mJ/m$^2$. The value of $\gamma_S$, $\gamma_S^d$ and $\gamma_S^p$ for PBA-SPU was higher than that of PTMG-SPU. Thus, the polar component was mostly decreased in PTMG-SPU. These results might be due to the carbonyl group of PBA has an effected to the polar component on the surface of SPU. Certainly, the $\gamma_S$ was dependent on the aggregation of hard segment in SPU chain and the type of polar component in polymer glycol.
Figure 3.14. Relationships between contact angle and different polymer glycols based SPUs.

Table 3.5 Surface free energy, the dispersion component and the polar component of different polymer glycols based SPUs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\gamma^d_s$ (mJm$^{-2}$)</th>
<th>$\gamma^p_s$ (mJm$^{-2}$)</th>
<th>$\gamma_s$ (mJm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated PP</td>
<td>27.1</td>
<td>1.5</td>
<td>28.6</td>
</tr>
<tr>
<td>Corona treated PP</td>
<td>25.4</td>
<td>75.7</td>
<td>101.1</td>
</tr>
<tr>
<td>PBA-SPU</td>
<td>25.8</td>
<td>20.7</td>
<td>46.5</td>
</tr>
<tr>
<td>PTMG-SPU</td>
<td>19.3</td>
<td>16.1</td>
<td>35.3</td>
</tr>
</tbody>
</table>
Figure 3.15 shows T-peel strength and single lap shear strength of SPUs with different polymer glycols. T-peel strength and single lap shear strength of PBA-SPU were higher than that of PTMG-SPU. T-peel strength of PBA- and PTMG-SPUs exhibited 2.01 and 1.23 MPa, respectively. In addition, single lap shear strength of SPUs exhibited in same trend of T-peel strength, namely PBA- and PTMG-SPUs exhibited 12.19 and 7.36 MPa, respectively. In both cases, PBA-SPU showed higher adhesive strength than PTMG-SPU. These results suggest that the carbonyl group in polyester polyol (PBA) chain can be induced the strong interaction between SPU adhesive and corona treated PP substrate compared with the ether group in polyether polyol (PTMG). Thus, the polymer glycols and corona discharge treatment for non-polar substrate such as PP strongly affect polyurethane adhesives.

![Figure 3.15. Effect of polymer glycol on T-peel strength and single lap shear strength (in MPa) of SPUs.](image-url)
Two types of SPUs were prepared using two different polymer glycols and non-polar substrate was treated by corona discharge treatment. This study can be concluded as followed:

1. Crosslinking can be induced by carbonyl group in PBA polyol better than that ether group in PTMG polyol.

2. The microphase separation of the polyether based SPU was stronger than that of polyester based SPU due to the strong intermolecular interaction in polyester based SPU, that is the hydrogen bonding was largely occurred from carbonyl group (C=O) of polyester based SPU compared with the ether group (-O-) of polyether based SPU.

3. The surface free energy, water wettability, single lap shear strength and T-peel strength of polyester based SPU exhibited high values because the increasing of hydrophilic component (polar component) on the SPU surface compared with polyether based SPU.
Chapter 4 The Influence of Curing Temperature on Microaggregation Structure and Adhesion Properties of Segmented Polyurethanes

4.1 Introduction

Segment polyurethane elastomers (SPUs) is one of block copolymers, which consists of soft segment formed with polymer glycol and hard segment done with diisocyanate and curing agent. These SPUs can be separated into two microstructures\(^1\). Hard domains play the role of physical crosslinks and act as filler in the soft matrix, whereas the soft phase gives extensibility to the polyurethane. The two microphase structure reveals excellent mechanical properties in the bulk properties of SPU, which brings SPU to be used in various ways such as daily life materials, elastomers and adhesives\(^2, 3\). The amounts of academic studies have been directed toward understanding the scope of microphase separation and its effect to the bulk properties\(^4-8\). In fact, hard segment domain is not only effects on microphase separation in bulk, but also on the surface properties owning to the distribution of polar hard segment domains. The microphase separation is quite important for adhesive and coating materials. In addition, the amount of crosslinks should lead to a structural change in SPU surface as the hard segment structure, thus it also changes in the adhesion properties of SPU. Several methods have also been applied to modify the surface as well as the interfacial properties of SPU such as additional nanosilicas\(^9\), primers\(^10\). The arrangement of the SPU chain such as linear or crosslink is considered to be the most useful method to improve the mechanical and adhesion properties simultaneously. This method is interesting due to the preparation of these SPU has the advantage of special additives and devices are not required and their properties can easily be controlled by changes in the starting materials, preparation condition, and so on. Thus, it would be interesting to examine the effect of the arrangement of SPU structure on the surface structure and properties.

