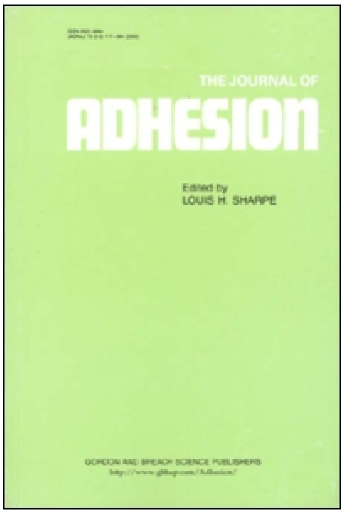

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Studies on The Modification of Epoxy Resin with Silicone Rubber†

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In order to find a compatibilizer for epoxy resin/silicone rubber systems, interfacial tension of epoxy resin mixed with modified silicone oils which had the compatible groups to epoxy resin was measured against RTV silicone rubber and silicone oil. From the results, it was found that one of polyether modified silicone oils (EtMPS) had strong interfacial activity. Then using the EtMPS as the compatibilizer, RTV silicone rubber or silicone diamine was filled in epoxy resin. The effects of silicone content of these materials on impact fracture energy and on peel strength were investigated. The impact fracture energy of epoxy resin was increased by the addition of RTV silicone rubber up to two times that of unmodified resin while silicone diamine had almost no effect which might be due to the small molecular weight. T-peel strengths of aluminium plates bonded by epoxy resin filled with RTV silicone rubber and with silicone diamine effectively increased with the increasing of silicone content showing the maximum at 10 ~ 20 phr. The fracture surfaces after the mechanical tests of these materials were observed by a scanning electron microscope. Many particles of silicone rubber in the size of 1 ~ 20 μ were observed over the fracture surface.

KEY WORDS Adhesives; fracture toughness; fracture surfaces; dispersing agent; T-peel strength; interfacial tension.

1 INTRODUCTION

Epoxy resins, because of their exceptional properties such as strength, heat resistance and adhesion, are widely used in paints, adhesives and moulding materials amongst other things. However, their peel and impact strength are low, and their general lack of toughness is a disadvantage. In order to improve these properties they are sometimes blended with thermoplastic resins, but frequently in these blends not only is heat resistance and shear adhesion strength lowered, but resistance to peeling and to impact too cannot be said to be satisfactory. In response to this, in recent years, methods of dispersing elastomers into epoxy resins have been developed, and it has become possible greatly to improve epoxy resins' weak points such as brittleness whilst preserving their other properties, by means of the same type of mechanism and structure as ABS and HIPS. The

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method currently in use involves mixing epoxy resin with reactive nitrile rubbers such as CTBN and ATBN. However, these rubbers lack heat resistance, and cannot be said to make adequate use of the special properties of epoxy resins. In contrast to this, if the improvement can be made using silicone rubber, which preserves stable physical properties over a broad range of temperatures, this would be more effective. However, as can be understood from the fact that silicone oil is used as a mould-releasing agent when epoxy resins are moulded, the relationship between epoxy resin and silicone rubber is like that of oil and water, and so dispersion filling of such resins with silicone rubber is generally difficult. Accordingly, little research has been carried out on this topic, although J. E. McGrath[1,2] reports that when epoxy resin is made to react with various piperidine terminated polysiloxanes and solubilized, and the resultant material blended with epoxy resin, fracture toughness (K_{IC}) increases.

However, even in the case of mutally-incompatible substances, if surface free energy is lowered using an appropriate surface active agent (compatibilizer), it is expected that is might be possible to compatibilize or microdisperse the two substances. The main objective of the present research is to find a material (compatibilizer) with a strong ability to reduce the interfacial tension between epoxy resin and silicone rubber. Accordingly, silicone oil modified by the introduction of atomic groups with strong compatibility with epoxy resin was mixed with epoxy resin, and the concentration dependency of its interfacial tension with silicone oil was investigated.

