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Effect on the toughness and adhesion properties of epoxy resin modified with silyl-crosslinked urethane microsphere

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Abstract

In order to give a toughness and improve adhesion properties of the cured epoxy system, modified epoxy resins, which have pre-reacted urethane microspheres formed using dynamic vulcanization method in liquid diglycidylether of bisphenol A, were prepared. It was found that the size of the particles decreased to sub-micro order with increase in solubility of urethane oligomers in epoxy resin, and coefficient of variance in the particle size distribution resulted in less than 15%. Fracture energy G_{1c} of the cured system was highly improved. Lap shear strength and peel strength were also improved. These mechanical and adhesion properties do not depend on any curing condition of epoxy resin because of the existing stable particles in the epoxy resin before curing. © 2001 Published by Elsevier Science Ltd.

Keywords: Epoxy resin; Toughness; Adhesion

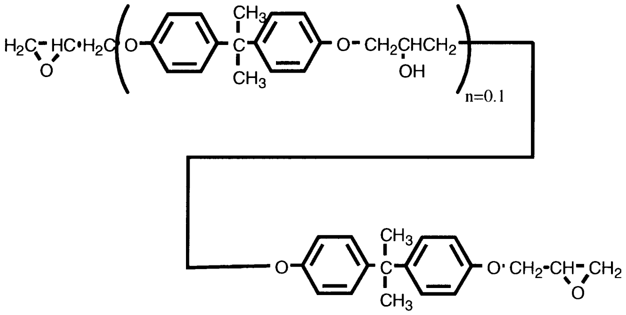
1. Introduction

There are a lot of studies to improve the toughness of epoxy resin without any lack of the nature of the epoxy resin, i.e. excellent heat resistance, mechanical properties and adhesion properties. For instance, using the reactive elastomer such as carboxyl-terminated acrylonitryl rubber (CTBN) was one of the most successful techniques [1–11]. However, the adhesion properties of the reactive elastomer system strongly depend on cure histories of epoxy resin. These systems generally show high viscosity, so that these disadvantages would limit the wide usage of epoxy resin adhesives. In previous reports [12,13], in order to solve these problems on the epoxy resin adhesives, modified epoxy resin that has silicone microsphere as a tougher was prepared by use of pre-reaction method prior to curing the epoxy resin. Fracture energy G_{1c}, lap shear strength and peel strength were evaluated. Following the previous work, in this study urethane structure was introduced into silyl-terminated oligomer to enhance oligomer in liquid epoxy resin. Several backbone structures of silyl-terminated oligomer were also used at the same time for the same objective.

2. Experimental

2.1. Materials

Epoxy resin used was diglycidylether of bisphenol A (DGEBA, Epikote 828, Yuka–Shell Epoxy Co., Mw = 380). Chemical structure is shown below.



Amidopolyamine (PA, Tomide 296, Mw = 1600, purchased from Fuji Kasei Co. Ltd) was used as a curing agent for DGEBA. The typical structure of PA is given

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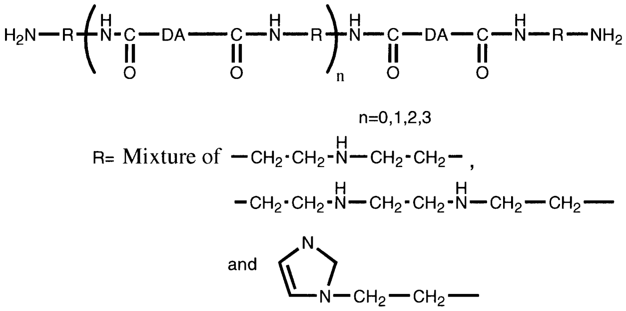
below [14]. PA (35 phr) was introduced into 100 phr of modified epoxy system.



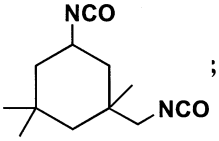
where DA was a mixture of dibasic acid of C_{16}-, C_{18}- and C_{20}–2COOH

Polypropylene oxide (PPG, purchased from MITSUI Chemical Co.), polytetramethylene diol (PTMG, purchased from SANYO Kasei Co.) and poly butylacrylate diol (p-BA, purchased from Nippon Shokubai Co.) were used as diol component in the urethane oligomer. Chemical structure, number average molecular weight (Mn) of these diols and abbreviation of entries are given in Table 1. Dibutyltindilaurate (DBTDL, purchased from Wako Pure Chemical Co.) was used as a pre-reaction catalyst of silyl group. The chemical structure is, $(C_4H_9)_2$–Sn–$(OCOC_{11}H_{23})_2$. Dimethoxysilyl terminated polypropylene oxide (Si-PPO, purchased from Kaneka Corp.) was used as a no-urethane structure system (Si-PPO system). The chemical structure and number average molecular weight of Si-PPO is also given in Tables 1 and 2.

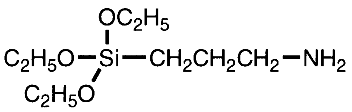
2.2. Synthesis of silyl-terminated urethane oligomer

The moisture contained after heat treatment was ca. 500 ppm, measured using Karl–Fischer moisture meter, so that a side reaction of isocyanate containing moisture would be negligible. Isophoronediisocyanate (IPDI, Desmodur I, purchased from Sumitomo–Beyer Urethane Co. Ltd Mw = 208) was used as an isocyanate source for urethane oligomers. The structure is given below.

