



Adhesion Properties between Microphase-Separated Segmented Polyurethane and Corona Treated PP Substrate

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Abstract

Segmented polyurethane elastomers (SPUEs) were prepared using two different polymer glycols, namely poly (oxytremethylene) glycol (PTMG) and poly (butylene adipate) glycol (PBA). In addition, polypropylene substrate (PP-Substrate) act as a non-polar substrate and PP substrates have limitations to their adhesion properties due to their non-polar nature and low surface tension. Corona treatment can make a free radical on the surface. 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), T-peel testing, single lap shear testing and contact angle measurement. In 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 means that the crosslink density affects the mobility of hard segment to pack itself correctly to form hard domains. 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 based different polymer glycols. It is noteworthy that the carbonyl group in PBA-SPU for adhesion, based T-Peel test and single lap shear test results, have good adhesive properties. The glass transition temperature (T_g), Melting temperature of soft segment ($T_{m,s}$) and melting temperature of hard segment ($T_{m,h}$) of PBA-SPU was higher than that of PTMG-SPU. The microphase separation of the polyether based SPU (PTMG-SPU) was stronger than that of polyester based SPU (PBA-SPU). It was easily expected that the polar hard segment component can be diffuse to the top surface of PTMG-SPU.

Keywords: Corona treatment, Surface free energy, Segmented polyurethane

Introduction

Segment polyurethane elastomers (SPUs), which consist of soft and hard segments, are well known to separate into two phases (Buist & Gudgeon, 1968). Hard domains participate in physical crosslinks in a soft matrix, whereas the soft phase provides extensibility to the polyurethane. The microphase-separated structure confers excellent mechanical properties in the bulk properties of SPU. Thus SPUs are used in various applications such as daily life materials, industrial parts, elastomers and adhesives (Petrovic, Javni, & Divjakovic, 1998; Nakamae, Nishino, Asaoka, & Sudaryanto, 1996,). 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. In contrast to the excellent mechanical properties of microphase-separated SPU, the adhesion properties will be reduced. Therefore, it is challenge that SPU has good mechanical properties and good adhesion properties. Therefore, control of morphology of SPUs is required to obtain high performance SPUs (Martin, Meijs, Renwick, Gunatillake, & McCarthy, 1996,; Petrovic et al., 1998; Mark, Gaylord, & Bikales, 1969; Kongpun, Motokucho, Kojio, & Furukawa, 2008). Normally, SPU consist of similar hard segments, but different of soft segment chemistries, including polyether and polyester. These different soft segments produce different surface chemistries and material properties.

Moreover, for adhesive field, the problem owing 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 (Owens & Wendt, 1969). However, PP substrates have limitations to their adhesion properties due to their non-polar nature and low surface tension so it cannot be adhered to the polar materials such as SPU. 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-], carbonyl [-C=O], ester [-C(C=O)-O-], carboxylic acid [-C(=O)-OH] and carbonate [-O(C=O)-O-] (O'Hare, Leadley, & Parbhoo, 2002). 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 (Figure 1) (Sellin & Campos, 2003). 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 (O'Hare et al., 2002; Sellin et al., 2003). 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 (Igor, Vladimir, & Ivan, 2006) (Figure 2). It 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. 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 (Sellin et al., 2003) and polyethylene substrate (Oosterom, Ahmed, Poulis, & Bersee, 2005).

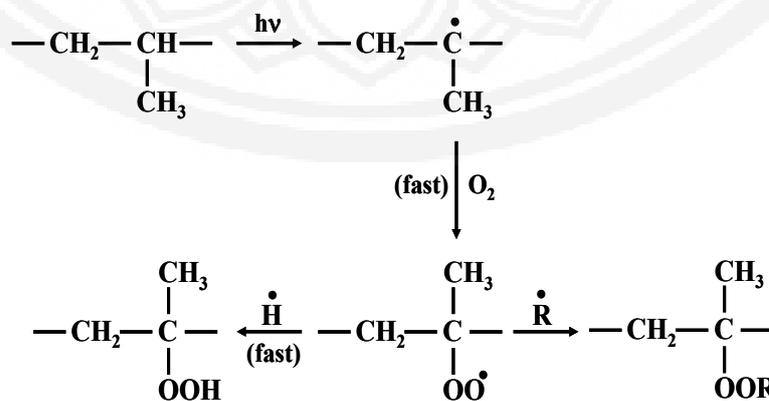


Figure 1 Surface oxidation during corona treatment of polypropylene (PP) (Sellin et al., 2003).