In this study, we controlled the SPU using different curing temperature and investigated the effect of curing temperature on the microaggregation structure and adhesion properties of SPUs. The crosslink density and the molecular weight between crosslinking points were measured by swelling. The microphase structure of SPUs was examined by the differential scanning calorimetry (DSC). Contact angle measurement, surface free energy and T-peel strength measurement were performed to study the adhesion properties of SPU to aluminum. Finally, the T-peel fracture behavior of SPU surface was observed by optical microscopy.
4.2 Experimental

4.2.1 Materials

Poly(oxytetramethylene)glycol (PTMG) with the average molecular weight ($M_n$) of 2018 and 4,4-diphenylmethane diisocyanate (MDI) were supplied by Nippon Polyurethane Industry, Japan. 1,4-Butanediol (BD) (Wako Chemicals Co., Ltd., Japan) were used as a chain extender for segmented polyurethanes. PTMG was dried with dried nitrogen under reduced pressure and BD was distilled prior to use. Toluene (Wako Chemicals Co., Ltd., Japan) was also distilled prior to use in swelling test. Methylene iodide which is used in contact angle measurement was supplied by Wako Chemicals Co., Ltd., Japan. Figure 4.1 shows the chemical structures of materials for synthesis of PTMG-MDI based segmented polyurethanes (SPUs).

**Polyol:** Poly(oxytetramethylene) glycol (PTMG $M_n = 2018$)

\[ \text{HO}-\left(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\right)_n\text{H} \]

**Diisocyanate:** 4,4’-diphenylmethane diisocyanate (MDI)

\[ \text{OCN}-\text{CH}_2\text{NCOOCN} \]

**Chain extender:** 1,4-Butanediol (BD)

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

*Figure 4.1.* Chemical structures of used materials for prepare PTMG-MDI based SPUs.
4.2.2 Polymer synthesis

SPUs were synthesized using the prepolymer technique. PTMG and MDI with a ratio of [NCO]/[OH] = 3.30 at 70 °C for 6 hours under a nitrogen atmosphere. The chain extender (BD) was added to the prepolymers with NCO index = [NCO]pre/[OH] = 1.05 and stirred for 3 min. [NCO]pre is the concentration of NCO groups in a prepolymer. The viscous product was then poured onto aluminium (Al) substrate and pressed with other Al plate by clip (0.2 mm in thickness). After that, the sample was cured for 24 hours at 50, 75, 100 and 125 °C under an air atmosphere. Synthetic scheme of the SPUs are shown in Figure 4.2. SPU with different curing temperatures was denoted as SPU-50, SPU-75, SPU-100 and SPU-125.

![Figure 4.2. Synthetic scheme of SPUs with various curing temperature.](image-url)
4.2.3 Characterization

Swelling measurement, macroscopic observation, thermal analysis, surface free energy measurement, T-peel strength and T-peel fracture behavior were used as the same condition, equation and method with chapter 2.

4.3 Results and discussion

Table 4.1 shows structural parameters and properties of SPUs at various curing temperature. The gel fractions in toluene exhibited more than 99% in all prepared SPUs. These results demonstrate that the polymerization reaction of SPUs was quantitatively proceeding. The degree of swelling of SPU-50, SPU-75, SPU-100 and SPU-125 with toluene was 2.40, 2.36, 2.13 and 2.06, respectively. Noteworthy, the degree of swelling of SPU-50 showed the highest value. This result might be suggested that SPU-50 was quite closed to linear. Crosslink density was calculated using Flory-Rehner’s equation. With increasing curing temperature, crosslink density increased from $4.74 \times 10^{-4}$ to $8.18 \times 10^{-4}$ mol/cm$^3$. The tendency of the crosslink density corresponded well to that of the degree of swelling. The results revealed that the increasing of curing temperature can be induced the crosslinking in the SPUs structure.
Figure 4.3 shows DSC thermograms of SPUs and Figure 4.4 shows the model of SPUs structure at the lower and higher curing temperature. Glass transition temperature ($T_g$) of soft segment chains of all SPUs were observed from -67.3 to -62.0 °C, and slightly shifted to the higher temperature side when increasing curing temperature. The melting temperature of hard segment ($T_{m,H}$) of SPU-50 and SPU-75 were observed at 143.7 and 153.8 °C, respectively. In addition, SPU-100 and SPU-125 were observed at the higher temperature side compared to the others that is observed within 180-210 °C. Moreover, with increasing curing temperature, the melting temperature of soft segment ($T_{m,s}$) was disappeared. It is supposed that the hard segments was not aggregated, thus the SPU chains were closed to linear chain structure at the lower curing temperature (Figure 4.4a). On the other hand, at the higher curing temperature, the hard segments were aggregated to form physical crosslinking. Thus, the strong intermolecular interaction between hard segments in SPUs chain can be observed as a result of high crosslinking density (Figure 4.4b).

