# Relation between the Phase Structure and Surface Structure of Films Made from Polyurethane Dispersions

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ABSTRACT: Segmented polyurethane dispersions (SPUD) having carboxyl groups in soft segments (SS) or hard segments (HS) were synthesized. Phase, surface, and interface structures of films made from those SPUD were examined by differential scanning calorimeter (DSC), contact angle, and X-ray photoelectron spectroscopy (XPS) measurements. Segmented polyurethanes (SPU) with the same structures as SPUD were also synthesized in the organic solvent system, and the properties and behaviors of these SPU films were compared with the SPUD films. It was indicated by the DSC measurements that the film made from SPUD having carboxyl groups in the soft segments (S-SPUD) had higher crystallinity and crystal growth rate than the film made from SPUD having carboxyl groups in the hard segments (H-SPUD) in spite of steric hindrance. On the other hand, the film made from SPU having carboxyl groups in the hard segments (H-SPU) had higher crystallinity than the film made from SPU having carboxyl groups in the soft segments (S-SPU). Further, the crystal growth rate of SPU was faster than that of SPUD, regardless of the position of carboxyl groups. These results indicated that the phase structure of SPUD film was affected by the phase structure in the dispersion particle. Surface and interface structure of SPUD film was rearranged with a change of the phase structure. But the degree of this change was higher in the surface structure than in the interface structure. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 741-748, 1999

Key words: polyurethane; dispersion; carboxyl group; surface; interface

# **INTRODUCTION**

Segmented polyurethane (SPU) is a multiblock copolymer having a hard segment (HS) and soft segment (SS) alternately. It is well known that SPU has a microphase separation structure, because of the incompatibility of HS and SS, and formation of a hard domain due to the hydrogen bond among urethane bonds in  $\text{HS.}^{1-3}$  SPU has very high cohesive strength because of this microphase separation structure, and this is widely used as adhesives, binder, paint base, and so on. However, there are a few studies about the surface or interface structure of SPU, related to phase structure.<sup>4,5</sup> It is important to understand the surface and interface structure to improve adhesive properties.

Nakamae et al.<sup>6,7</sup> reported the relation between the phase structure and the surface and interface structure of SPU film, having various amounts of the functional group in HS or SS. In their articles, the following was found. For SPU, having a functional group in HS, the modulus was decreased because of cohesion of the HS was disturbed by a steric hindrance of the functional group, and it was difficult for the functional group to orient to the interface because of the low mobility of HS. For SPU having a functional group in

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Monomer	Abbreviation	Structural Formula	
Isophoron–diisocyanate	IPDI	CH <sub>3</sub> CH <sub>3</sub>	
		OCN CH <sub>2</sub> NCO	
		H/ VCH3	
1,4-Butanediol	BDO	$HO-(CH_2)_4-OH$	
Dimethylolpropionic-acid	DMPA	$HO-CH_2-C-CH_2-OH$	
Poly convolution of iol	PCLD	COOH O O	
r ory-caprolactoneulor	relb	$\mathbf{H} - (\mathbf{O}(\mathbf{C}\mathbf{H}_2)_5\mathbf{C})_n - \mathbf{R} - (\mathbf{C}(\mathbf{C}\mathbf{H}_2)_5\mathbf{O})_n - \mathbf{H}$	
Poly-caprolactonediol having COOH	PCLD-COOH	$H - (O(CH_2)_5C)_n - R - (C(CH_2)_5O)_n - H$	
Piperazine	PZ	соон	
		ни ин	

Table I Structural Formulas of Used Monomers and Oligomers

SS, there was no decrease in modulus because microphase structure was maintained, and the functional group tended to orient to the interface because of the high mobility of SS.

As for adhesives, paint base, and so on, the conversion from an organic solvent system to a nonsolvent system or waterborne system has been advanced recently, from the point of view of environmental pollution and safety. As for segmented polyurethane dispersion (PUD), the development is required as an alternative to organic solvent systems for polyurethane. One of the ways for polyurethane to be dispersed in water is to introduce hydrophilic groups, such as a carboxyl group, to the polyurethane chain. But there is no report about surface or interface structure of film made from SPUD, the relation between the phase structure and the surface or the interface structure of film, and the effect of a functional group such as a carboxyl group on these structure.