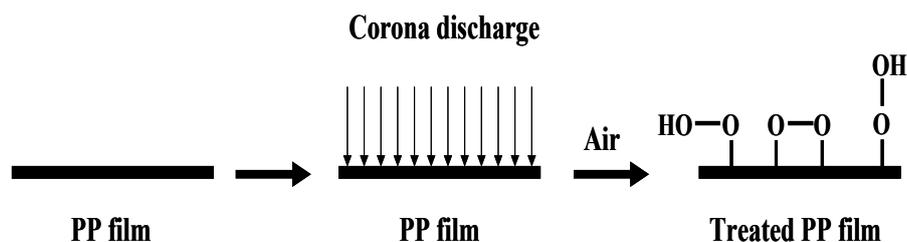


Figure 2 Corona discharge for polypropylene (PP) film.

In recent years, the development of polyurethane adhesive with various substrates has been conducted. (Xu & Liu, 2003) improved the hydrophilic properties of polyester fabric by corona discharge irradiation at different voltages and reported that dye-uptake ratio and dyeing speed were improved after the treatment. (Castell, Wouters, de With, Fischer, & Huijs, 2004) 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., 2005) 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.

Methods and Materials

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 gas 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).

Surface modification of polypropylene (PP) substrate

PP films were treated by corona discharge (Kasuga Denki Co., Ltd., PS-601c model). The PP samples were cut into $100 \times 25 \text{ mm}^2$ and $152 \times 25 \text{ mm}^2$ 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.

SPUs synthesis

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 $70 \text{ }^\circ\text{C}$ 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 $100\text{ }^\circ\text{C}$ for 24 hours under air atmosphere.

Characterization

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.

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 $60\text{ }^\circ\text{C}$, using the following formula: $g = W_b/W$, 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).

$$q = 1+Q \tag{1}$$

$$Q = \left[\frac{(W_a - W_b) / d_s}{W_b / d_p} \right] \tag{2}$$

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.

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 $10\text{ }^\circ\text{C}/\text{min}$ from $-140\text{ }^\circ\text{C}$ to $250\text{ }^\circ\text{C}$ under a nitrogen atmosphere.

Surface free energy measurements

Surface free energy were investigated using contact angle (θ) measurements with water and

methylene iodide (Lugscheider, Bobzin, & Moller, 1999; Lugscheider & Bobzin, 2001). 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 (Takahashi, Kita, & Kaibara, 2002; Mochizuki, Senshu, Seita, Yamashita, & Koshizaki, 2000). The surface free energy (γ_s) can be expressed as follows;

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{4}$$



where γ_s^d is from the dispersion (nonpolar) component and γ_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 (Owens et al., 1969) extended the Young's equation using geometric means, as follow;

$$1 + \cos\theta = 2\sqrt{\gamma_s^d \left(\frac{\sqrt{\gamma_L^d}}{\gamma_{LV}} \right)} + 2\sqrt{\gamma_s^p \left(\frac{\sqrt{\gamma_L^p}}{\gamma_{LV}} \right)} \quad (5)$$

where subscripts L , S and V are the liquid, solid and vapor states, respectively. The superscripts d and p refer to the dispersion force and polar force components, respectively.

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 mm² 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.

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).

Single Lap shear strength

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 mm². 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.

Results and Discussion

Density and swelling measurement

Table 1 shows properties of PTMG-SPU and PBA-SPU. Density of PTMG- and PBA-SPUs was 1.07 and 1.18 g/cm³, 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 polyol better than that ether group in PTMG polyol.

Table 1 Properties of PTMG-SPU and PBA-SPU.

Sample	Density d_p (g/cm ³)	Gel Fraction (%)	Degree of Swelling in Toluene	Crosslink density (mol/cm ³)x10 ⁻³	Molecular weight between crosslinks (g/mol)x10 ²
PTMG-SPU	1.07	99.5	1.89	1.18	8.47
PBA-SPU	1.18	99.1	1.33	5.03	1.99

Thermal Behavior

Figure 3 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).

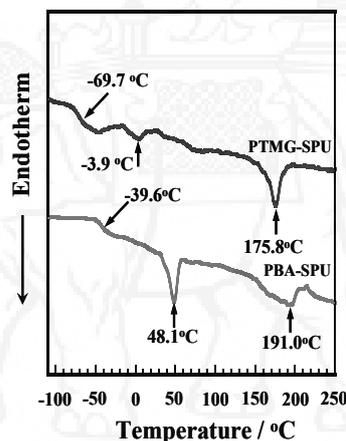


Figure 3 DSC thermograms of various polymer glycols based SPUs.