Using modified silicone rubber, which displayed the greatest interfacial activity, RTV (room temperature vulcanizing) silicone rubber or silicone diamine was dispersed in epoxy resin. Impact fracture tests and peel strength tests were carried out, and the fracture surfaces were examined using a scanning electron microscope. The results were as predicted, with the silicone rubber microdispersing inside the epoxy resin, bringing about a large increase in impact fracture strength and peel strength. These results are reported here.

2 EXPERIMENTS

2.1 Test Materials

2.1.1 *Epoxy resin* Epikote 828, a bisphenol A type from Yuka Shell Epoxy Ltd., was used as the main epoxy resin. Bis (paraaminocyclohexyl) methane (PACM) and diaminodiphenyl methane (DDM) were used as hardening agents.

2.1.2 *Silicone resin* The silicone resins used in the measurement of interfacial tension with epoxy resin in order to choose a compatibilizer were silicone oil (PDMS, Shinetsu Chemicals Ltd KF96) and RTV silicone rubber (Shinetsu Chemicals Ltd KE108). The silicone resins used for the modification of epoxy resin were RTV silicone rubber and silicone diamine (SDA, Shinetsu Chemicals Ltd X.22.161C). The reason for using silicone diamine was that, since McGrath (*vide supra*) found that it would not mix with epoxy resin, if it could be dispersion filled by means of a compatibilizer, a bridge-formation reaction with epoxy resin by means of amino groups would become possible, giving an even better result.

2.1.3 *Compatiblizer (modified silicone oil)* The modified silicone oils used are shown in Table I. For the ether-modified silicone oils (EtMPS), three types with differing ether content were used. The polyether blocks of EtMPS(1) and EtMPS(2) are made up solely of polyethylene oxide, whilst EtMPS(3) includes polypropylene oxide. Furthermore, the polyether terminals of EtMPS(1) and EtMPS(3) are methyl groups, but those of EtMPS(2) are hydroxide groups. Epoxy-modified silicone (EpMPS) includes polyethylene oxide as well as epoxy groups. Silicone diamine is the same as that previously mentioned as a modifying agent. All of these modified silicone oils are manufactured by Shinetsu Chemicals Ltd. Glycidyloxypropyltrimetroxysilane (GPTMS) is generally used as a silane coupling agent.

2.1.4 *Preparation of silicone-rubber-filled epoxy resin* If a fixed quantity of compatibilizer is added to epoxy resin, stirred, degassed and, whilst stirring vigorously at 50°C a fixed quantity of silicone rubber containing a catalyst added, the rubber particles disperse, and a sticky, milky-white liquid is obtained. After degassing this, hardening agent (30 phr of both PACM and DDM) was added, the mixture stirred once again, degassed, poured into a mould and thermally hardened at 165°C for two hours.

2.2 Methods

2.2.1 *Measurement of interfacial tension* The measurement of interfacial tension was carried out using the sessile drop method. Since this method has already been described in detail in a published work,[3] we will describe briefly its application in the present experiment. The principle of measurement is shown in Figure 1.

TABLE I
Modified silicone oils used for compatibilizers

			Composition (mole fraction)			
Modified silicone	Abbr.	Mw	silicone	ethylene oxide	propylene oxide	epoxy
Polyether Modified Silicone Oil	EtMPS(1)	3900	15	85	0	—
Polyether Modified Silicone Oil	EtMPS(2)	3700	17	83	0	—
Polyether Modified Silicone Oil	EtMPS(3)	12000	13	66	20	—
Epoxy Modified Silicone Oil	EpMPS	1700	14	79	—	7
Silicone Diamine	SDA	3900				
Glycidyloxypropyltrimethoxysilane	GPTMS	236		—	—	—

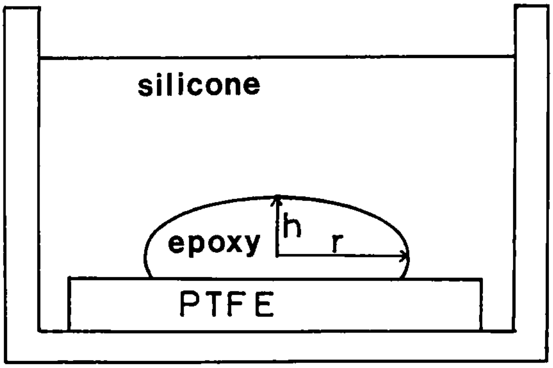


FIGURE 1 Scheme of sessile drop method of the interfacial tension measurement.