γ-Aminopropyltriethoxysilane (APTES, A-1100, purchased from Nippon–Unicar Co. Ltd Mw = 221) was used as a terminal group of the urethane oligomer. The structure is given below



; Isophorondiisocyanate, IPDI



The preparation of the silyl-terminated urethane oligomer was carried out in two steps. In the first step, 1 mole weight of diol was reacted with 2 mole weight of IPDI. DBTDL (200 ppm) was added to the reaction mixture. This reaction was controlled at 78°C for 3 h under a dry nitrogen atmosphere. In the second step, 2 mole weight of APTES was added to react with the terminal isocyanate group. The reaction condition in the second step was 65°C for 3 h under dry nitrogen atmosphere. Resultant molecular weights (Mn) of oligomers were determined by using polystyrene standard sample with GPC. In the first step of the urethane oligomer synthesis with a mole ratio of NCO/OH = 2 : 1, trimer, pentamer and heptamer were obtained as main products [15]. Mole weight of oligomers synthesized is given in

Table 1
Chemical structures and mole weight of raw materials

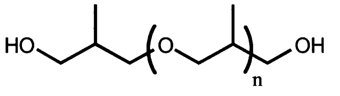
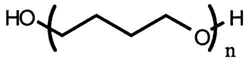
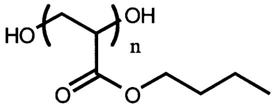
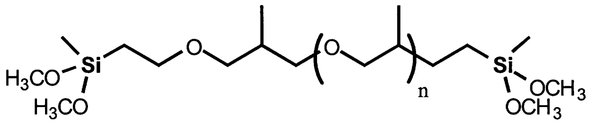
Entry	Diols	Mn of diols	Abbreviation
1		2150	PPG
2		2850	PTMG
3		2500	p-BA
4			Si-PPO

Table 2
Mole weight of oligomers prepared

Entry	Abbreviation	M_w of oligomers	Theoretical[a] M_w
1	IPDI–PPG	8546	7724
2	IPDI–PTMG	9546	9824
3	IPDI–*p*-BA	9855	8774
4	Si-PPO	8084	

[a] Heptamer as a theoretical structure.

Table 3
Residue of alkoxysilyl group on oligomers and boundary temperature of oligomer with the DGEBA

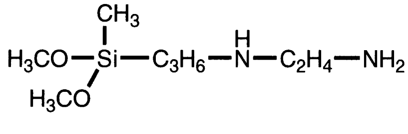
Entry	T_b (°C)	Residue (%)
1	15	10
2	35	9
3	48	10
4	41	11

Table 2, compared with theoretical mole weight. It is seen from Table 2 that the experimental values agree with the theoretical ones.

2.3. Pre-reaction of the silyl-terminated urethane oligomer in the DGEBA

The modified epoxy systems were obtained by pre-reacting an ethoxysilyl group on both the termini of the urethane oligomer with DBTDL catalyst. The pre-reaction temperature started at the soluble state was kept at $T_b + 10°C$ in order to control the spinodal phase separation of oligomers from epoxy resin, where T_b is a homogeneous/heterogeneous boundary temperature of the oligomer/DGEBA system. T_b of each oligomer in the DGEBA is given in Table 3. Here, oligomer content in each system is 20 wt%. T_bs were measured by setting the mixture on the temperature gradient stage (MFT-4, Rika Industry Co. Ltd) [13]. All systems in this study showed the upper critical solution temperature (UCST) type phase diagram. The reaction was running at $T_b + 10°C$ for 5 h under ambient conditions, then degassed under vacuum condition. The residual silyl group of oligomers after pre-reaction is also given in Table 3. Residual silyl group was estimated using FT-IR method reported earlier [13]. The amount of residual silyl group in the four systems was around 10%. This result indicated that the reaction of the silyl group in the systems were on the same pathway. The appearance of the mixture of systems changed from clear to white after pre-reaction so that the IPDI-diols phase separated from the DGEBA as it is followed in the silyl group reaction (pre-reacted system). The status of these white viscous systems is stable in storage. These results indicate that all oligomers having several backbones assemble themselves in the liquid DGEBA by the pre-reaction.

On the Si-PPO used system (entry 4 in Table 1), 1 wt% of *N*-β-(aminoethyl)-γ-aminopropyl-dimethoxysilane (AMS, Mw = 222, purchased from Nippon–Unicar Co.) was added when pre-reaction started by addition of DBTDL. The chemical structure of AMS is given below:



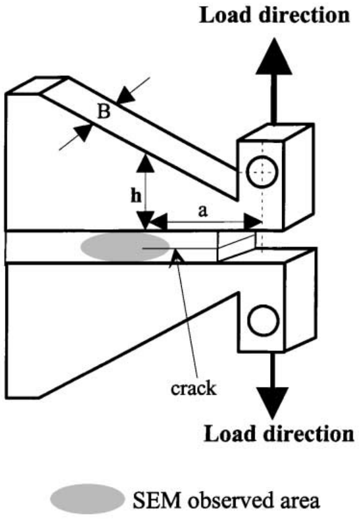
$$\mathrm{H_3CO{-}\underset{H_3CO}{\overset{CH_3}{Si}}{-}C_3H_6{-}\overset{H}{N}{-}C_2H_4{-}NH_2}$$

In this system, AMS would act as a compatibilizer between the Si-PPO and the DGEBA reported earlier [12,13]. These pre-reacted systems were then placed under vacuum condition for 5 min to remove the bubbles. PA (35 phr) was mixed with 100 phr of each of the pre-reacted systems and pre-cured at several temperatures for 2 h, prior to the post-curing at 140°C for 4 h. On the other hand, non-prereacted system having IPDI–PPG structured oligomers synthesized without pre-reaction was also cured with 35 phr of PA in the same curing conditions (non-prereacted system). Pre-reacted and non-prereacted systems were compared with cured DGEBA/PA system (unmodified system) in adhesion and dynamic mechanical properties.

