

Thermodynamic Work of Adhesion and Peel Adhesion Energy of Dimethoxysilyl-Terminated Polypropylene Oxide/Epoxy Resin System Jointed with Polymeric Substrates

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ABSTRACT: The characterization of the interfacial surface of a dimethoxysilyl-terminated polypropylene oxide (DMSi-PPO)/diglycidylether of bisphenol A (DGEBA) system, which has the phase structure of DGEBA particles in a DMSi-PPO matrix, was investigated by using model joints with polymeric substrates. The surface free energy (γ) of the DMSi-PPO/DGEBA system had varied with the γ of each substrate. When the system contacted to low surface free energy materials such as Teflon, polypropylene, and polyethylene, the γ of the system showed about 14.3–31.6 mJ/m²; on the other hand, when the system contacted to high surface free energy substrates such as polyethylene-terephthalate and polyimide, the γ of the system showed 50.4 and 64.6 mJ/m², respectively, because the concentration of the DGEBA as a polar component in the system changed around these interfaces. In the low surface energy substrates used, the actual peel adhesion energy value was in good agreement with the thermodynamic work of adhesion (W_a) determined independently. However, in the high surface energy materials used, the peel adhesion energies were 10^3 – 10^4 times larger than W_a because the energy was dissipated viscoelastically at the jointed points. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1920–1930, 2001

INTRODUCTION

Epoxy resins have been widely used for adhesives, paints, and molding compounds in the civil engineering, construction, automobile, and electronic material fields because cured epoxy resins show good adhesion strength, stiffness, thermal durability, and mechanical and electronic properties. Cured epoxy resins had lacked the properties of toughness and peel adhesion, but these have been improved through various investigations, which have typically utilized a polymer blend

technique using a reactive elastomer or various types of polymer, such as carboxyl-terminated butadiene acrylonitrile rubber (CTBN),^{1–14} acrylic core-shell particles,^{14–20} and crosslinked urethane microsphere or silicone elastomer.^{21–25} These investigations have focused on enhancing toughness without losing the other advantages of cured epoxy resins. On the other hand, an elastic epoxy resin material, dimethoxysilyl-terminated polypropylene oxide (DMSi-PPO)/bisphenol A type epoxy resin (DGEBA) system, had been developed for use as an adhesive and a sealant. The DMSi-PPO/DGEBA system shows a phase structure that is the reverse of the other epoxy resin systems mentioned. Therefore, the cured system has a phase-separated structure with

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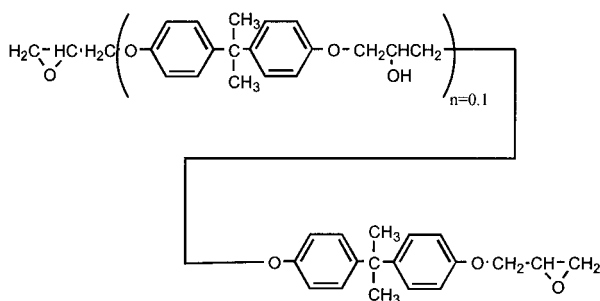
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the DMSi-PPO network as the matrix phase reinforced by dispersing DGEBA microparticles. There are reports in the literature on the relationship between adhesion strength and the phase structure of the DMSi-PPO/DGEBA system against an aluminum substrate.²⁶⁻²⁷ We had previously raised concerns about the adhesion strength and interfacial chemistry of a DMSi-PPO/DGEBA blended system against some polymeric materials that have a lower surface free energy than the metal substrates. The aim of the current study was the estimation of the thermodynamic work of adhesion (W_a) between the separated surface of the DMSi-PPO/DGEBA system and polymeric substrates by using contact-angle measurement and making a comparison of its actual peel adhesion energy with its W_a .

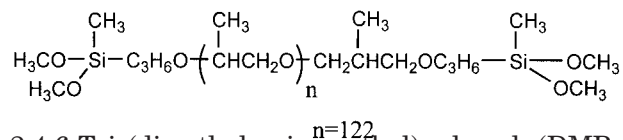
EXPERIMENTAL

Raw Materials and Substrates

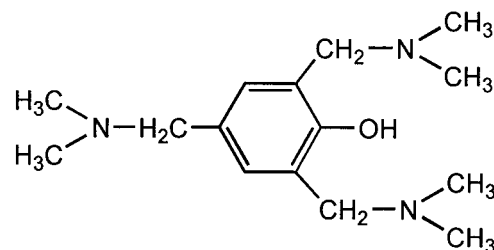
Diglycidylether of bisphenol A (DGEBA; Epikote 828, Yuka-Shell Epoxy Co., Japan; $M_w = 380$) was used as an epoxy resin. Its chemical structure is given in Structure 1.



The reactive oligomer used was dimethoxysilyl-terminated polypropylene oxide (DMSi-PPO; Siril, KANEKA Corp.; $M_w = 5500$). Its chemical structure is given in Structure 2.

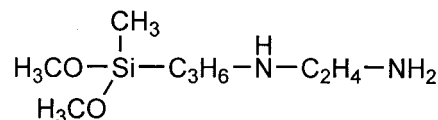


2,4,6-Tris(dimethylaminomethyl) phenol (DMP; Anchormine K54, BTR Japan Co.; $M_w = 256$) was the curing agent used for the DGEBA. Its chemical structure is given in Structure 3.



Dibutyltindilaurate (DBTDL), from the WAKO Pure Chemical Company, was used as the catalyst for DMSi-PPO. Its chemical structure is $(C_4H_9)_2-Sn-(OCOC_{11}H_{23})_2$.