### Table 4.1 Structural parameters and properties of SPUs with various curing temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gel fraction (%)</th>
<th>Degree of swelling in Toluene</th>
<th>Crosslink density (mol/cm$^3$)$\times 10^{-4}$</th>
<th>Molecular weight between crosslinks (g/mol)$\times 10^3$</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPU-50</td>
<td>100.0</td>
<td>2.40</td>
<td>4.74</td>
<td>2.11</td>
<td>-67.3</td>
<td>143.7</td>
</tr>
<tr>
<td>SPU-75</td>
<td>99.5</td>
<td>2.36</td>
<td>5.00</td>
<td>2.00</td>
<td>-66.2</td>
<td>153.8</td>
</tr>
<tr>
<td>SPU-100</td>
<td>99.8</td>
<td>2.13</td>
<td>7.41</td>
<td>1.35</td>
<td>-65.7</td>
<td>189.7, 210.0</td>
</tr>
<tr>
<td>SPU-125</td>
<td>99.8</td>
<td>2.06</td>
<td>8.18</td>
<td>1.22</td>
<td>-62.0</td>
<td>180.3, 209.8</td>
</tr>
</tbody>
</table>
Figure 4.3. DSC thermograms of various SPUs measured at 10 °C min\(^{-1}\); (1) SPU-50, (2) SPU-75, (3) SPU-100 and (4) SPU-125.
Figure 4.5 shows polarized optical micrographs of SPU with different curing temperature. The spherulite sizes of SPU-100 and SPU-125 were 20-25 µm and 25-30 µm, respectively. No spherulites were observed for SPU-50 and SPU-75 whereas it was clearly seen for SPU-100 and SPU-125. The reason that SPU with lower curing temperature was closed to linear chain, hence the aggregated hard segment are not occurred. These spherulites are found to be negative spherulites; that is, polymer chains oriented perpendicular to the radial direction. It is known that the spherulites were composed of a small soft segment components and a lot of hard segment components\textsuperscript{11)}. SPU cured at 100 °C had many small negative spherulites with well-defined Maltese cross. However, the structure of spherulites of SPU cured at 125 °C turn into loose spherulites, so-called sheaf-like\textsuperscript{4, 12)}. This result indicates that the ordered soft segment structure hardly changes at low curing temperature. As the curing temperature of 100 and 125 °C, the intermolecular interaction between hard segments to form physical crosslinking can be occurred. Therefore, the curing temperature above 100 °C (lower than melting of hard segments) dominantly influences the aggregative morphology of SPUs.

Figure 4.4. The SPUs structure; (a) at low curing temperature and (b) at high curing temperature.
Figure 4.5. Polarizing optical microscopic images of SPUs with various curing temperature; (a) SPU-50, (b) SPU-75 (c) SPU-100 and (d) SPU-125.
Figure 4.6 shows the relationships of contact angle and curing temperature. The contact angle of water and methylene iodide of SPUs was found from 66.2 to 99.8 degree and 59.7 to 73.3 degree, respectively. The contact angle of water increases in the order of SPU-50 < SPU-75 < SPU-100 < SPU-125, indicates the good wetting decreases sequentially from SPU-50 to SPU-125. It can also be seen that the values for the contact angle of methylene iodide obtained for interfacial SPU surfaces fall in increasing order of cure temperature, that is, SPU-50 > SPU-75 > SPU-100 > SPU-125. These results can be suggested that in the case of lower cure temperature, the strong intermolecular interaction between SPUs surface and water, namely the high hydrophilic component on the surface of SPUs. The increasing of hydrophilic component (polar component) in SPUs might be due to the diffusion of hard segment on the surface of these SPUs. In the case of higher cure temperature (SPU-125), the physical crosslinking can be formed cause the aggregated hard segments, thereby the amount of segregated hard segments on the top surface of SPUs was decreased. These results mean that the numerous of non-polar component (dispersion component, namely the soft segment components was found at the top surface of SPUs as result of large contact angle of water. It is noteworthy that the change of curing temperature are primarily improved the wettability and adhesion properties of SPUs.
Figure 4.6. Relationships between contact angle and curing temperature for the various SPUs.
Table 4.2 shows the value of total surface free energy (γS) and its components for SPUs cured at different temperatures. The γS of SPUs was evaluated using contact angle measurements, according to an extended equation (4) and (5). The relationships of γS, γSd, γSp and cure temperature are shown in Figure 4.7. The γS of SPUs has been determined to be in the range between 30 and 49 mJ/m². With increasing cure temperature, the value of γS and γSp for SPUs decreased. In contrary, γSd exhibited differ from γS and γSp. Furthermore, the polar component was mostly decreased by curing up to 125 °C. These results might be due to the segregation of hard segments on the surface of SPUs decreased largely. Certainly, the γS was dependent upon the aggregation of hard segment in SPUs chain.

Table 4.2 The value of γS and its components for SPUs cured at different temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>γSd (mJ/m²)</th>
<th>γSp (mJ/m²)</th>
<th>γS (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPU-50</td>
<td>22.0</td>
<td>26.4</td>
<td>48.4</td>
</tr>
<tr>
<td>SPU-75</td>
<td>22.9</td>
<td>22.4</td>
<td>45.3</td>
</tr>
<tr>
<td>SPU-100</td>
<td>25.6</td>
<td>9.3</td>
<td>34.9</td>
</tr>
<tr>
<td>SPU-125</td>
<td>27.1</td>
<td>3.0</td>
<td>30.1</td>
</tr>
</tbody>
</table>
Figure 4.7. Effect of cure temperature on surface free energy (in mJm\(^{-2}\)) of SPUs.