2.4. Measurements

The glass transition temperature (T_g) and tensile modulus of cured systems were determined using a non-resonance forced vibration viscoelastometer (Rheogel E4000, UBM Co. Ltd). The frequency was adjusted to 10 Hz and the heating rate was 2°C/min at the ambient temperatures. T_g was identified as a peak temperature of the loss tangent in each system.

The fracture energy G_{1c} of the adhesive joints were determined by tapered double cantilever beam specimens with pre-crack according to ASTM D3433-85. The shape of the specimen is shown in Scheme 1 (shape of the specimen in fracture energy G_{1c} measurement). The specimen was



Scheme 1.

mounted on an Instron-type tensile machine (TENSILON UTM-5T, Toyo-Boldwin Co. Ltd) and loaded at a constant crosshead speed adjusted to 0.5 mm/min. The experiments were conducted at room temperature. The value of G_{1c} were calculated from the following equations:

$$G_{1c} = 4L^2m/EB^2$$

$$(m = 3a^2/h^3 + 1/h)$$

where, L is the load at crack initiation, E is the tensile modulus of the substrate, B is the specimen width, a is the crack length, h is the thickness of the substrate at a point of crack tip, and m is a geometric factor. In this evaluation, the geometric factor, m, is ca. 23–28. Abraded steel plates (ISO E235B) were used as substrates. The substrates were polished with sandpaper (No. 280) and washed with acetone. The thickness of the adhesive layer was adjusted to 0.5 mm with Teflon sheet. A sharp pre-crack was formed by carefully tapping with a fresh razor blade.

The lap shear strength of adhesive joints were measured at a crosshead speed of 50 mm/min using an Instron-type tensile machine (TENSILON UTM-5T, Toyo–Boldwin Co. Ltd) according to ASTM D1002-74 at 20°C. Aluminum plates (ISO Al 95.0, 2.0 mm thickness) were used as substrates. The aluminum plates were degreased with acetone vapor. The thickness of the adhesive layer was adjusted between 30 and 50 μm by using a thin Teflon spacer. The T-peel strength of adhesive joints was measured in the same manner as the lap shear strength measurement. An extended aluminum plates (ISO Al 95.0, 0.5 mm thickness) were used as substrates. The Al plates were degreased with acetone vapor, abraded with sandpaper (No. 280), and then wiped with cotton cloth soaked in acetone.

The morphology of the fractured surfaces was observed with a scanning electron microscope (SEM, JSM-6100, JEOL Ltd). Average particle diameter and the surface area of dispersed phase were calculated using the pin drop method [16] from SEM results. The coefficient of deviation (CV) value in each system was calculated by the use of following equation:

$$\mathrm{CV} = \mathrm{SD}/D_n \times 100$$

where D_n is the number average particle diameter in μm and SD is a standard deviation of its particle diameter in μm.