Used as the compatibilizer of both DMSi-PPO and DGEBA was γ -aminoethyl-aminopropyl ethoxysilane (AMS; Nippon UNICAR Co.; $M_w = 222$). Its chemical structure is given in Structure 4.



This study used six types of polymeric substrates, all 0.025 mm thick. Those eventually chosen were:

1. Teflon (TE), Engineering Test Service Company.
2. Polyethylene (PE), Engineering Test Service Company.
3. Random polypropylene (RPP), Engineering Test Service Company.
4. Oriented polypropylene (OPP), Engineering Test Service Company.
5. Polyethylene terephthalate (PET), Engineering Test Service Company.
6. Polyimide (PI), Kapton 100H Toray-Dupont Company.

Preparation of DMSi-PPO/DGEBA System

One hundred parts DMSi-PPO and 75 parts DGEBA were poured into a 300-mL separable round-bottom flask equipped with a mechanical stirrer and a vacuum pump. These were then stirred for 1 h at room temperature under vacuum. One part DBTDL, 7.5 parts DMP, and 3 parts AMS were added to these mixture, which was then stirred for an additional 5 min under vacuum. The DMSi-PPO system and the DGEBA system were prepared as follows: 100 parts

DMSi-PPO was stirred in a flask equipped as described above for 1 h under vacuum; then 1 part DBTDL and 0.4 parts distilled water were added and mixed for an additional 5 min. Then 100 parts DGEBA was stirred under the same conditions as that for the DMSi-PPO, and 10 parts DMP was then added to the flask and mixed for an additional 5 min. The DMSi-PPO and DGEBA systems were used as references. These mixtures were cured at 25°C for 2 days, then at 50°C for 3 days as adhesives. The DMSi-PPO/DGEBA system was a clear viscous liquid at first, which means the DGEBA was almost soluble in the DMSi-PPO. Then it changed from clear to white. This result suggests that the solubility of DGEBA in DMSi-PPO changed with the reaction of both DGEBA with DMP and of DMSi-PPO with DBTDL.

Measurement of Dynamic Mechanical Properties of DMSi-PPO/DGEBA System

The dynamic mechanical property of the cured DMSi-PPO/DGEBA system was determined with a nonresonance forced-vibration viscoelastometer (Rheogel E-4000, UBM Co., Japan). The frequency was adjusted to 10 Hz, and the heating rate was 2°C/min in ambient air. The glass-transition temperature of the cured system was decided as the temperature at peak of loss tangent and was determined by dynamic mechanical analysis. The tensile moduli of both polyethylene-terephthalate and polyimide were determined with the same measurement.

Observation and Analysis of Phase Structure of the Cured System

The phase structure of the cured DMSi-PPO/DGEBA system was obtained by observing the fractured surface with a scanning electron microscope (SEM; JSM-6100, JEOL, Ltd.). The volume fraction of the dispersed DGEBA phase in several parts of the cured system was calculated from the SEM results using the pin-drop method.²⁸ In the pin-drop test small pins or needles are dropped and laid on the SEM photographs; then the number of cross points of the pins across the domains (p) and the number of hit points of the pin on the domain (h) are counted. The particle diameter (D) is calculated with the following equation: $D = 2P/3Lh$

where L is the length of the pin converted in the photo scale (μm).

The volume fraction (V) is calculated with:

$$V = h/2N$$

where N is the number of trials. In this study the number of pin drops was 400 in each case.

FT ATR-IR Measurement

Fourier transform attenuated total reflection infrared spectroscopy (FT ATR-IR; SPECTRUM 2000, PerkinElmer, Ltd.) was used to estimate the composition of the DMSi-PPO/DGEBA system near the surface. The number of scanings was 45 in each test.

Contact-Angle Measurement

In order to evaluate the surface free energy and to determine the thermodynamic work of adhesion (W_a) for each substrate joints, equilibrium contact angles were determined at 20°C for distilled water and diiodomethane on samples of the molded, rubbery DMSi-PPO/DGEBA sheet and on each substrate. When a polyimide sheet was used, the polyimide-DMSi-PPO/DGEBA bonded system showed a cohesive fracture of the adhesive so that we could not measure the contact angle of the adhesive surface; therefore, pure aluminum foil was substituted for polyimide. The Al foil contacted on the DMSi-PPO/DGEBA system was dissolved in 0.1N HCl aqueous solution for 5 days. Prior to the above substitution, we had already ascertained that the contact angle of the DMSi-PPO/DGEBA system soaked in the HCl solution for 5 days was the same as that of the surface cured under ambient conditions; therefore, the cured DMSi-PPO/DGEBA surface was considered not to change in the HCl treatment. Al substitution for PI is acceptable for the surface free-energy evaluation in this study. The diiodomethane used was research grade of high purity (purity > 99.5%). Contact angles were measured by using a contact-angle analyzer (Face CA-Z, Kyowa Surface Science Co.), which allowed a minimum change of 0.1° to be detected. The measured angles were the average of at least 25 determinations, and repeatability was within 1.5°

Determination of Adhesion Failure Energies

Adhesion failure energies for each adhesive-substrate joint were determined with the T-shape adhesion test, using an Instron-type tensile ma-

Table I Surface Free Energies of Water and Diiodomethane

Liquid	Surface Free Energy (mJ/m ²)		
	γ_L^D	γ_L^P	γ_L
Water	22.0	50.2	72.2
Diiodomethane	48.5	2.3	50.8

γ_L^D : dispersion force component of surface free energy.
 γ_L^P : polar force component of surface free energy.
 $\gamma_L = \gamma_L^D + \gamma_L^P$

chine (AGS 100A, Shimadzu Co.) with a cross-head speed of 10 mm/min at 20°C, according to ISO4578-1990. The measured results were revealed on section paper mounted on the X-Y plotter. These test pieces were prepared by pressing the spread adhesive into the substrates and curing the adhesive for 2 days at room temperature followed by 3 days at 50°C. At least 15 specimens were sampled for measuring adhesion strength in each substrate. Adhesion failure energies were calculated with the total area surrounded on the section paper.