A Teflon sheet is placed on the bottom of a glass sample cell and silicone resin is poured in. Epoxy resin mixed with a compatibilizer is then dropped in, and a drop of epoxy resin forms on top of the Teflon sheet, as shown in the diagram. This is kept horizontal inside an isothermal container maintained at a set temperature. When it reaches a state of equilibrium, the drop's greatest radius (r) and the distance (h) between the level at which r occurs and the uppermost point of the drop are measured using a cathetometer. Surface tension γ_{12} was calculated using Porter's equation.

$$\gamma_{12} = \Delta\rho g h^2 \left| 0.5 - 0.3047\left(\frac{h}{r}\right) + 1.219\left(\frac{h}{r}\right)^3 \right| \tag{1}$$

Here, $\Delta\rho$ is the difference of density between silicone resin and epoxy resin in the test material, and g is the acceleration of gravity.

The density necessary for these calculations was obtained using a picnometer at room temperature, and by dilatometry at high temperature.

2.2.2 *Izod Impact testing* In accordance with JISK7110, a test piece measuring 12.7 × 12.7 × 63.6 mm was cut from the hardened material mentioned above, a notch cut to a depth of 2.54 mm along the centre, and Izod impact testing carried out.

2.2.3 *Peel testing* Aluminium sheeting with a thickness of 0.3 mm was cut into 150 mm × 200 mm sections, and these were polished with emery paper. After thorough washing and drying with Triclene, they were bonded using the silicone-rubber-filled epoxy resin described above, and the adhesive hardened by two hours of heat and pressure at 165°C. An aluminium sheet of 0.3 mm thickness was used as a spacer in order to control the thickness of the adhesive. A 25 × 150 mm sample piece was cut off, and T-peel testing was carried out at a crosshead speed of 300 mm/min at 20°C.

2.2.4 *Electron scanning microscope examination* The fracture surfaces of test pieces after Izod impact fracture testing and peel testing were examined using a scanning electron microscope, and the distribution of the rubber particles investigated.

3 RESULTS AND DISCUSSION

3.1 Interfacial activity of compatibilizers

In general, the thermodynamic relationship between surface tension (γ_{12}) and temperature (T) is as follows:

$$\gamma_{12} = E^{1}-S^{1}T \tag{2}$$

Here, E^{I} is surface energy, and S^{I} is surface entropy. Figure 2 shows the relationship between interfacial tension (γ_{12}) and temperature for epoxy resin and GPTMS mixed systems against silicone oil, and the good linearity of the relationships.

3.1.2 *Relationship between interfacial tension and modified silicone concentration* Figure 3 shows the relationship between the concentration of modified silicones and interfacial tension (γ_{12}) for epoxy resin with 1~2% mixture of various modified silicones in contact with silicone oil. For each modified silicone, γ_{12} decreases as concentration increases, but there are large differences in the degree of reduction. Despite the fact that they both have epoxy groups, epoxy modified silicone (EpMPS) and GPTMS both have low surface activity. In general, for molecules made up of two components to have interfacial activity, it is necessary for each of the components to have a chain length longer than normal. As shown in Table I, EpMPS and GPTMS have molecular weights of 1700 and 236 respectively, which are small when compared with the others,

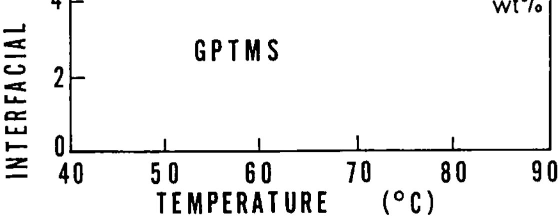


FIGURE 2 Temperature dependence of interfacial tension for (epoxy resin + glyidyloxypropyltrimethoxysilane) systems against silicone oil.