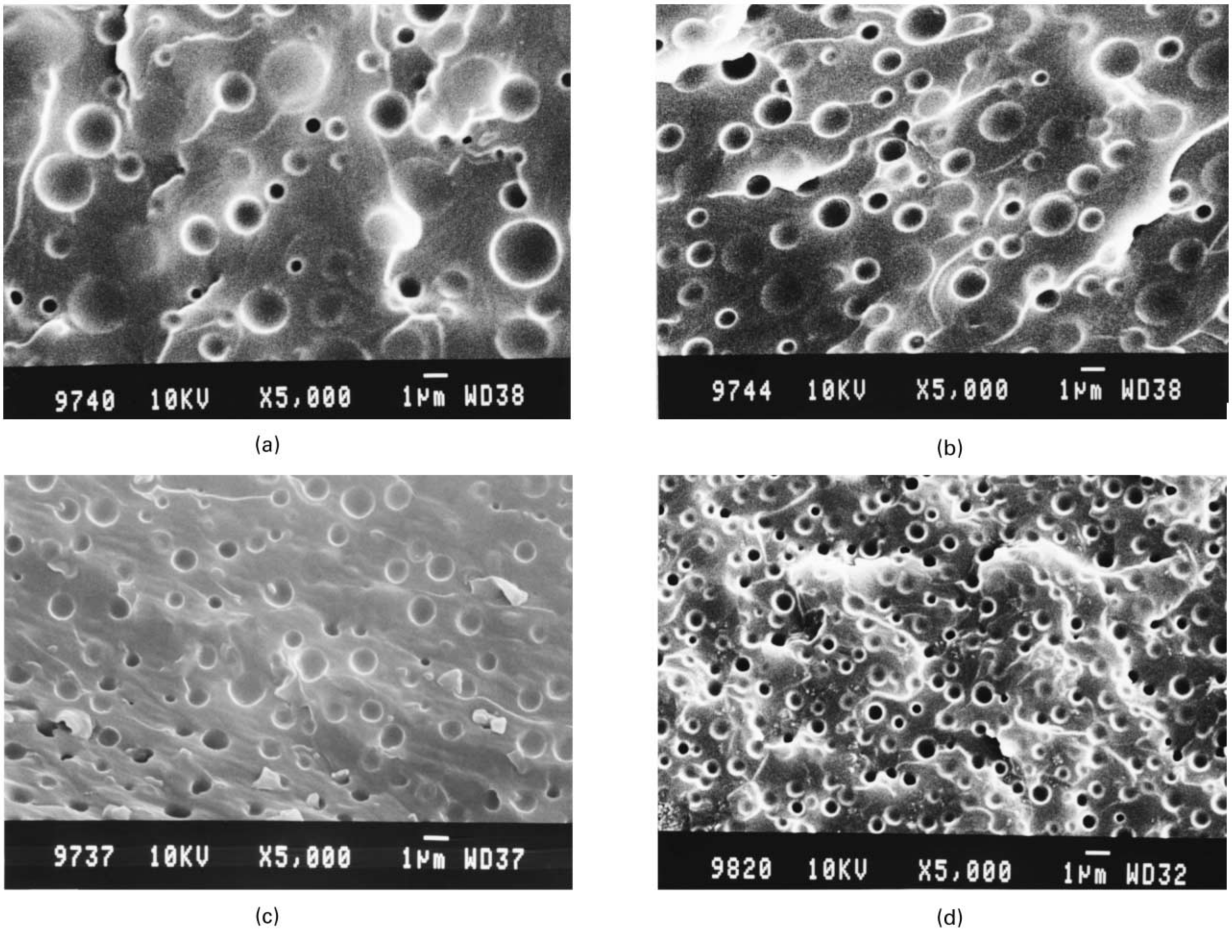
3. Results and discussion

3.1. Dispersion state of microspheres in cured epoxy resin

In order to investigate the relationship between the solubility of oligomers to DGEBA and phase structure of the cured system, SEM observation photos, number average particle diameter (D_n), solubility parameter value of oligomers and CV values are shown in Fig. 1. Solubility parameter value (δ, SP value) at 27°C of each oligomer was calculated by Small's method and mentioned in Fig. 1 comparing with SP value of DGEBA ($\delta_{\mathrm{DGEBA}} = 20.58\ (\mathrm{J/cm^3})^{0.5}$). We have already evaluated the solubility of the Si-PPO into the DGEBA [13]. Number average particle diameter and CV values of Si-PPO system (Fig. 1a, Si-PPO, $\delta = 16.06$) were 1.29 μm and 51.7%, respectively, and bimodal particle diameter distribution was observed. This result indicates that the surface of Si-PPO particles is not fully stabilized so that it brought bimodal particle distribution even if it had small amount of AMS as a compatibilizer. When the SP value of oligomers comes into contact with the SP value of DGEBA, the particle diameter goes to 1.07 μm (Fig. 1b, IPDI-poly BA, $\delta = 23.59$) and the CV value is 28.7%, and then to 0.83 μm (Fig. 1c, IPDI–PTMG, $\delta = 22.85$). Basically, oligomer is able to dissolve into the DGEBA when the SP value comes close to that of the DGEBA so that the interface between elastomer and the DGEBA become stable, but pre-reacted oligomer separates from the liquid DGEBA because the solubility of oligomer decreased with growth in the network structure during the pre-reaction. The resultant particle diameter and CV value reached 0.72 μm and 14.9% in IPDI–PPG system, respectively, which has the nearest SP value ($\delta = 20.91$) to that of the DGEBA. The high compatibility of the oligomer in DGEBA was considered to achieve the highly stabilized surface of pre-reacted elastomer particles. In the viewpoint of CV value, Omi et al. reported that the particles having less than 15% of CV value was considered as unimodal particles; moreover, particles having less than 10% of CV value was absolutely unimodal [17]; therefore, it is considered that the IPDI–PPG system has fine dispersed phase. The particle diameter was decreased and CV value was also decreased so that the fine morphology was obtained with the change in the solubility of backbone of oligomer synthesized after the pre-reaction. In this section, the epoxy resin system having the controlled sub-micro ordered elastomer particles is obtained.

3.2. The relationship between the fracture energy G_{1c} and phase structure of the cured modified system

To give an excellent toughness to the cured epoxy resin, in some studies of elastomeric dispersed phase, which were reactive elastmers, acrylic microspheres [18–23], silicones [24–29] were introduced into the cured epoxy phase. In this study, it will also be expected that the cured system, which have fine dispersed phase of pre-reacted oligomer, show a high toughness. Fig. 2 shows the relationship between adhesion fracture energy G_{1c} and total surface area of dispersed phase. Total surface area of particles was calculated in 240 $\mu\mathrm{m}^2$ in SEM photo view. In this figure, black squares refer to the pre-reacted systems having IPDI-diols structure in oligomers and white squares refer to the pre-reacted Si-PPO systems.



(a) (b)

(c) (d)

Fig. 1. SEM observation results and CV value of dispersed phase in cured systems. $\delta_{\mathrm{DGEBA}} = 20.58$ J$^{1/2}$/cm$^{3/2}$.

Controlling not only the solubility of olgomers but also the amount of the oligomer in DGEBA varied surface area of dispersed phase. Changing the amount of AMS controlled phase structure of Si-PPO systems [13]. The fracture energy G_{1c} increased with the increase in the surface area of the dispersed phase. Fig. 2 also showed that the G_{1c} value of IPDI-diols system (■) was higher than that of the Si-PPO system (□), and the system of entry 1 resulted in 2660 J/m^2 as the highest value in all system. This result was consistent with the phase structure shown in Fig. 1d. This G_{1c} value was ca. 6.7 times that of the unmodified system shown as dotted line in Fig. 2. These results indicate that the pre-reacted system that have IPDI-diols structure in the oligomer backbone bring good toughness to the cured epoxy system.