Table 2 Glass transition temperature and melting temperature of SPUs.

SPU	Glass transition temperature (T_g) (°C)	Melting temperature of soft segment ($T_{m,S}$) (°C)	Melting temperature of hard segment ($T_{m,H}$) (°C)
PTMG-SPU	21.8	51.0	72.8
PBA-SPU	49.5	1.3	50.8

Surface free energy measurements

Figure 4 shows contact angle of different polymer glycols based SPUs. The value of total surface free energy (γ_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. 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 polyether 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 γ_s of PP film showed the extremely high value when the corona discharge treatment time was used, namely the γ_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 γ_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 γ_s , γ_s^d and γ_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 γ_s was dependent on the aggregation of hard segment in SPU chain and the type of polar component in polymer glycol.

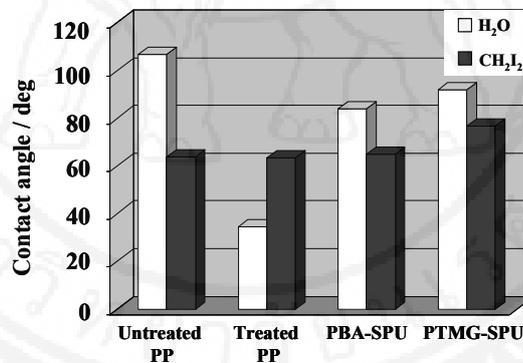


Figure 4 Contact angle of different polymer glycols based SPUs.

Table 3 Surface free energy, the dispersion component and the polar component of different polymer glycols based SPUs.

Sample	γ_s^d (mJm^{-2})	γ_s^p (mJm^{-2})	γ_s (mJm^{-2})
Untreated PP	27.1	1.5	28.6
Corona treated PP	25.4	75.7	101.1
PBA-SPU	25.8	20.7	46.5
PTMG-SPU	19.3	16.1	35.3

Adhesive strength and adhesive behavior

Figure 5 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). For PBA based SPUs, the interaction between adhesive and PP treated substrate can be occurred in both segments that is, in hard segment and soft segment because soft segment also has polar groups. In contrast, for PTMG based SPUs, the interaction between adhesive and PP treated substrate can be occurred in one phase that is, hard segment. Thus, the polymer glycols and corona discharge treatment for non-polar substrate such as PP strongly affect polyurethane adhesives.

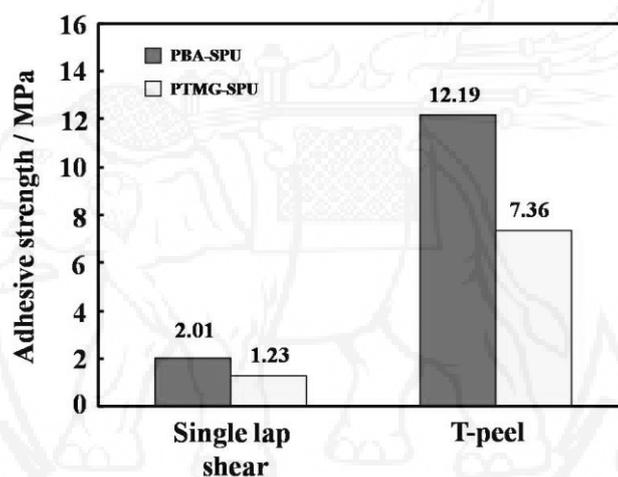


Figure 5 Effect of polymer glycol on T-peel strength and single lap shear strength (in MPa) of SPUs.

Conclusion

Two types of SPUs were prepared using two different polymer glycols and non-polar substrate was treated by corona discharge treatment for studied the adhesion properties. Crosslinking can be induced by carbonyl group in PBA polyol better than that ether group in PTMG polyol. Therefore, the microphase separation of the polyether based SPU was stronger than that of polyester based SPU. Furthermore, polyester based SPU has strong intermolecular interaction in soft segment because polar component (carbonyl group (C=O) of polyester) can be interacted with other segment and

also interacted with PP treated substrate. From surface free energy, water wettability, single lap shear strength and T-peel strength results, polyester based SPU exhibited high values because the increasing of hydrophilic component (polar component) on the SPU surface compared to polyether based SPU. After corona discharge treatment, the small contact angle was found and the surface free energy of PP film showed the extremely high value. Moreover, polar functional group such as $-CO$, $-C=O$ and $-COO$ were introduced on PP film surface. PP film had changed from non-polar to polar substrate so PP treated substrate can be adhered with both SPUs, especially to polyester based SPU (PBA-SPU).



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