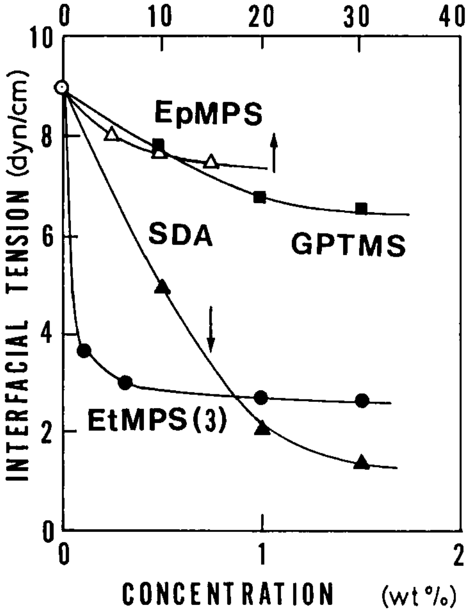


FIGURE 3 Interfacial tension for (epoxy resin + modified polysiloxanes) systems against silicone oil as a function of the concentration of modified polysiloxanes at 40°C.

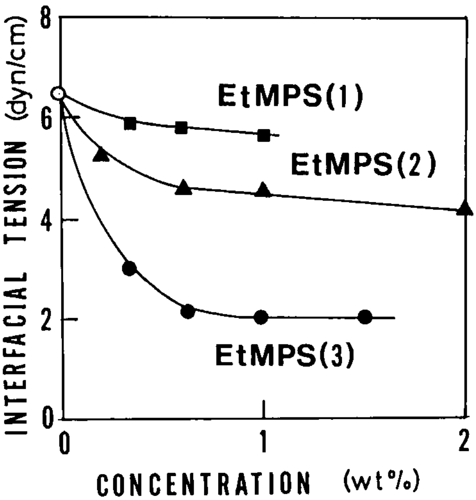


FIGURE 4 Interfacial tension for (epoxy resin + polyether modified polysiloxanes) systems against RTV silicone as a function of the concentration of polyether modified polysiloxanes at 40°C.

and it is thought that their surface activity is low because the chain length of the silicone is short. In silicone diamine (SDA) and polyethyl modified silicone (EtMPS(3)), γ_{12} decreases suddenly as concentration increases. In particular, it can be seen that EtMPS(3) has extremely strong surface activity which causes γ_{12} to decrease from 8.9 dyn/cm to 2.7 dyn/cm in the space of only 1% change in concentration.

Figure 4 shows the concentration dependency of γ_{12} of epoxy resin mixed with three types of ether-modified silicone against RTV silicone rubber. Here too γ_{12} decreases as concentration increases, but for EtMPS(1) and EtMPS(2), in which the polyether blocks are made up solely of polyethylene oxide, the value of the decrease in γ_{12} is small, but EtMPS(3), which includes polypropylene oxide in its polyether blocks, showed strong surface activity. For this reason, it was decided to use EtMPS(3) as the compatibilizer in the present research.

Here, γ_{12} of epoxy resin not containing modified silicone against silicone oil is 8.99 dyn/cm, and the value against the RTV silicone surface is 6.48 dyn/cm, a difference of 2.5 dyn/cm. This is due to the fact that RTV silicone has silanol as its terminal groups, so that its compatibility with epoxy resin is increased.

3.2 Effect of the addition of silicone rubber on impact fracture energy

Figure 5 shows the relationship between silicone content (phr) and impact fracture energy (*E*) for epoxy resin filled with RTV silicone rubber using the addition of 1 wt% EtMPS(3) as a compatibilizer and DDM as hardener. *E* increases with the addition of silicone rubber. In particular, at 5 phr, *E* is approximately double the value for unmodified material.