\(\gamma_s^d\); surface free energy of the dispersion component.

\(\gamma_s^p\); surface free energy of the polar component.
Figure 4.8 shows T-peel strength of SPUs with various cure temperature. To understand the aggregated hard segment affect adhesive strength in SPUs in Figure 4.8, the schematic model of the aggregated hard segment components at the SPUs/aluminum interface was drawn in Figure 4.9. T-peel strength of SPUs decreased as the curing temperature increased that is decreased from 20.87 MPa of SPU-50 to 12.37 MPa of SPU-125. These results can be attributed to the aggregation of hard segments to formed physical crosslinking was found in SPUs with higher cure temperature. For SPU-50 and SPU-75, a lot of hard segment component which is segregated at the top surface of SPUs can greatly adhere to aluminum surface. Thus, the strong interaction between SPUs and aluminum surface can be attained. On the other hand, opposite phenomena happened to SPU-100 and SPU-125. The physical crosslinking in these SPUs induced the formation of non-linear chains and causes phase mixing trend between soft and hard segment components. It seems that this phenomenon occurs ever at the surface region of SPUs.

![Figure 4.8](image-url)  
*Figure 4.8. Effect of cure temperature on T-peel strength of SPUs.*
Figure 4.9. Schematic model of the aggregated hard segment components at the SPU/aluminum interface.

Figure 4.10 shows optical microscopic images for (a) SPU-50, (b) SPU-75, (c) SPU-100 and (d) SPU-125. To understand the failure behavior of SPUs in Figure 4.10, the schematic model of T-peel fracture behavior of SPUs was drawn in Figure 4.11. Only cohesive failure was observed in SPUs. Cohesive failure is fracture occurring within the adhesive layer that is when the adhesive was subjected to a peeling force, it is deformed and the fracture was arisen within the adhesive layer as shown in Figure 4.11(b). This fracture was due to the interaction between adhesive and substrate as large as the intermolecular interaction in SPUs.
Figure 4.10. Optical microscopic images of aluminum surface after T-peel testing for SPUs; SPU-50, (b) SPU-75, (c) SPU-100 and (d) SPU-125.

Figure 4.11. Schematic model of T-peel fracture behavior of SPUs; (a) original specimen, (b) peeling specimen and (c) peeled specimen.
4.4 Conclusion

Four types of PTMG-MDI based SPUs were prepared using four different cure temperatures.

1. Crosslinking density and the melting temperature of hard segments in SPUs were increased with increasing cure temperature.

2. When the cure temperature was increased, SPUs were closed to non-linear chain and the physical crosslinking was greatly formed, hence the hard segments were aggregated to form spherulites.

3. The surface free energy, water wettability and T-peel strength of SPUs decreased because the polar hard segment component could not segregate at the top surface of SPUs when the curing temperature was increased.

4. Only cohesive failure was observed in all SPUs. These were explained by the interaction between SPUs adhesive and aluminium substrate as large as the intermolecular interaction in SPUs adhesive layer due to a phase separation trend of hard and soft segment chains, thus a lot of hard segments can be segregated at the top surface of SPUs.
Chapter 5 Effect of Humidity on the Micro-aggregation Structure and Adhesion Properties of Segmented Polyurethanes

5.1 Introduction

Polyurethane is used in various application fields such as sealant production\(^1\), coating\(^2\) and adhesive\(^3\) because the isocyanate group has a high reactivity and it can react with almost any compound possessing active hydrogen atom, even at room temperature. Free hydroxyl group in the polymer react with isocyanates to form urethane linkages. A three dimensional urethane network is formed when there are two or more reactive sites on each reactant. However, reactions leading to the formation of urethane linkages are influenced by external conditions. When water is present, the isocyanate group reacts with water to form an amine, and the amine reacts with another isocyanate to form urea linkages. The source of water is typically a high reactive humidity or water absorbed into the system. Amines are more nucleophilic than alcohols, the formation of urea linkages will dominate the process, and the polyl will be difficult to crosslink with the isocyanate group properly. In addition, byproducts of the side reaction between isocyanate and water will affect the properties of the resulting products in various applications.