In this study, SPUDs having carboxyl groups as functional groups in HS or SS were synthesized, and the effect of the position of carboxyl groups on the phase structure and the surface or interface structure was investigated. The SPUs were also synthesized in an organic solvent system, whose compositions were equal to those of SPUDs, and we compared the film structure of the organic solvent system with that of the waterborne system.

### EXPERIMENTAL

#### Materials

As a diisocyanate, isophoron-diisocyanate (from Hulls Co. Ltd. Veatanat IPDI) was used as received. As oligomeric diols, poly-caprolactonediol (from Daicel Chemical Co. Ltd. PLACCEL-220,  $M_n = 2000$ ) (PCLD) and carboxyl group, containing poly-caprolactonediol (from Daicel Chemical Co. Ltd. PLACCEL-220A,  $M_n = 2000$ ) (PCLD-COOH) were used after dehydration at 80°C for 12 h. Dimethylolpropionic-acid (from International Menerol Co. Ltd.) (DMPA) was used to introduce carboxyl groups in HS of SPUD and

For DSC Measurement		For Contact Angle Measurement	
S-SPU disp.	$50^{\circ}\mathrm{C}  imes 48\mathrm{H}$	$50^{\circ}\mathrm{C}  imes 8\mathrm{H} + \mathrm{vacuum}$	
H-SPU disp.	$50^{ m oC} imes 48{ m H}$	$50^{\circ}\mathrm{C}  imes 8\mathrm{H} + \mathrm{vacuum}$	
S-SPU sol.	$50^{\circ}\text{C} \times 48\text{H} + 80^{\circ}\text{C} \times 8\text{H} + \text{vacuum}$	$80^{\circ}C \times 8H + vacuum$	
H-SPU sol.	$50^{\circ}C \times 48H + 80^{\circ}C \times 8H + vacuum$	$80^{\circ}C \times 8H + vacuum$	

 Table II
 Condition for Film Preparation

SPU. 1,4-Butanediol (from Wako Pure Chemical Industrials Ltd.) (BDO) was dehydrated with molecular sieves prior to use. Piperazine (from Wako pure Chemical Industrials Ltd.) (PZ) was used as received. Triethyl amine (TEA), methyl ethyl ketone (MEK), and dimethyl formamide (DMF) (from Wako Pure Chemical Industrials Ltd.) were also dehydrated with molecular sieves prior to use. Distilled-deionized water was used in all experiments.

#### **Synthesis**

The basic formulations of samples used are shown in Table I. As a reactor, 1000-mL cylinder-shape, four-necked separable flask with a mechanical stirrer, condenser, thermometer, and nitrogen tube inlet was used. Reaction was carried out in an oil bath with a temperature controller.

SPUD having carboxyl groups in SS (S-SPU) and SPUD having it in HS (H-SPU) were synthesized as follows. IPDI, PCLD-COOH or PCLD and BDO or DMPA were first mixed in a flask and the reaction was carried out at 80°C for 4 h in MEK to synthesize NCO-terminated urethane prepolymer. The reaction time was determined separately with a standard dibuthylamine back-titration method. Then the system was cooled to 40°C and TEA was added to the prepolymer. Stirring rotation rate was increased, and water was added to the prepolymer at once to emulsificate. After confirming the emulsification, PZ water solution was added to the dispersion and chain extension reaction was carried out at 30°C for 3 h. Finally, MEK was distilled at 40°C under a vacuum condition, and SPUD, which was a complete waterborne system, was obtained.

SPU having a carboxyl group in SS (S-SPU) and SPU having it in HS (H-SPU) were synthesized as follows. IPDI, PCLD-COOH or PCLD, and BDO or DMPA were first mixed in a flask and the reaction was carried out at 80°C for 4 h in DMF to synthesize NCO-terminated prepolymer. Then the system was cooled to 40°C and PZ DMF solution was added slowly. Synthesized SPU was reprecipitated with water and solved in DMF again.