RESULTS AND DISCUSSION

Surface Free Energy of DMSi-PPO/DGEBA System Separated from Several Substrates

The respective values of the dispersion force component, γ_L^D , and the polar force component, γ_L^P , to the total surface free energy, γ_L , of water and diiodomethane are shown in Table I. The surface free energy of the materials was determined from

the measured contact angles, θ , and the reported values of γ_L^D , γ_L^P , and γ_L by using expanded Fowkes's equations:

$$Wa = \gamma_{Li}(1 + \cos \theta_i) = 2(\gamma_S^D \gamma_{Li}^D)^{1/2} + 2(\gamma_S^P \gamma_{Li}^P)^{1/2}$$

$$Wa = \gamma_{Lw}(1 + \cos \theta_w) = 2(\gamma_S^D \gamma_{Lw}^D)^{1/2} + 2(\gamma_S^P \gamma_{Lw}^P)^{1/2} \quad (1)$$

where γ_S^D is the dispersion force component and γ_S^P is the polar force component of the surface free energies of materials. The total surface free energy, γ_S , is then simply the sum of these components. The θ_i is a contact angle of diiodomethane; the θ_w is that of water. In this analysis it is acceptable to write a pair of the above simultaneous equations derived for water, w , and for diiodomethane, i , on one solid surface. These equations were solved to yield the dispersion force component, γ_S^D , and the polar force component, γ_S^P , to the surface free energy of the solid.

The measured contact angles of these liquids on surface free energies calculated by using eq. (1) of the substrates are shown in Table II. Our results showed that the surface free energy of PE was slightly higher than that of both random and oriented polypropylene. In general, the surface free energy of polyethylene is almost the same as that of polypropylene; therefore, the difference in our results should be acceptable. There are references from the literature in Table II as comparisons with our results.²⁹⁻³⁴ The contact angles from our investigation coincide with data from literatures. Table II shows that surface free energy of the system changed from 16.5 (TE) to 51.2 mJ/m² (PI), with an increase in the dispersion force component from 14.7 of TE to 43.4 mJ/m² of

Table II Contact Angles and Surface Free Energies of Substrates

Substrates	Contact Angle (°)		Surface Free Energy (mJ/m ²)			
	Water	Diiodomethane	Experimental			From Literature
			γ_S^D	γ_S^P	γ_S	γ_S
TE	103.8	82.4	14.7	1.8	16.5	18.5 ^{29,30}
OPP	90.1	55.6	28.9	2.3	31.2	29.8 ³³
RPP	94.5	51.0	33.0	0.8	33.8	31.9 ³³
PE	89.2	43.8	36.3	1.4	37.7	35.7 ³²
PET	73.3	21.6	43.0	4.9	47.9	45.1 ³⁴ 43.8 ³¹
PI(Al)	66.1	13.3	43.4	7.8	51.2	

Table III Surface Free Energies of DMSi-PPO/DGEBA Systems

Interface	Contact Angle (°)		Surface Free Energy (mJ/m ²)		
	Water	Diiodomethane	γ_S^D	γ_S^P	γ_S
TE	100.2	67.5	23.3	1.0	24.3
OPP	88.3	59.4	26.0	3.5	29.5
RPP	91.6	59.6	26.6	2.4	29.0
PE	91.3	54.8	29.7	1.9	31.6
PET	60.8	25.4	38.2	12.2	50.4
PI	32.7	21.1	34.2	30.4	64.6

PI. The polar component also increased slightly. Therefore, the change in the dispersion force component strongly affected the total value of surface free energy of the substrates.

The measured contact angles and surface free energies of the separated surface of the cured DMSi-PPO/DGEBA system are shown in Table III. This result shows that the surface free energy of the DMSi-PPO/DGEBA system varied with the substrate.

Figure 1 shows the relationship between the γ_S of the substrates and the γ_S of the separated DMSi-PPO/DGEBA system as compared with both the DMSi-PPO and the DGEBA systems. The γ_S of the DMSi-PPO (○) system had few relations with the γ_S of substrates. This result indicates that the surface free energy of the DM-

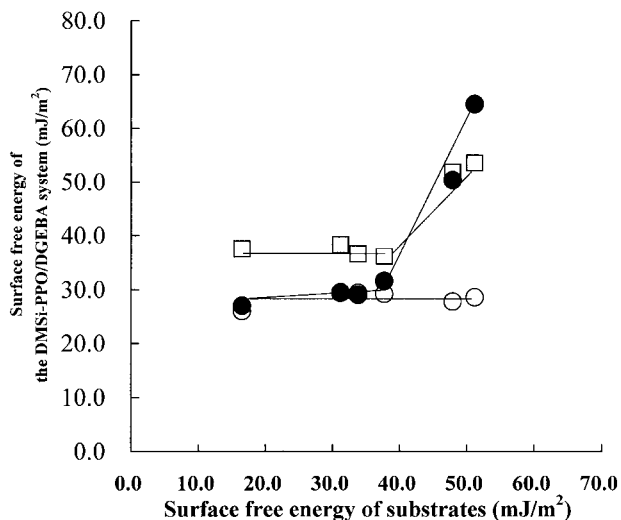


Figure 1 Relationship of surface free energy between DMSi-PPO/DGEBA system and substrates compared with DMSi-PPO system and DGEBA system (●: DMSi-PPO/DGEBA, ○: DMSi-PPO, □: DGEBA/DMP),