Werner \textit{et al.}\(^4\) investigated the effect of the relative humidity of the ambient air on the dentin bonding efficiency of four self-etching primer adhesives. Eight specimens were prepared for each of the adhesives and each of the following six conditions prior to application of the bonding agents and a hybrid-type resin composite material: air dried, wet, or stored for 1 h at 33\%, 50\%, 75\%, and 100\% relative humidity (RH). Shear bond strength (SBS) was determined after 24 h of storage in water at 37 °C. They found that the self-etching primer adhesives tested are unaffected by the degree of dentin wetness or ambient air humidity exposure prior to application. Unless considered necessary for other clinical reasons, use of rubber-dam is not compulsory. Burrow \textit{et al.}\(^5\) studied the effect of temperature and relative humidity (RH) on the early tensile bond strength to bovine dentine of two bonding systems (Liner Bond System and Scotchbond Multi-purpose) of resin composite, and an experimental system (KB-110) were tested. They found that the different bonding system due to the different experimental system may be more or less sensitive to changes in RH and temperature. Moreover, the bond strengths of the systems tested tended to exceed the early cohesive strengths of the resin composite. Asahara \textit{et al.}\(^6\) studied the effect of humidity during storage on the crosslinking reactions of isocyanate groups using attenuated total
reflectance Fourier transform infrared spectroscopy with pressure-sensitive adhesive (PSA) composed of poly[ethyl acrylate-co-(2-ethylhexyl acrylate)-co-(2-hydroxyethyl methacrylate)] as a base resin and polyisocyanate as a crosslinker. They have found that the isocyanate groups in the PSA films stored under the humid condition were consumed earlier than the films stored under the dry condition. In addition, more urea linkages were produced in the PSA films stored under the humid condition than in the films stored under the dry condition.

The object of this study was to investigate the effect of humidity on the micro-aggregation structure and adhesion properties of segmented polyurethanes (SPUs).

5.2 Experimental

5.2.1 Materials

Poly(oxytetramethylene)glycol (PTMG) with the average molecular weight ($M_n$) of 2018 and 4,4-diphenylmethane diisocyanate (MDI) were supplied by Nippon Polyurethane Industry, Japan. 1,4-butanediol (BD) (Wako Chemicals Co., Ltd., Japan) were used as a chain extender for segmented polyurethanes. PTMG was dried with dried nitrogen under reduced pressure and BD was distilled prior to use. Toluene (Wako Chemicals Co., Ltd., Japan) was also distilled prior to use in swelling test. Methylene iodide which is used in contact angle measurement was supplied by Wako Chemicals Co., Ltd., Japan. Figure 5.1 shows the chemical structures of materials for synthesis of PTMG-MDI based segmented polyurethanes (SPUs).
5.2.2 Polymer synthesis

SPUs were synthesized using a prepolymer method. Synthetic scheme of SPUs is shown in Figure 5.2. The prepolymer was prepared from PTMG and MDI with a ratio of $[\text{NCO}]/[\text{OH}] = 3.30$ at 70 °C for 6 h under a nitrogen atmosphere. The curing agents was added to the prepolymers with $\text{NCO INDEX} = [\text{NCO}]_{\text{pre}}/\text{[OH]} = 1.05$ and stirred for 5 min, where $[\text{NCO}]_{\text{pre}}$ is the concentration of NCO groups in a prepolymer. The viscous product was then poured into a mold constructed by a spacer of 0.5 mm thickness. The two aluminum plates were heated at 130 °C prior to use. The sample was cured for 24 h at 100 °C under an air atmosphere with various relative humidity (RH), 37, 50, and 75%. SPUs under various humid conditions were denoted as SPU-37, SPU-50 and SPU-75.

**Figure 5.1.** Chemical structures of all materials for synthesis SPUs.
5.2.3 Characterization

Swelling measurement, macroscopic observation, thermal analysis, surface free energy measurement, T-peel strength and T-peel fracture behavior were used as the same conditions, equations and methods with chapter 2.

Figure 5.2. Synthetic scheme of SPUs cured under different relative humidity (%RH).
5.3 Results and Discussion

Table 5.1 shows structural parameter and properties of SPUs. The gel fraction of all three SPUs showed similar value that is greater than 99%. It is supported that the polymerization of SPUs progressed enough. The degree of swelling decreased with increasing relative humidity that is decreased from 2.30 to 1.85. It is noteworthy that the degree of swelling of SPU-75 showed the lowest value. This result suggests that SPU-75 was close to the network structure. With increasing relative humidity, the crosslink density increased from $5.48 \times 10^{-4}$ to $12.90 \times 10^{-4}$ mol/cm$^3$. On the other hand, the molecular weight between crosslink points and the degree of swelling decreased with increasing relative humidity. This result indicates that the relative humidity can be induced the crosslinking into the SPUs structure.

Table 5.1. Structural parameters and properties of SPUs cured under different relative humidity (%RH).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm$^3$)</th>
<th>Gel fraction$^a$ (%)</th>
<th>Degree of swelling$^a$</th>
<th>Crosslink density (mol/cm$^3$)$\times 10^{-4}$</th>
<th>Molecular weight between crosslink (mol$^{-1}$)$\times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPU-37</td>
<td>1.08</td>
<td>99.05</td>
<td>2.30</td>
<td>5.48</td>
<td>1.83</td>
</tr>
<tr>
<td>SPU-50</td>
<td>1.08</td>
<td>99.33</td>
<td>2.03</td>
<td>8.93</td>
<td>1.12</td>
</tr>
<tr>
<td>SPU-75</td>
<td>1.09</td>
<td>99.14</td>
<td>1.85</td>
<td>12.90</td>
<td>0.78</td>
</tr>
</tbody>
</table>