All samples have the same HS content and COOH content.

#### **Preparation of Films**

Films were prepared by drying SPU or SPUD in a clean chamber under a vacuum condition. Full and detailed conditions are given in Table II. Films were annealed at 80°C for 48 h and stored at 20°C, 60% of relative humidity before measurements.

#### Measurements

# DSC

DSC chart was obtained on the Shimadzu DSC-50 system. The heating rate was  $10^{\circ}$ C/min, the measurement range was between -50 and  $250^{\circ}$ C, and sample weight was approximately 10 mg.

#### **Contact Angle**

Contact angles were measured for both the surface and interface removed from PET film at 20°C and 60% relative humidity. The static contact angle was measured with the CA-Z autocontact angle measurement system (Kyowa Interface Science Co. Ltd.). The PET film was washed with water and acetone prior to use. The surface free energy was calculated with eqs. (1) and (2), proposed by Owens et al.<sup>8</sup>

$$\{(1 + \cos \theta)\gamma_l\}/2 = (\gamma_s^d \gamma_l^d)^{1/2} + (\gamma_s^p \gamma_l^p)^{1/2}$$
(1)

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{2}$$

where  $\gamma_s$  and  $\gamma_l$  are the surface free energy of the solid and liquid, respectively, and  $\gamma^d$  and  $\gamma^p$  are the dispersion and the polar force components, respectively. Because at least two kinds of liquids are needed to evaluate  $\gamma_s$ ,  $\gamma_s^d \gamma_s^p$ , water and meth-

Sample	HS Content (wt %)	$M_w$	$M_w/M_n$
S-SPUD	31.0	3,400,000	2.1
H-SPUD	32.1	2,700,000	2.7
S-SPU	32.0	2,200,000	3.4
H-SPU	33.7	1,600,000	4.0

 Table III
 Molecular Weight of Samples

ylene iodide was used. The dispersion and the polar force components of the surface free energy of water are 21.5 and 51.0 mJ/m<sup>2</sup>, and those of methylene iodide are 48.5 and 2.3 mJ/m<sup>2</sup>, respectively.

#### XPS

XPS spectra was obtained on the Shimadzu ESCA-500 with MgK $\alpha$  X-ray source. The X-ray gun was operated at 6 kV, 30 mA.

# **RESULTS AND DISCUSSION**

#### **Polymer Characterization**

Molecular weight of each sample determined by gel permeation chromatography (GPC) by using polystyrene as a standard is given in Table III. Molecular weight of SPUD was two times as large as SPU. This was mainly caused by the difference of the chain extension method. It is assumed that the few differences in the molecular weight did not affect the results.

The general properties of SPUD are shown in Table IV. It was suggested that the amount of carboxyl groups at the particle of S-SPUD was approximately equal to that of H-SPUD because the particle size and pH of S-SPUD were same as H-SPUD. It was also confirmed by the  $\zeta$ -potential measurements.

#### **SPUD**

#### **DSC** Measurements

A typical DSC chart obtained by SPUD film is shown in Figure 1. An endothermic peak at

Table IV General Properties of Used SPUDs

Sample	Conc. (wt %)	Vis. (cps)	pН	<i>d</i> (nm)
S-SPUD H-SPUD	$\begin{array}{c} 20.9 \\ 20.9 \end{array}$	4.8 17.9	$7.97 \\ 7.91$	$\begin{array}{c} 116.0\\ 119.8\end{array}$



Figure 1 Typical DSC curves for SPUD.

around 50°C was observed. It was assigned to melt the crystal formed by SS. The peak area changed with stored time, and it indicated that crystallinity increased with stored time. In Figure 2, the relationships between heat of fusion ( $\Delta H$ ) calculated from the DSC peak and the stored time is shown for S-SPUD and H-SPUD. In the case of S-SPUD,  $\Delta H$  increased in 0 to 20 days, and after 20 days,  $\Delta H$  was still unchanged, while, in the case of H-SPUD, a significant change of  $\Delta H$  was not observed in 0 to 10 days.  $\Delta H$  increased after



**Figure 2** Plots of heat of fusion for SS ( $\Delta H$ ) vs. stored time for films made from SPUDs. Open ( $\bigcirc$ ) and filled ( $\bigcirc$ ) circle represent S-SPUD and H-SPUD, respectively. Solid (—) and dotted ( $\cdots$ ) straight lines show  $\Delta H$  for PCLD and PCLD-COOH, respectively.