Si-PPO system is stable against various free energy surfaces. In the DGEBA/DMP system, the γ_S (□) was also stable against TE, PE, and PP; however, when the substrates were PET and PI, the γ_S of the system gradually rose. Nakamae et al.³⁵ have reported that competitive adsorption of amine compound occurred for DGEBA/methylenedianiline system on the aluminum hydroxide surface because of an acid-base interaction between cationic nitrogen in the NH₂ group and anionic oxygen in the OH group. The change in γ_S of DGEBA/DMP system against high surface free-energy materials can be explained by adsorption of the DMP to PET and PI following this mechanism. The value of γ_S of DMSi-PPO/DGEBA system (●) was divided into two regions. In lower region the value was stable when contacted with lower substrates, and these values were almost the same as those of DMSi-PPO. This result indicates that the interfacial character of the DMSi-PPO/DGEBA system separated from TE, OPP, RPP and PE is similar to that of DMSi-PPO and that the DMSi-PPO is not able to form a surface that has a lower free energy than the DMSi-PPO surface itself. In the higher region when contacted with PET and PI, the value increased with an increase the value of the substrate. For instance, the γ_S of the system separated from PET and PI were 50.4 and 64.6 mJ/m², respectively. These changes in γ_S were larger than that of the DGEBA/DMP system. It was considered that the γ_S of the DMSi-PPO/DGEBA system strongly depended on the surface character of substrates above the energy of the DMSi-PPO. These results suggest that the DMSi-PPO/DGEBA system is able to change its surface free energy and adapt the character of the interfacial surface on substrates.

Table IV Intensity Ratio of IR Peaks of Separated Surfaces Against Each Substrate

Contacted to	1507 cm ⁻¹			1243 cm ⁻¹			1100 cm ⁻¹		
	Surface	Internal	Ratio	Surface	Internal	Ratio	Surface	Internal	Ratio
TE	0.89	0.99	0.899	2.13	2.05	1.039	21.51	17.51	1.228
OPP	1.19	1.02	1.167	2.93	2.01	1.458	20.15	17.53	1.149
RPP	1.28	1.05	1.219	2.85	1.98	1.439	20.35	17.51	1.162
PE	1.33	1.02	1.304	2.75	1.9	1.447	20.3	17.52	1.159
PET	1.63	1.04	1.567	3.65	2.01	1.816	17.11	17.5	0.978
PI(Al)	1.56	0.98	1.592	3.79	1.99	1.905	17.02	17.55	0.970

Characterization of the Interfacial Surface of the DMSi-PPO/DGEBA System

We reported above the important finding of a correspondence of the γ_S of the separated DMSi-PPO/DGEBA system with the γ_S of each substrate. Now we will focus on the characterization of the surfaces by means of FT ATR-IR technique to explain the change in the surface free energy against substrates. Table IV shows the peak intensity ratio of 1507 cm⁻¹, 1243 cm⁻¹, and 1100 cm⁻¹ of IR peaks of the separated surfaces against each substrate. There were three intrinsic peaks for determining the DMSi-PPO and DGEBA, at 1507 cm⁻¹, 1243 cm⁻¹, and 1100 cm⁻¹, which were derived from in-plane bending of the benzene ring in DGEBA, in-plane bending of phenoxy structure in DGEBA, and rotation of the aliphatic ether in DMSi-PPO, respectively. Table IV shows the evaluation of the peak intensity ratios from the respective peak area of the surfaces divided by that of the internals. Figure 2 shows the specific IR peak intensity ratios of the surface/internal of the DMSi-PPO/DGEBA systems separated from the substrates. The respective peak intensity was detected by calculation of the peak area using FT ATR-IR measurements. The dotted line in Figure 2 indicates that the peak intensity ratio, surface/internal, was unity. The ratio of 1100 cm⁻¹, which derived from aliphatic ether in the DMSi-PPO, was slightly decreased with an increasing γ_S ; however, the ratio of both the 1507 cm⁻¹ and the 1243 cm⁻¹, which derived from the bisphenol A structure in the DGEBA, clearly increased with an increasing γ_S . It is well known that FT ATR-IR measurement is not able to characterize the pure surface. In this study infrared radiation was induced to the surface with 60° in ATR equipment. Therefore, the FT ATR-IR analyzes about 2 μm deep

from a surface; however, the qualitative characterization and comparison of components of the DMSi-PPO/DGEBA surfaces mentioned above would be acceptable. These results indicate that the DGEBA component would localize around the interface as the γ_S of the DMSi-PPO/DGEBA system increases. In general, the polarity of the DGEBA is considered higher than that of the DMSi-PPO because it has an OH group that would contribute to hydrogen bonding with other molecules and also has benzene rings saturated with π electrons. An affinity of the DMSi-PPO/