$^a$ in toluene solvent
Figure 5.3 shows DSC thermograms of SPUs cured under various relative humidity (%RH). Glass transition temperature of the soft segment chains ($T_g$) elevated from -63.2 to -51.7 °C with an increase in relative humidity. Melting temperature of hard segment domains ($T_{m,H}$) observed from 171.8 to 189.1 °C. It is well known that increasing $T_g$ of soft segment in SPUs means an increase in miscibility of two components on account of the molecular interaction between soft and hard segments. Moreover, the shifted of $T_{m,H}$ to the higher temperature side when increased relative humidity can be suggested that the humidity induced crosslink into SPUs structure. The change of SPUs structure with different relative humidity can be explained as follows. For the lower relative humidity, the hard segment possesses a linear urethane chain, resulting in high crystallizability. On the other hand, for higher relative humidity, the crystalline structure was disturbed by the penetration of crosslinking reactions. Thus, the degree of the crystalline was reduced. These results indicate that the degree of microphase separation of the SPU became weaker toward the higher relative humidity.
Figure 5.3. DSC thermograms of various SPUs measured at 10 °C min$^{-1}$. 
Figure 5.4 shows polarized optical micrographs of SPUs cured under different relative humidity. The spherulite size of SPU-37, SPU-50 and SPU-75 were 12-20, 10-18 and 8-16 μm, respectively. When the relative humidity increased, the spherulite size decreased. These spherulites are found to be negative spherulites; that is, polymer chains oriented perpendicular to the radial direction. It is known that the spherulites were composed of a small soft segment component and a lot of hard segment component. These results mean that the chemical crosslinking which was formed by diisocyanate and water in air interrupt the aggregation of hard segments to form spherulites. Thus, the small spherulites were observed in high relative humidity.

Figure 5.4. Polarized optical microscopic images of SPUs; (a) SPU-37, (b) SPU-50 and (c) SPU-75.
The relationship between contact angle and relative humidity is shown in Figure 5.5. With increasing relative humidity, the contact angles of water and methylene iodide of SPUs increased from $92.7^\circ$ to $99.0^\circ$ and decreased from $72.6^\circ$ to $68.3^\circ$, respectively. The contact angle of water increased in the order of SPU-37 < SPU-50 < SPU-75. In contrast, the contact angle of methylene iodide decreased with increased relative humidity. SPU-37 had the highest wettability by water, i.e. smallest contact angle, indicating the highest surface free energy. These results suggest that the excellent intermolecular interaction between SPUs surface and water, that is, the high hydrophilic component (polar component) on the surface of SPUs.

![Figure 5.5. Relationships between contact angle and relative humidity for SPUs.](image.png)
Figure 5.6 shows $\gamma_S$, $\gamma_S^d$ and $\gamma_S^p$ of the SPUs cured under various relative humidity. The value of total surface free energy ($\gamma_S$), dispersion component ($\gamma_S^d$) and polar component ($\gamma_S^p$) of the SPUs are summarized in Table 5.2. These values were calculated by equation (4) and (5) in chapter 2. The $\gamma_S$ of SPU-37, SPU-50 and SPU-75 were 35.9, 33.9 and 32.4 mJm$^{-2}$, respectively. The value of $\gamma_S$ for the SPUs decreased with increasing relative humidity. $\gamma_S^p$ exhibited same trend as well. In contrary, the value of $\gamma_S^d$ increased with increasing relative humidity. It means that the $\gamma_S^p$ of SPU-37 is the highest in the three SPUs due to the large diffused hard segment components at the top of surface. For SPU-75, the segregation of the hard segment chains at the top of surface was suppressed by the crosslinking point in SPUs.

Figure 5.6. Effect of relative humidity on surface free energy (in mJm$^{-2}$) of SPUs.

$\gamma_S^d$: surface free energy of the dispersion component.
$\gamma_S^p$: surface free energy of the polar component.
Figure 5.7 shows T-peel strength of SPUs cured under different relative humidity (%RH). T-peel strength of SPUs decreased as the relative humidity increased namely decreased from 16.35 MPa of SPU-37 to 12.29 MPa of SPU-75. To understand the adhesive strength in Figure 5.7, see Figure 2.8 in chapter 2. These results suggest that the moisture vapor readily causes the curing reaction, that is, the reaction between residual diisocyanates end group and water result in the formation of urea linkages (scheme 5.1). Thus, the SPU structure at higher relative humidity was changed from a linear to crosslinked form. As a result, poor T-peel strength can be obtained. In contrary, SPU with lower relative humidity showed excellent T-peel strength due to the lower crosslinking density in the SPU structure. These results can be attributed to the reaction between diisocyanate and water was slightly obtained and hard segment can be segregated at the top of SPU surface. Therefore, the strong interaction between SPU and substrate was found.