**Figure 3** Plots of contact angle  $\theta$  of water on surface of films made from SPUDs vs. stored time. Open ( $\bigcirc$ ) and filled ( $\bullet$ ) circle represent S-SPUD and H-SPUD, respectively.

10 days, and it came to equilibrium after 30 days. Moreover,  $\Delta H$  of S-SPUD in the equilibrium state was higher than that of H-SPUD in the equilibrium state.  $\Delta H$  of PCLD, which was a oligomer for H-SPUD, had higher crystallinity than PCLD– COOH, which was a oligomer for S-SPUD. It might be caused by the steric hindrance of the COOH side chain. However, for SPUD, S-SPUD had higher crystallinity and a faster crystalline rate than H-SPUD, despite steric hindrance in SS. The meaning of the results is discussed later by comparing them with the results obtained from the SPU system.

#### **Contact Angle**

The relationships between the contact angle of water and stored time for S-SPUD and H-SPUD are shown in Figure 3. In the case of S-SPUD, the contact angle of water decreased in 0 to 20 days, that is, the hydrophilicity of the surface increased, and it came to an equilibrium state after 20 days, while, in the case of H-SPUD, the change of contact angle was not observed in 0 to 10 days, and it changed slightly in 10 to 30 days and came to equilibrium state after 30 days. The results obtained from the contact angle measurements corresponded to the results obtained from DSC measurements. It indicated that the surface structure changed accompanying changes of the phase structure with storage time.

When the contact angle in the equilibrium region of S-SPUD was compared with H-SPU in Figure 3, the hydrophilicity of the S-SPUD surface was higher than that of the H-SPUD surface. To investigate the difference in hydrophilicity and the change of contact angle with stored time, surface free energy ( $\gamma$ ), its dispersion component ( $\gamma^d$ ), and its polar component ( $\gamma^p$ ), were calculated by using the contact angle of water and methylene iodide. The time dependence of  $\gamma$ ,  $\gamma^d$ , and  $\gamma^p$  are shown in Figure 4.

It was confirmed that the surface free energy increased with stored time, and the tendency agreed with the change of the hydrophilicity of the surface for both SPUDs. For S-SPUD, the increase of surface free energy depended on the increase of both dispersion and polar component. It is suggested that the increase of dispersion component can be attributed to the increase of the density of the polymer at surface, following the crystallization of SS, and the increase of the polar component can be attributed to the orientation of carboxyl groups near the surface. That is, the increase of both the dispersion and polar component for S-SPUD indicated that the SS near the surface formed crystals, going with crystallization in the bulk, and the density of carboxyl groups that were in the SS near surface increased as crystallization of SS near the surface, while, for H-SPUD, the polar component was unchanged and the increase of surface free energy depended on the increase of dispersion component, that is, the increase of crystallinity near the surface.

The value of the dispersion component at the equilibrium state for S-SPUD was larger than



**Figure 4** Plots of surface free energy  $(\gamma)$ , polar component  $(\gamma^p)$  and dispersion component  $(\gamma^d)$  vs. stored time. White and black symbols represent S-SPUD and H-SPUD, respectively.

Sample	Cs/Cav	Os/Oav	Ns/Nav
	(wt %)	(wt %)	(wt %)
S-SPUD	108.0	93.8	$29.5 \\ 53.2$
H-SPUD	99.9	109.0	

Table VResults of XPS Measurement

that for H-SPUD. The value of  $\Delta H$  for S-SPUD was also larger than that for H-SPUD (see Fig. 2). These results indicated that both S-SPUD surfaces were mainly covered with SS, and the tendency was especially remarkable for S-SPUD.