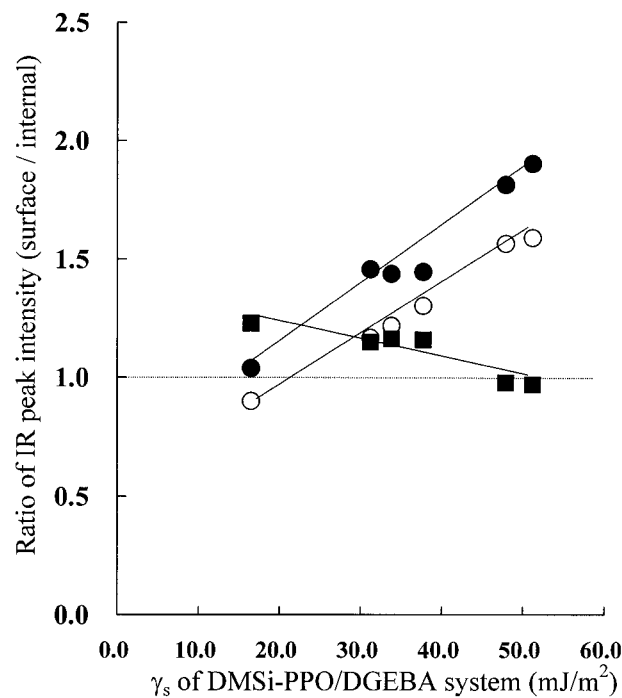
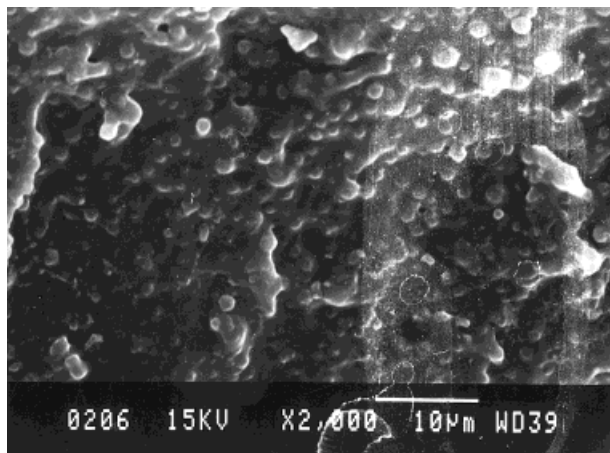
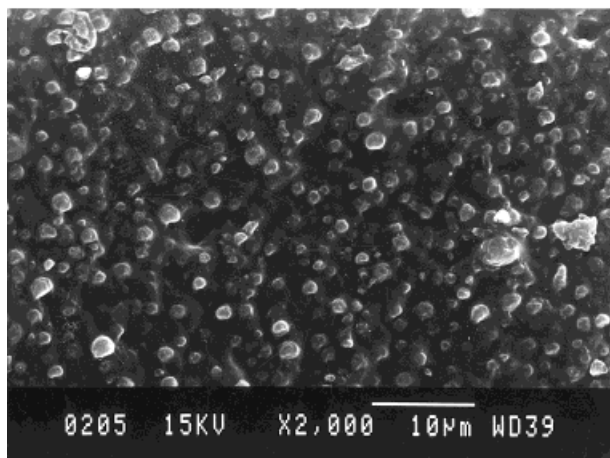


Figure 2 Relationship between IR peak intensity ratio and γ_S of the DMSi-PPO/DGEBA surfaces (○: 1507 cm⁻¹, ●: 1243 cm⁻¹, ■: 1100 cm⁻¹).



3-1) Neighborhood in the interface
Vol. Fraction of DGEBA: 34.8



3-2) Internal of the cure system
Vol. Fraction of DGEBA: 41.1

Figure 3 SEM photographs of fractured surfaces of the DMSi-PPO/DGEBA system contacted to Teflon. The theoretical volume fraction of the DGEBA phase is 40.24.

DGEBA system for several substrates would attribute to the alternative character of both DMSi-PPO and DGEBA.

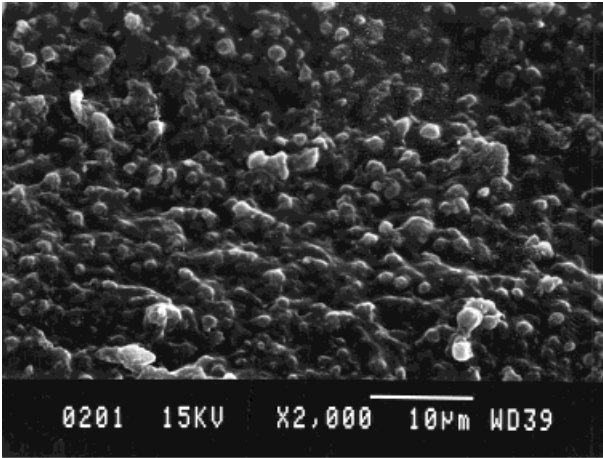
Figure 3 shows the features in the neighborhood of the interfacial surface [Fig. 3-1] and the inner fractured section [Fig. 3-2] of the DMSi-PPO/DGEBA system contacted with TE as seen through SEM observations. In these photos there are submicro-order spherical domains in black matrix. These white domains are DGEBA cured

by DMP, and DMSi-PPO is indicated as matrix. It is already known that this cured system shows a phase-separated structure.^{26,27} During the phase-separation process between DMSi-PPO and DGEBA, the DGEBA gathered itself in the DMSi-PPO matrix because the value in solubility parameter of the DGEBA ($9.94 \text{ cal/cm}^3)^{1/2}$ was higher than that of the DMSi-PPO ($7.85 \text{ cal/cm}^3)^{1/2}$. The SEM result of fractured surface of the internal reveals spherical domains of 41.1 vol % in Figure 3-2. The theoretical volume percentage of the DGEBA in this system is 40.24, so that this result indicates most of the DGEBA added can be observed as spherical domains. The result of the fractured surface around the TE interface in Figure 3-1 shows that the observed amount of the DGEBA is 34.8 vol %; therefore, the amount of the DGEBA is less than that of the internal by 6.3 vol %. This result indicates that the amount of the DGEBA around the interface between TE and DMSi-PPO/DGEBA is smaller than in the internals.