Table 5.2 The value of $\gamma_S$ and its components for SPUs cured under various relative humidity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\gamma_S^d$ (mJm$^{-2}$)</th>
<th>$\gamma_S^p$ (mJm$^{-2}$)</th>
<th>$\gamma_S$ (mJm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPU-37</td>
<td>21.6</td>
<td>14.3</td>
<td>35.9</td>
</tr>
<tr>
<td>SPU-50</td>
<td>22.7</td>
<td>11.2</td>
<td>33.9</td>
</tr>
<tr>
<td>SPU-75</td>
<td>24.2</td>
<td>8.1</td>
<td>32.4</td>
</tr>
</tbody>
</table>
**Figure 5.7.** T-peel strength of SPUs cured under different relative humidity.

Scheme 5.1. The hydrogen bonded structure between diisocyanate and moisture in air.
To investigate directly the surface failure of the SPUs, we made optical microscopy observations for the aluminum plate surface. Figure 5.8 shows optical microscopic images of aluminum surface after T-peel testing for (a) SPU-37, (b) SPU-50 and (c) SPU-75. Only cohesive failure was observed after T-peel test. When the adhesive was subjected to a peeling force, it is deformed and the high residue of SPU adhesive was found on aluminum surface area and the fracture was occurred within the adhesive layer (figure 4.10 in chapter 4). These results clearly imply the strong interaction between SPU and aluminum plate surface, which is caused from the weak network structure in SPU chains and the polar components were greatly segregated at the surface of SPU.

![Optical microscopic images of aluminum surface after T-peel testing for (a) SPU-37, (b) SPU-50 and (c) SPU-75.](image)

**Figure 5.8.** Optical microscopic images of aluminum surface after T-peel testing for SPUs; (a) SPU-37, (b) SPU-50 and (c) SPU-75.

### 5.4 Conclusion

Three SPUs were prepared using three different relative humidity.

1. Crosslinking density in SPUs increased whereas the degree of swelling decreased with increasing relative humidity.

2. When the relative humidity was increased, SPUs were close to network structure and the crosslinking was greatly formed, hence the crosslinking points suppressed the aggregation of hard segments to form spherulites. In addition, the degree of
microphase separation of the SPUs became weaker towards the higher relative humidity.

3. The surface free energy, water wettability and T-peel strength of SPUs decreased because the polar hard segment component cannot segregated at the top surface of SPUs when the relative humidity increased.

4. Only cohesive failure observed in all SPUs. These were explained by the interaction between SPUs adhesive and aluminum substrate as large as the intermolecular interaction in SPUs adhesive layer due to a lot of hard segment components can be segregated at the top surface of SPUs.
References

Chapter 6 Summary

Polyurethane adhesives (PUAs) are normally defined as those adhesives that contain a number of urethane groups in the molecular backbone, regardless of the chemical composition of the rest of the chain. PUAs have some advantages as follows: 1) SPU readily forms hydrogen bonds to the substrates. 2) SPU forms covalent bonds with substrates that have active hydrogen. 3) SPU effectively wet the surface of most substrates. 4) SPU with small molecular size allows them to permeate porous substrates. The primary bonding mechanisms of urethane adhesives is believed to be through isocyanate (-NCO) and polar groups (-NH and -C=O) that are capable of forming strong chemical and physical interactions with surfaces having active hydrogen.

The purpose of this study is investigation of the effect of the aggregation structure of segmented polyurethanes (SPUs) on their adhesion properties. SPUs were synthesized by a prepolymer method, and were used as hot melt adhesives and reactive adhesives. An attempt to control the morphology and adhesion between adhesive and substrate was done by performing the different conditions. This study might develop the segmented polyurethanes having good adhesion properties.

Chapter 1 included the general introduction about polyurethane adhesives and precious researches, the purpose and the outline of this thesis.

In Chapter 2, the effect of curing agent ratio of diol to triol on the micro-aggregation structure and adhesion properties of SPU were investigated. Four SPUs were prepared by different blend ratios of 1,4-butanediol/1,1,1-trimethylol propane (BD/TMP) (BD/TMP = 100/0, 90/10, 75/25 and 50/50). With increasing the blend ratio of TMP, the adhesive strength and wettability decreased because the polar hard segment contents cannot segregate at the top surface of SPUs. Moreover, three failure modes were observed after T-peel testing. That is, the cohesive failure, the cohesive-interfacial failure and the interfacial failure which are observed for the SPU with low, moderate and high TMP blend ratios, respectively. These were explained by the strong chemical network structure and the SPU did not interact with aluminum surface due to a phase mixing trend of soft and hard segment chains, thus this fracture led to the interfacial failure and the strong interaction between SPU and the aluminum plate surface led to the cohesive failure.