The surface elemental concentrations for S-SPUD and H-SPUD measured by XPS are given in Table V compared with the average concentration of each element calculated by composition. As can be seen from Table V, the nitrogen concentration at the surface was especially low compared with the bulk for both S-SPUD and H-SPUD. It was noted that the surface was mainly covered with SS. Besides, the tendency was more remarkable for the S-SPUD surface. These results were consistent with the results of the contact angle measurements.

The relationships between the contact angles of water on the interface removed from the PET film and stored time for S-SPUD and H-SPUD are shown in Figure 5. The change of contact angle at the interface had same tendency as that at the surface (see Fig. 3). The result indicated that the interface structure was also influenced by the al-



**Figure 5** Plots of contact angle  $\theta$  of water on interface of films made from SPUDs vs. stored time. Open ( $\bigcirc$ ) and filled ( $\bullet$ ) circle represent S-SPUD and H-SPUD, respectively.



**Figure 6** Plots of heat of fusion for SS ( $\Delta H$ ) vs. stored time for films made from SPU. Open ( $\bigcirc$ ) and filled ( $\bigcirc$ ) circle represent S-SPU and H-SPU, respectively. Solid (—) and dotted ( $\cdots$ ) straight lines show  $\Delta H$  for PCLD and PCLD–COOH, respectively.

teration of bulk structure with stored time, as well as the surface structure. However, the degree of alteration at the interface was lower than that at the surface. This might be caused by the decrease of mobility of the molecule because of adsorption of the molecule on PET.

#### SPU

#### **DSC** Measurements

At around 50°C, an endothermic peak assigned to melt the crystal formed by SS was also observed in the SPU film as well as in SPUD film. In Figure 6. the relationships between  $\Delta H$  calculated from the DSC peak and stored time are shown. After annealing,  $\Delta H$  increased rapidly and came to an equilibrium state in either case of the S-SPU and H-SPU. It indicated that the SS crystallized and phase structure came to equilibrium rapidly in either case. Moreover,  $\Delta H$  of H-SPU at the equilibrium state was higher than PCLD-COOH, which was an oligomer for S-SPU. It indicated that H-SPU had higher crystallinity than S-SPU for SS because SS in H-SPU had no steric hindrance of the COOH side chain. This tendency was different from the tendency in water-borne systems.

# Contact Angle

The relationships between the contact angle of water on the surface and stored time for H-SPU



**Figure 7** Plots of contact angle  $\theta$  of water on surface of films made from SPU vs. stored time. Open ( $\bigcirc$ ) and filled ( $\bullet$ ) circle represent S-SPU and H-SPU, respectively.

and S-SPU are shown in Figure 7, and the relationships between the contact angle of water on the interface removed from the PET film and stored time are shown in Figure 8. In either case, the contact angle of the water came to an equilibrium state rapidly after annealing, and these results corresponded to the results obtained by DSC measurements. It indicated that the surface and interface structure of SPU also changed, accompanying changes of phase structure with stored time, as well as these structure of SPUD. Moreover, the surface and interface structure of films made from the organic solvent system changed and came to an equilibrium state more rapidly than those of SPUD.

In the case of S-SPU, the hydrophilicity of surface decreased and the hydrophilicity of interface increased in 0 to 10 days. This indicated that the decrease of hydrophilicity of the surface was attributed to hiding in bulk for the carboxyl groups near the surface, to avoid contacting more hydrophobic air than bulk, and the increase of hydrophilicity of the interface was attributed to the orientation of carboxyl groups near the interface, accompanying adsorption of the molecule on PET, while, in the case of H-SPU, the hydrophilicity of surface and interface did not change. S-SPU, which had carboxyl groups in SS, had more remarkable changes in hydrophilicity of the surface and interface than H-SPU. This was caused by a higher mobility of SS with the carboxyl groups in S-SPU than that of HS with the carboxyl groups in H-SPU. Moreover, the hydrophilicity in the equilibrium state decreased for the interface of S-SPU, the interface of H-SPU, the surface of S-SPU, and the surface of H-SPU.

#### Comparison of SPUD and SPU

According to the comparison of Figures 2 and 6, the crystal growth rate of SPU was faster than that of SPUD, regardless of the position of carboxyl groups.