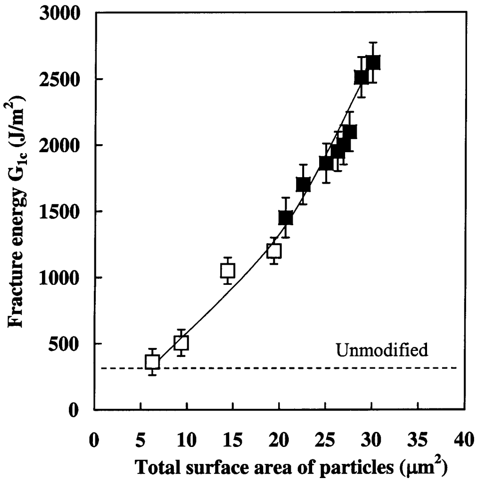
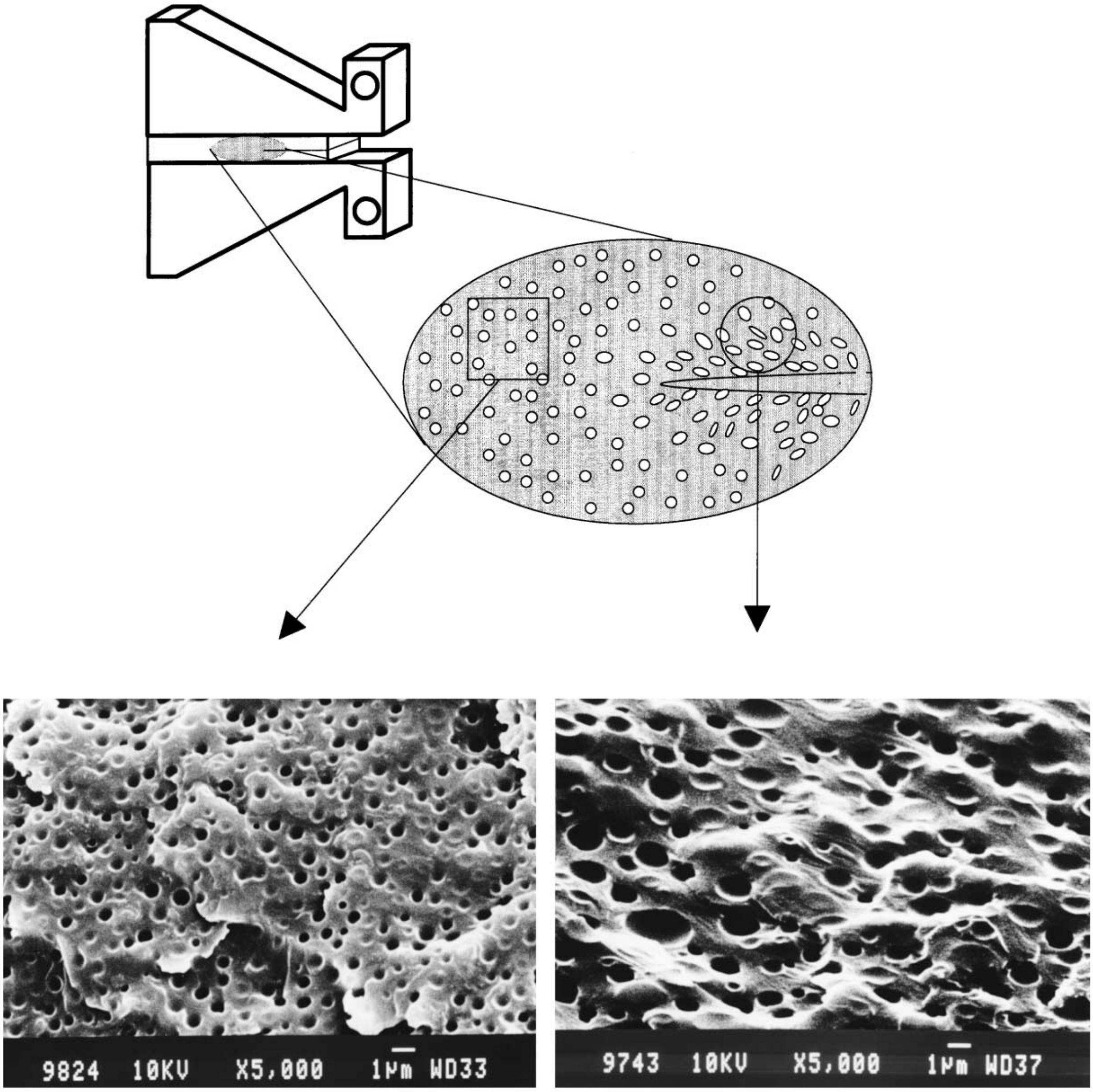


Fig. 2. Relationship between the surface area of particles and fracture energy G_{1c} of cured system. Curing condition: 120°C-2 h + 140°C-4 h, ■: IPDI-diols sysrems, □: Si-PPO systems.

A lot of discussions have been existing in the nature of toughening of the brittle plastic materials, in particular, there is an interest in studying the relationship between a toughening mechanism and morphology in elastomer modified epoxy resin system. Wu et al. [30] reported earlier that the thickness of the matrix 'ligament' is shown to be the single parameter determining when a polymer/rubber blend will be tough or brittle, where ligament is defined as a region of the matrix between two neighboring rubber particles. His report indicated that the critical thickness of the ligament of nylon-66 matrix was 0.3 μm in nylon-66/rubber blend. The cured epoxy resin system is considerably more brittle than nylon-66 so that the critical thickness in our systems should be less than 0.3 μm. The ligament thickness of IPDI–PPG system (Fig. 1d) had been measured 0.7 μm so that the ligament thickness is not a single parameter evaluating the toughness in our system. To study the toughening mechanism, some microscopic techniques were studied. Fig. 3 shows the position observed by the SEM. A stress was applied for about 95% of the crack initiation stress of the tapered double cantilever beam specimen, and then a small block in vicinity of the crack was cut off in liquid N_2. This small block was molded with the DGEBA/tertiary amine system for fixing the state around the crack. This molded block was cut again in liquid N_2 for SEM observation. SEM micrographs of fractured surfaces near the crack tip are also shown in Fig. 3. At the point A (Fig. 3a) which is ca. 15 mm distant from the crack tip, there is a dispersed phase with an average particle diameter of 0.72 μm. On the other hand, at the point B (Fig. 3b), which is fairly close to the crack tip, the diameter of the elastomer phase is 1.4 μm which is greater than the phase at the point A. This result shows that the cavitations of the elastomer phase occurred near the crack tip by loading. And it was also shown in Fig. 3b) that the elastomer phase was deformed, an ellipsoid in shape along the direction of the applied stress. From these micrographs, it might be concluded that the toughening mechanism in the system modified with the pre-reacted elastomer particles is cavitation of the particles followed by the shear deformation of the epoxy matrix. Yee [8,9] has already reported a toughening mechanism for the epoxy resin system modified with CTBN copolymer. In his report, the cavitations of rubber particles and the shear deformation of