In Chapter 3, the influence of curing temperature on the micro-aggregation structure and adhesion properties of SPU were studied. Four SPUs were prepared using four different curing temperatures (50°C, 75°C, 100°C and 125°C). Crosslinking density and the melting
temperature of hard segments ($T_{m,H}$) in SPUs were increased with increasing curing temperature. SPUs were closed to crosslink structure, hence the hard segments were aggregated to form spherulites and the polar hard segment components cannot segregate at the top surface when the curing temperature was increased. Additionally, $T_g$ of soft segment increased with increasing curing temperature and $T_{m,S}$ of soft segment was disappeared at the high curing temperature. These results indicate that the microphase separation of SPU became weaker toward the higher curing temperature. The surface free energy, water wettability and T-peel strength of SPUs decreased because the polar hard segment component could not segregate at the top surface of SPUs when the curing temperature was increased. Thus, the adhesion properties decreased at high curing temperature.

In Chapter 4, the effect of humidity on the micro-aggregation structure and adhesion properties of SPU were investigated. Three SPUs were prepared using three different relative humidity (37%RH, 50%RH and 75%RH). Crosslinking density in SPUs increased whereas the degree of swelling decreased with increasing relative humidity. $T_g$ of soft segment increased with increasing relative humidity. Therefore, it is conceivable that SPUs were closed to network structure As the result, the crosslinking point suppressed the aggregation of hard segments to form spherulites. The adhesive strength decreased when relative humidity increased because the polar hard segment component cannot segregate at the substrate/adhesive interface. Moreover, only cohesive failure was observed in all SPUs.

In Chapter 5, the effect of polymer glycols on the microaggregation structure, mechanical and adhesion properties of SPU were studied. For mechanical properties (chapter 5.1), the spherulite size graded polyurethane elastomers were successfully prepared by using different temperature of mold plates and different polymer glycols, namely poly(oxytetramethylene) glycol (PTMG), poly(hexamethylene adipate) glycol (PHA) and poly(ethylene adipate) glycol (PEA), 4,4-diphenylmethane diisocyanate (MDI) and BD/TMP as a curing agent by a prepolymer method. Polyether based PUE showed strong microphase separation compared with polyester based PUE. The polyether based PUE had largely graded mechanical properties from the lower temperature to the higher temperature, while the polyester based PUE had slightly graded mechanical properties. The important knowledge was found to develop novel functionally graded polyurethane elastomers. For adhesive properties (chapter 5.2), the SPUs was prepared from two polymer glycols, namely poly(oxytetramethylene) glycol (PTMG) and poly (butylene adipate) glycol (PBA), MDI and BD as a chain extender by a prepolymer method. The corona discharge can lead to increasing the high reactive free radical oxygen in non-polar polymer (PP surface). Upon the condition of corona discharge
treatment, the contact angle and surface free energy showed optimum value and the surface free energy of PP film showed the extremely high value when the corona discharge treatment time was used. Moreover, polar functional groups, such as -CO, -C=O, and -COO were introduced on the PP film surface after corona discharge treatment. Comparative studies of SPU adhesive containing different polymer glycols indicate that the adhesive strength of polyester based SPU (PBA-SPU) was higher than polyether based SPU (PTMG-SPU) because the carbonyl group of PBA polyol is also segregated at the surface of PBA-SPU. Thus, the interfacial interaction between PBA-SPU adhesive and substrate was stronger than that of PTMG-SPU adhesive and substrate.

Finally, the polyurethane adhesives are not only replacing screws, rivets and nails but are becoming a preferred alternative to spot welding, soldering and brazing. Interestingly, the use of polyurethane adhesives can produce joints of higher strength and allow the assembly of components without to need to drill or perforate them. Additionally, polyurethane adhesives can avoid the heat distortion resulting from high temperature jointing processes. Thus, the polyurethane adhesive are widely developed and used in many industrial applications. The development of SPUs having good adhesion properties can be successfully prepared by changing the condition in the preparation step, for instance, curing agent ratio, curing temperature, relative humidity, polymer glycol. Moreover, the surface modification (corona discharge treatment) was also used to improve the nonpolar substrate. In addition, the nonpolar substrate after modified surface was lead to a very strong adhesive strength between substrate/adhesive interfaces.
Paper lists of thesis

1. Published Papers


2. Proceeding paper

3. Basic paper related to this thesis

ACKNOWLEDGEMENT

I would like to express my gratitude towards my supervisor, Prof. Dr. Mutsuhisa Furukawa for kindly helpful, commendations and suggestions in this thesis. I am very grateful for my co-supervisor, Prof. Dr. Makoto Egashira, Prof. Dr. Masayuki Hasaka, and my assistant professor, Dr. Ken Kojio for their valuable reviews and suggestions in this thesis. I am also obligate to Dr. Suguru Motokucho and Mr. Mitsuru Egasira for their technical assistance and kindly helpful in this thesis.

I am also very grateful for the Ministry of Education, Culture, Sports, Science and Technology of Japan for supporting the scholarship in this thesis and doctorate course.

I would like to extend my appreciation to all staffs and friends from the Super-structural Materials Science Laboratory, Department of Materials Science for their kindly helpful and pleasant experience for this research.

Finally, I am forever indebted to my parents and my family for their understanding, endless patience and encouragement when it was most required. I am also grateful to Miss Naphat Intaravichian for her kindly helpful and cheering up.