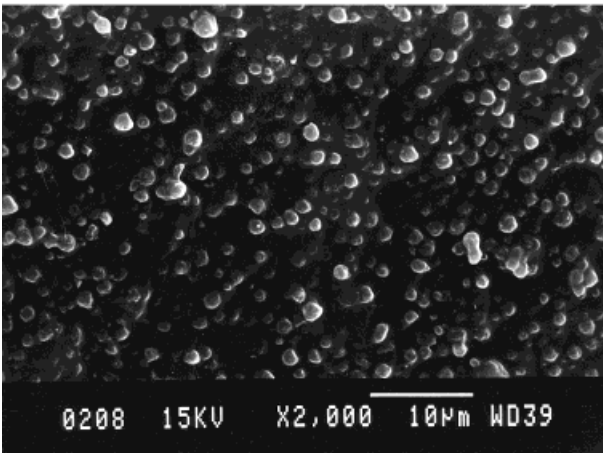
Figure 4 shows the features in the neighborhood of the interfacial surface [Fig. 4-1] and the inner fractured section [Fig. 4-2] of fractured surfaces of systems contacted with PI. Figure 4-2 shows the SEM result for the fractured surface of the internal, revealing spherical domains of 40.6 vol %. This calculated value also is in good agreement with the theoretical value. The observed result of the fractured surface around the PI interface [Fig. 4-1] shows that the amount of the DGEBA is 52.5 vol %; therefore, the amount of the DGEBA is larger than that of the internal by 12.26 vol %. The photo in Figure 4-1 reveals that the shape of the DGEBA phase is not spherical but continuous because too much DGEBA has coagulated in the neighborhood of the interface of PI. This result indicates that the amount of the DGEBA around the interface between PI and DMSi-PPO/DGEBA is much larger than in the internals. The results in Figures 3 and 4 are consistent with the FT ATR-IR investigations mentioned above. As a result, the DMSi-PPO/DGEBA system is considered to have a surface similar to the surface free energy of substrates in a curing process.

Relationship between Thermodynamic Work of Adhesion and Peel Adhesion Failure Energy

The previous section revealed that the surface free energy of the DMSi-PPO/DGEBA system



4-1) Neighborhood in the interface
Vol. Fraction of DGEBA: 52.5



4-2) Internal of the cure system
Vol. Fraction of DGEBA: 40.6

Figure 4 SEM photographs of fractured surfaces of the DMSi-PPO/DGEBA system contacted to polyimide. Theoretical volume fraction of the DGEBA phase is 40.24.

varies with the substrates contacted. These results indicate that the DMSi-PPO/DGEBA system optimizes thermodynamic adhesion energy between the system and substrates by arranging its phase structure around the interface. To discuss the relationship and compare the actual peel adhesion failure energy of systems with thermodynamic work of adhesion (W_a), actual peel adhesion failure energies of each adhesive-substrate

joint were evaluated, and the W_a deduced from these calculated surface free energies (Tables III and IV) by eq. (1) are shown in Table V. The results show that the W_a of the joint increases with an increase in the surface free energy of a DMSi-PPO/DGEBA system that has contacted with substrates. It was hypothesized that the peel adhesion failure energy of the joint would increase with an increase in the W_a .

Figure 5 shows the relationship between the thermodynamic work of adhesion and the peel adhesion failure energy of the DMSi-PPO/DGEBA-substrate jointed system. Adhesion failure was observed on all joints without PI used in the system. In systems that used PI, cohesive fracture of adhesive occurred so that adhesion energy of the PI system would refer to the cohesive energy of the cured DMSi-PPO/DGEBA system. The peel adhesion failure energy of the system shows an gradual increase from 410 at TE up to 998 mJ/m² at PE. The adhesion energy value of systems that contacted to TE, OPP, RPP, and PE were larger by at most one order compared to the corresponding W_a . This small difference could be caused by an anchor effect in the adhesion interface because of an unevenness of the substrate surface, by an uneven thickness of the adhesive, or by both. Then the adhesion energy abruptly

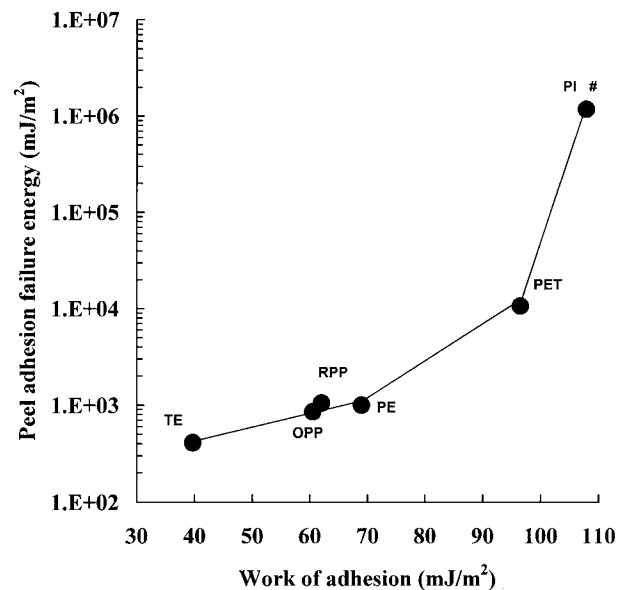


Figure 5 Relationship between the work of adhesion and the peel adhesion failure energy of DMSi-PPO/DGEBA-substrate jointed system. #: cohesive fracture of DMSi-PPO/DGEBA system.