(a) (b)

Fig. 3. SEM observation results of the fractured surfaces of the IPDI–PPG system.

epoxy matrix near the crack tip is the main mechanism for toughening of CTBN-modified system. It is considered that this mechanism would be adopted in this system, and this is the reason why the G_{1c} of the system improved which would be explained by the increase in the stress transfer from the matrix to elastomer particles with increase in total surface area of the particles.

3.3. Effect of the phase structure on the dynamic mechanical properties of cured IPDI–PPG system

Fig. 4 showed that the temperature dependence of the tensile modulus and loss tangent (tan δ) of the pre-reacted (●) and non-prereacted (▲) IPDI–PPG systems compared with unmodified system (□). Curing condition was 60°C-2 h followed by 140°C-4 h for post-curing. In the pre-reacted system, the glass transition temperature (T_g) of the epoxy matrix and dispersed elastomer particles phase were clearly observed at 110 and −38°C, respectively. This result indicated that the IPDI–PPG pre-reacted system has a two-phase structure and also showed good agreement with the microscopic photo in Fig. 1d. The glass transition of unmodified system was observed at 114°C. Therefore, the T_g was hardly affected by the existence of the elastomer phase in the cured systems. The tensile modulus around room temperature was slightly affected and lower than that of the unmodified system by the T_g of the elastomer phase.

In the non-prereacted IPDI–PPG system, two relaxation peaks were also obtained at −50 and 56°C, and the tensile modulus on rubber region was lower that that of the both pre-reacted system and unmodified system. These results would indicate that the heat resistance of the non-reacted system decreased since some amount of the IPDI–PPG oligomer was dissolved into DGEBA matrix during cure process and small amount of the oligomer could be separated from the matrix. These results suggest that the T_g of the matrix in non-prereacted IPDI–PPG system would be dependent on the pre-curing condition of the system.

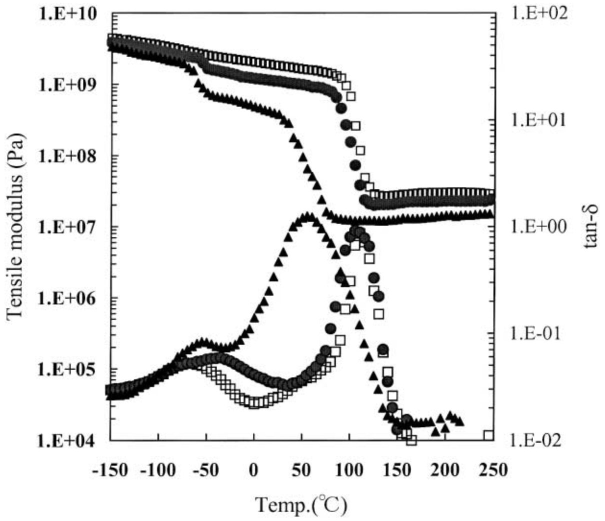


Fig. 4. Dynamic mechanical properties of cured IPDI–PPG systems; ●: pre-reacted system, ▲: non-prereacted system, □: DGEBA/PA system. Curing condition, 60°C-2 h + 140°C-4 h.

For clarification of this discussion from microscopic standpoint, comparison of the phase structure, CV value and histogram of the particles in both the pre-reacted and non-prereacted IPDI–PPG systems pre-cured at 60°C, showed a different result between them on T_g and adhesion strengths, and are shown in Fig. 5. The difference in adhesion strengths is shown in Figs. 7 and 8. The average particle diameter of non-prereacted system (Fig. 5a) was 2.85 μm and CV value was 61.4%. Non-prereacted system has large particle diameter and the wide diameter distribution. The volume fraction of the particle was 11.7%. This value was lower than the value of 16.3%, the theoretical one. This result showed that 28% of the added oligomer dissolved into the matrix. The decrease in the T_g of the non-prereacted system (Fig. 4) is explained. On the other hand, the average particle diameter of the pre-reacted IPDI–PPG system (Fig. 5b) was 0.76 μm and its CV value was 14.6%. There was a fine sub-micro ordered phase with monodisparsibility in the IPDI–PPG system. The volume fraction of the dispersed phase was 16.0% so that most of the elastomer existed as dispersed phase. Fig. 6 showed the relationship between the glass transition temperature (T_g) of the IPDI–PPG system and pre-cure temperature, and its T_g was compared with the non-prereacted system. The T_g of the non-prereacted system increased with increasse in the pre-curing temperature. In Fig. 6, the T_g of non-prereacted system pre-cured at 60°C was 56°C. There was a large difference in T_g between the non-prereacted system cured at 60°C and unmodified system at 114°C. The non-prereacted system cured at 60°C had poor heat resistance. It was concluded from the result in Fig. 5a that the low T_g in the system is due to the dissolved elastomer acting as plasticizer in the cured system. We have already described earlier that some amount of the oligomer in the non-prereacted system is dissolved into the DGEBA matrix, so that the result of the change in T_g of the system would be explained by the change in an amount of the dissolved oligomer at each pre-curing temperature. On the other hand, the T_g of the pre-reacted IPDI–PPG system was independent of the cure condition and it was almost coinciding with the T_g of the unmodified system. This result indicates that the nature of the matrix in the pre-reacted IPDI–PPG system which is same as that of the unmodified system, because pre-reacted sub-micro order particles existed in the cured DGEBA matrix without dissolution in the matrix. From these results, it is inferred that the cured resin of the pre-reacted IPDI–PPG system has good heat resistance stable under any curing history.