The organic solvent systems are homogeneous systems because DMF used as a solvent is a good solvent for both HS and SS, and polymer chains are solvated in the organic solvent system. In the case of SPU, there is little restriction on the dynamics of polymer chains during the film formation. Therefore, crystallization of SS was faster and the phase structure came to an equilibrium state more rapidly. On the other hand, the water-borne systems are heterogeneous systems, and they have an interface between particles in their film-forming process. It is considered that a long time is needed to make the interface disappear between particles. For example, in the case of acrylic emulsion whose  $T_{a}$ is 18°C, the coalescence of particles does not completely occur until about 4 months at 25°C.<sup>9</sup> Another reason is that there is not enough space for the molecule to move in a particle. The molecular weight of SPUD was about 10<sup>6</sup>, and according to the following eq.:

$$S = (nl^2/6)^{0.5} \tag{3}$$

where S is a diameter of random coil, n is bond number, and l is bond length; a diameter of random coil is about 10 nm. There is not enough space for the molecular chain to move in a particle because the diameter of the particle is about 100 nm, and this size is only 10 times as large as the



**Figure 8** Plots of contact angle  $\theta$  of water on interface of films made from SPU vs. stored time. Open ( $\bigcirc$ ) and filled ( $\bigcirc$ ) circle represent S-SPU and H-SPU, respectively.



**Figure 9** Schematic representation for the phase structures in the dispersion particle. (A) SPUD; (B) surface of the particle for S-SPUD; (C) surface of the particle for H-SPUD.

diameter of the random coil. Therefore, the existence of an interface between particles and less space in a particle made the crystal growth rate of SS lower in the water-borne system than in the organic solvent system.

By DSC measurements, the film made from S-SPUD had higher crystallinity and a higher rate of crystal growth than the film made from H-SPUD, despite steric hindrance. In the waterborne system, most carboxyl groups exist in the surface of particles to stabilize particles in water. Carboxyl groups are in SS for S-SPUD, and they are in HS for H-SPUD, and it is considered that the phase structures in the dispersion particle shown in Figure 9 are formed. In the film-forming process with these structures, SS is rich in S-SPUD and HS is rich in H-SPUD in their interface between particles. Therefore, S-SPUD had higher crystallinity than H-SPUD for SS, despite steric hindrance. For H-SPUD, crystallization of SS is difficult because of its strong restriction on mobility of the polymer chain in a particle. Therefore, crystal growth rate of SS is lower.

According to the comparison of Figure 3 and Figure 7, the contact angle of water on the surface of SPU was higher than SPUD, that is, the surface of SPUD has higher hydrophilicity. This was caused by the particle structure having many carboxyl groups on the surface of the particle (see Fig. 9). Especially, as for S-SPU, the tendency to decrease the hydrophilicity showed, as for S-SPUD, the reverse tendency, that is the tendency of increasing the hydrophilicity. It was suggested that carboxyl groups oriented on the surface of S-SPUD. It was considered that carboxyl groups could hide in bulk by not contacting air for the organic solvent system because there was little restriction on mobility of the polymer chain. On the other hand, for the water-borne system, it was considered that there were many SSs having carboxyl groups at the interface between particles, and crystallization of SS progressed with restriction on their mobility.

# **CONCLUSION**

Segmented polyurethane having carboxyl groups in HS or SS was synthesized in the water system and solvent system, and the phase, surface, and interface structure of these films were investigated. The following was concluded. (1) In the case of films made by SPUD, S-SPUD had a higher crystallinity and rate of crystal growth for SS than H-SPUD despite steric hindrance of the carboxyl groups. (2) Surface and interface structure of films made by PUD rearranged as a change of phase structure. However, the degree of change at the interface was lower than that at the surface. (3) In the case of films made by the organic solvent system, H-SPU had a higher crystallinity for SS than S-SPU. The crystal growth rate of SS was faster than that of films made by PUD, regardless of the position of the carboxyl groups. (4) It was indicated that phase and surface structure of films made by SPUD were affected by the phase structure in the dispersion particles.

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