Table V Thermodynamic Work of Adhesion (W_a)

Interface	Substrates		DMSi-PPO/DGEBA		W_a (mJ/m ²)
	γ_s^D	γ_s^P	γ_s^D	γ_s^P	
TE	14.7	1.8	23.3	1.0	39.70
OPP	28.9	2.3	26.0	3.5	60.50
RPP	33.0	0.8	26.6	2.4	62.03
PE	36.3	1.4	29.7	1.9	68.93
PET	43.0	4.9	38.2	12.2	96.52
PI	43.4	7.8	34.2	30.4	107.85

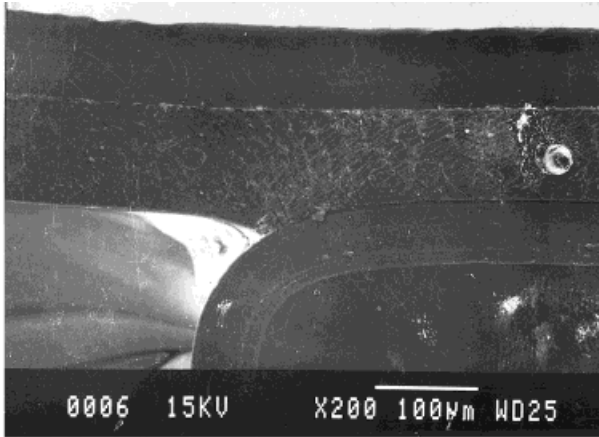
increases to 10,850 at PET. This value is 112 times higher than that of the corresponding W_a . This result suggests that another effect could have existed while the peel adhesion test was conducted—for instance, viscoelastic energy dissipation by the deformation of the adhesive layer or an elongation of the substrate film. The tensile modulus of the PET and of the DMSi-PPO/DGEBA at 20°C was 5.3×10^9 Pa and 1.6×10^7 Pa, respectively, so that the deformation of the adhesive layer would occur much easier on the latter than on the PET. In our experiment the elongation of any substrate film while undergoing the peel adhesion test was negligible. Therefore, it was considered that the viscoelastic energy dissipation from the deforming adhesive layer would reflect on the high peel adhesion failure energy of the PET jointed system. In the PI jointed system there was a more than 11,000 times difference in value between the peel adhesion failure energy and the W_a . Much attention needs to be paid to the cohesive fracture of the adhesive layer on the PI system. The tensile modulus of the PI film was 7.7×10^9 Pa at 20°C; so this unusual value of the peel adhesion energy of the PI jointed system would derive from both the cohesive energy and viscoelastic energy dissipation from the deformation of the adhesive layer. Figure 6 shows the features of the adhesive layers contacted to PET [Fig. 6-1] and PI [Fig. 6-2] under the peel situation. In Figure 6-1 the deformation of the adhesive layer can be observed at the point of peeling toward the loaded direction of the PET film. This result suggests that the peel adhesion failure energy of the PET jointed system was evaluated under an applied energy dissipation during the measurement. In Figure 6-2 bright adhesive cleavage can be observed. This bright field was not coated with Au in pretreatment for SEM ob-

servation; therefore, the cohesive fracture of the adhesive layer can be observed. This observation is in good agreement with fracture mode in the peel adhesion energy measurement (Fig. 5). A deformation of the adhesive layer also occurred in the PI jointed system. These observational results indicate that the enormous peel adhesion failure energy of the PI jointed system was evaluated during the measurement under applied energy dissipation by cohesive fracture of the system and deformation of the layer. These results indicate that a great amount of peel adhesion failure energy were consumed in the both PET and PI system. This energy consumption would explain the discrepancy between the actual peel adhesion failure energy and the W_a in jointed systems in PET and PI. However, an attempt to evaluate quantitatively the viscoelastic energy dissipation of DMSi-PPO/DGEBA and to divide the actual peel adhesion failure energy into W_a and viscoelastic energy consumption still has not been done.

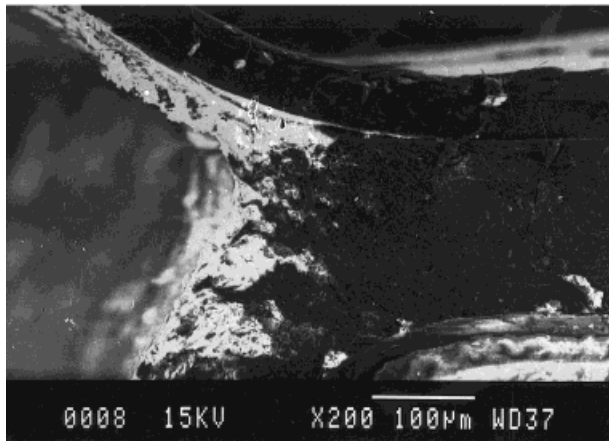
CONCLUSIONS

The following conclusions can be drawn from this study:

1. The DMSi-PPO/DGEBA system is able to change its surface free energy for obtaining maximum thermodynamic work of adhesion (W_a) against several polymeric substrates. The surface free energy of the system changes from 24.3 mJ/m² to 64.6 mJ/m². In the components of the surface free energy, the polar component changes sharply from 1.0 mJ/m² to 30.4 mJ/m² with Teflon and polyimide. The change in the



6-1) PET-jointed system



6-2) PI-jointed system

Figure 6 SEM observation results of jointed systems during peel test.

surface free energy of this system strongly depends on the change in the polar component.