3.4. Effect of the elastomer microsphere on the adhesion properties of cured system

In this section, IPDI–PPG system, which involves

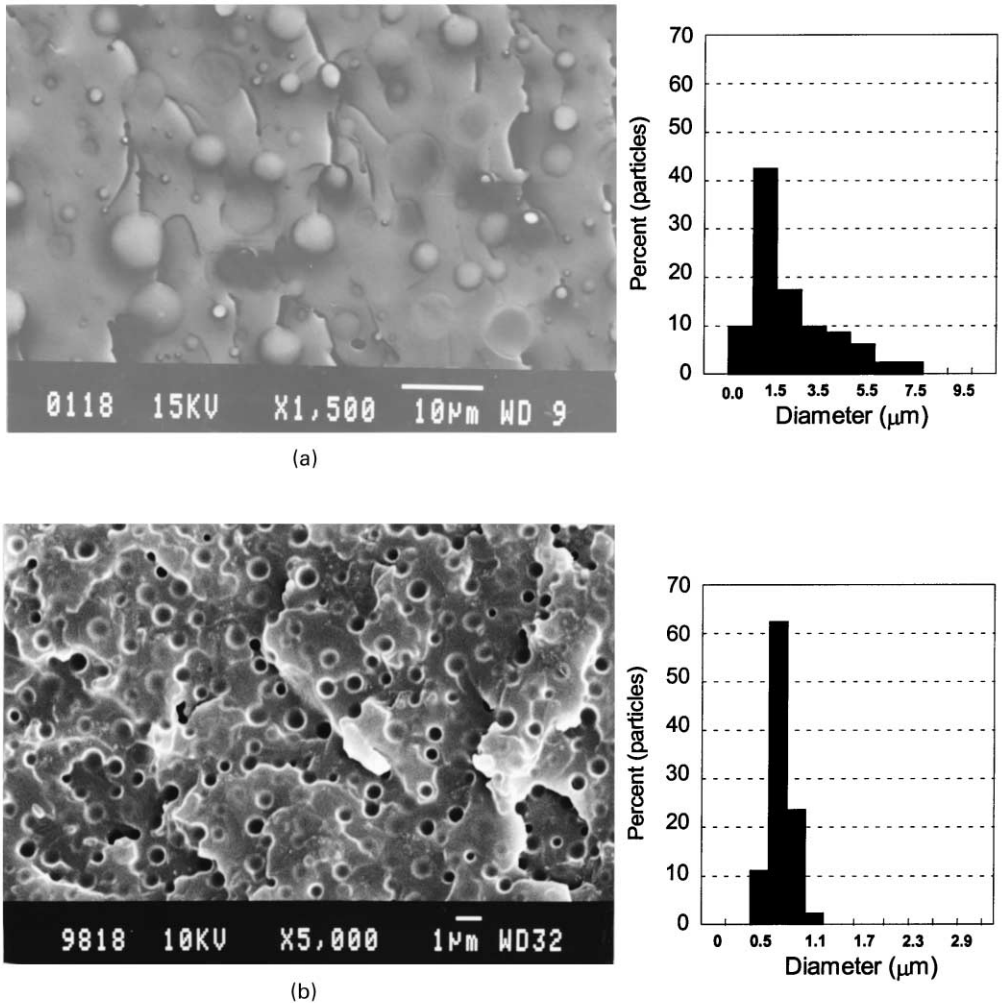


Fig. 5. Results of SEM observation and particle analysis of pre-reacted IPDI–PPG system compared with non-prereacted system. Curing condition, 60°C-2 h + 140°C-4 h.

20 wt% of the pre-reacted oligomer in DGEBA, was used as a typical example of the adhesion system because of showing the highest G_{1c} in this study. Fig. 7 showed the relationship between the lap shear strength and pre-curing temperature of the pre-reacted IPDI–PPG system compared with the non-prereacted system. White circles refer to the system modified with the pre-reacted IPDI–PPG and black circles refer to non-prereacted system, which had same oligomer involving 20 wt% in the DGEBA. The result of unmodified system is shown as a dotted line. These systems were post-cured at 140°C for 4 h.

Prior to the evaluation of adhesion strengths, conversions of the glycidyl group in Figs. 7 and 8 were determined by FT-IR measurement [13] and have reached almost 100% after post-cure treatment, therefore, the phase structure is considered as a single parameter for adhesion strength. The lap shear strength of non-prereacted system increased with increase in pre-curing temperature. This result indicated that the lap shear strength depended on the pre-curing temperature. This tendency was often seen on epoxy resin adhesives modified with reactive elastomers in general. The adhesion

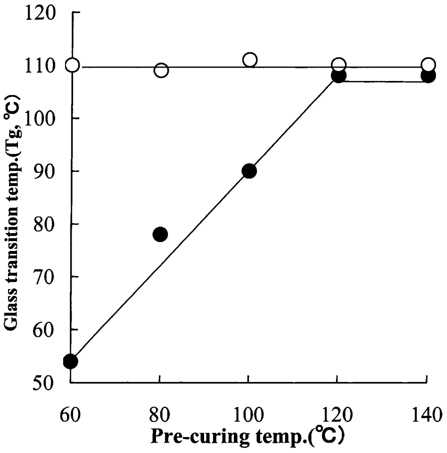


Fig. 6. Relationship between T_g and pre-curing temperature of IPDI–PPG system. Post-curing: 140°C-4 h, T_g of the unmodified system: 114°C; ○: pre-reacted system, ●: non-prereacted system.

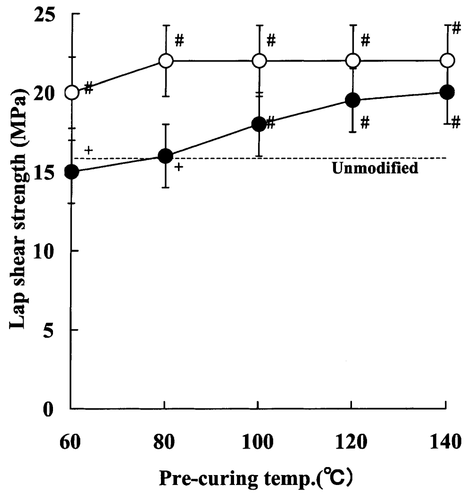


Fig. 7. Relationship between lap shear strength and pre-curing temperature of IPDI–PPG system. Post-curing: 140°C-4 h, +: surface failure, #: cohesive fracture. Symbols as in Fig. 6.

property of the epoxy resins modified with reactive oligomer such as CTBN depends on the phase separation phenomena between epoxy resin matrix and elastomer phase that was decided by the reaction rate of the epoxy resin [31], in other words, it was decided by curing temperature of the epoxy resin. On the other hand, lap shear strength of the pre-reacted IPDI–PPG system was stable and the strength was higher than that of the non-prereacted system. This result indicated that the lap shear strength of the IPDI–PPG system was not affected by curing temperature because it already had sub-micro size, monodispersed urethane microspheres in the DGEBA before curing (Fig. 1d).

Fig. 8 showed that the relationship between T-peel adhesion strength and pre-curing temperature of the IPDI–PPG system compared with non-prereacted system. The result of unmodified system is shown as a dotted line. The T-peel strength of non-prereacted system decreased with increase in pre-cure temperature by 80°C. This result suggested that dissolving some amount of the elastomer in the DGEBA matrix during the curing would ductilize cured system. The dissolving oligomer would bring comparative high peel adhesion strength of the system on a 60°C pre-cured system, however with the pre-cured at 80°C, more amount of oligomer was not dissolved into the matrix so that the cured system became brittle. Therefore, T-peel strength pre-cured at 60°C was higher than that of 80°C pre-cured system. Then the adhesion strength increased with increase in the pre-cure temperature by 140°C. On the other hand, the T-peel strength of the pre-reacted IPDI–PPG system was stable between 60 and 140°C of pre-cure temperature and improved more than 7.3 times as that of the unmodified system. These results indicate that the cured resin including IPDI–PPG particle showed high adhesion properties both of lap shear strength and T-peel strength. Fracture occurred within the cured resin in both lap shear strength and T-peel strength on pre-reacted system, so that the improving of the toughness estimated with the fracture energy G_{1c} would contribute to high adhesion property both of the lap shear and T-peel strengths. The results shown in Figs. 7 and 8 suggest that the finely controlled microsphere in the DGEBA matrix before curing of epoxy resin gave not only high lap shear strength but also high T-peel strength and good stability against cure temperature.

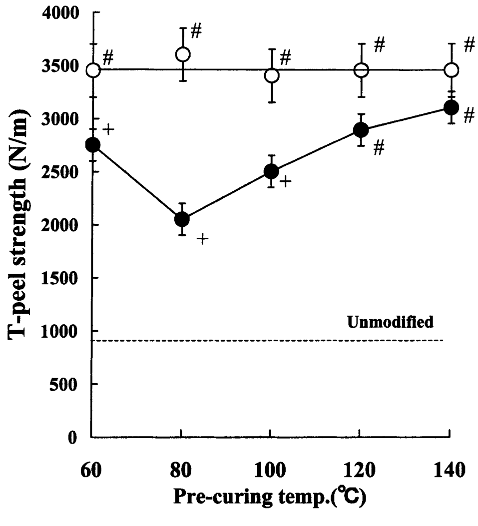


Fig. 8. Relationship between T-peel strength and pre-curing temperature of IPDI–PPG system. Post-curing: 140°C-4 h. Symbols as in Fig. 6.

4. Conclusions

The following conclusions were derived from the results and discussion:

1. Controlled dispersed phase of urethane-structured elastomer that is designed to adjust the solubility parameter of oligomers to that of the DGEBA matrix is obtained. The best results are 0.72 μm in diameter and 14.9% in the CV value of diameter distribution at the pre-reacted IPDI–PPG system.
2. The toughness of the cured epoxy resin system having pre-reacted urethane microsphere increases considerably with both increase in the total surface area of particle and minimizing CV value of the diameter of dispersed phase.
3. Both lap shear strength and T-peel strength of the system are higher than that of unmodified system. In particular, T-peel strength of the modified system was improved by 7.3 times. Adhesion properties are independent of curing temperature of the epoxy system. The glass transition temperature of the system is also independent of the curing history and is as same as the unmodified system. This stability of the system is explained by fixed phase structure of the system prior to curing the epoxy matrix.

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