2. The polar component of the system consists of the DGEBA. FT ATR-IR investigations and SEM observation results reveal that the DGEBA phase greatly localizes in the interface on polar substrates such as PET and PI. On the contrary, the DGEBA phase does not concentrate around the surface on TE, OPP, RPP, and PE.
3. The actual peel adhesion failure energies of TE, OPP, RPP, and PE jointed systems

agree considerably with those of W_a ; however, in a PET jointed system peel adhesion failure energies observed were 112 times higher than those of W_a , and in the PI jointed system difference was more than 11,000 times. These discrepancies of adhesion energies can be explained by the viscoelastic energy consumption effect of the DMSi-PPO/DGEBA system.

REFERENCES

1. Ochi, M.; Yamashita, K.; Shimbo, M. *Kobunshi Ronbunshu* 1988, 45, 817.
2. Pearson R. A.; Yee, A. F. *J Mater Sci* 1986, 21, 2475.
3. Shimbo, M.; Ochi, M.; Okazaki, M. *Nippon Settyaku Gakkaishi* 1982, 17, 192.
4. Bucknall, C. B.; Gilbert, A. H. *Polymer* 1989, 30, 213.
5. Chem, T. K.; Jan, Y. H. *Polym Eng Sci* 1991, 31, 577.
6. Ochi, M.; Yamada, H. *Kobunshi Ronbunshu* 1992, 49, 499.
7. Ochi, M.; Katayama, T.; Mimura, K.; Yamada, H. *Kobunshi Ronbunshu* 1993, 50, 621.
8. Ochi, M.; Koyama, A. *J Soc Mater Sci Jpn* 1994, 43, 1513.
9. Guild, F. J.; Kinloch, A. J. *J Mater Sci* 1995, 30, 1689.
10. Ochi, M.; Yamauchi, M.; Kiyohara, O.; Tagami, T. *J Adhes Sci Technol* 1995, 9(12), 1559.
11. Pearson, R. A.; Yee, A. F. *J Mater Sci* 1991, 26, 3828.
12. Yee, A. F.; Pearson, R. A. *J Mater Sci* 1986, 21, 2462.
13. Kinloch, A. J.; Hunston, D. L. *J Mater Sci Lett* 1987, 6, 137.
14. Ochi, M.; Mimura, K.; Kiyohara, O.; Tagami, T. *Die Angewandte Makromolekulare Chemie* 1996, 240, 4295, 17.
15. Pearson, R. A.; Dimonie, V. L.; El-Aasser, M. S. In *Proc. 25th SAMPE Tech. Conf. (California)*; 1993, p 40.
16. Sue, H. J.; Bertram, J. L.; Garcia-Martin, E. I.; Wilchester, J. W.; Walker, L. L. *Colloid Polym Sci* 1994, 272, 456.
17. Pearson, R. A.; Dimonie, V. L.; El-Aasser, M. S. *J Appl Polym Sci* 1995, 58, 439.
18. Baghri, R.; Pearson, R. A. *J Appl Polym Sci* 1995, 58, 427.
19. Ashida, T.; Ochi, M. *J Adhes Sci Technol* 1997, 11, 519.
20. Ashida, T.; Ochi, M. *J Adhes Sci Technol* 1998, 12, 749.
21. Ochi, M.; Takemiya, K. *Key Eng Mater* 1998, 137, 220.
22. Ochi, M.; Takemiya, K.; Kiyohara, O.; Nakanishi, T. *Polymer* 1998, 39, 725.

23. Ochi, M.; Shimaoka, S. *Polymer* 1999, 40, 1305.
24. Okamatsu, T.; Kitajima, M.; Hanazawa, H.; Ochi, M. *Nippon Settyaku Gakkaishi* 1997, 33, 33.
25. Okamatsu, T.; Kitajima, M.; Hanazawa, H.; Ochi, M. *J Adhes Sci Technol* 1998, 12, 813.
26. Okamatsu, T.; Kitajima, M.; Hanazawa, H.; Ochi, M. *Nippon Settyaku Gakkaishi* 1995, 31, 398.
27. Okamatsu, T.; Kitajima, M.; Hanazawa, H. Ochi, M. *J. Adhes Sci Technol* 1999, 13, 109.
28. Watanabe, H. *Funtaikougaku Kenkyukaiishi* 1971, 8, 39.
29. Dettre, R. H.; Johnson Jr., R. E. *J Phys Chem* 1967, 71, 1529.
30. Fox, H. W.; Zismann, W. A. *J Colloid Sci* 1950, 5, 514.
31. Ellison, A. H.; Zismann, W. A. *J Phys Chem* 1954, 58, 503.
32. Kitazaki, Y.; Hata, T. *Nippon Settyaku Kyoukaishi* 1972, 8, 174.
33. Schonhorn, H.; Ryan, F. W. *Advances in Chemistry Series 87*; American Chemical Society: Washington, DC, 1968; p 140.
34. Andrews, E. H.; Kinloch, A. J. *Proc R Soc London, Ser A* 1973, 332, 385.
35. Nakamae, K.; Nishino, T.; Airu, X.; Asaoka, S. *Int J Adhesion and Adhesive* 1995, 15, 15.