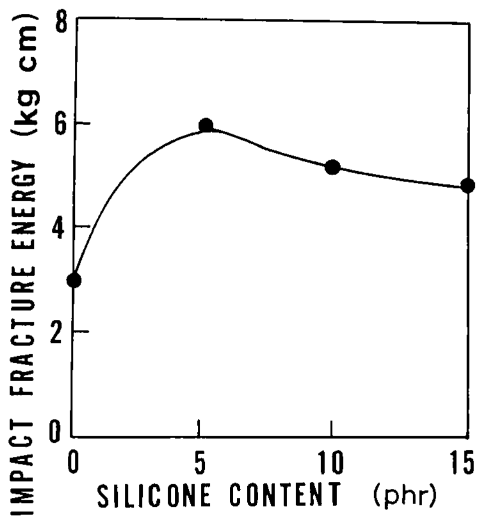


FIGURE 5 Impact fracture energy for RTV silicone rubber filled epoxy resins as a function of silicone rubber content.

Figure 6a shows a SEM photograph of the fracture surface of a system with 5 phr of silicone rubber added and hardened with PACM (compatibilizer 1 wt%). Rubber particles of 1 ~ 20 μm can be seen dispersed across the entire surface. From this it is apparent that EtMPS(3) is performing adequately as a compatibilizer. Figure 6b shows an enlarged photograph of the rubber particles. It can be seen that small fragments of epoxy resin are adhering to the surface of the rubber particles, suggesting the existence of a bonding force between the epoxy resin and the surface of the silicone rubber particles.

Next, we report on the results obtained by the addition of silicone diamine

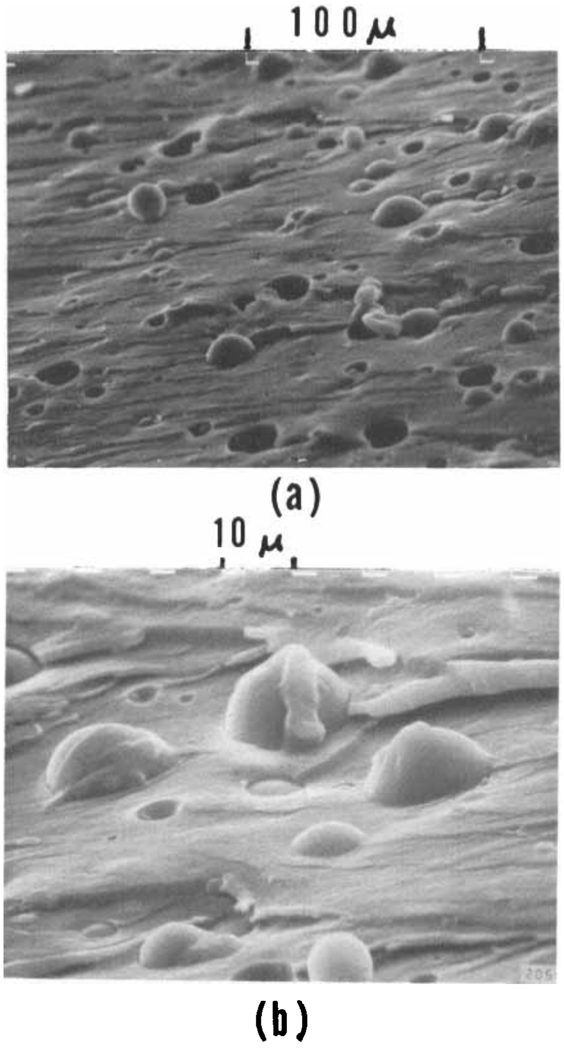


FIGURE 6 Scanning electron micrographs of impact fracture surfaces for RTV silicone rubber filled epoxy resin (silicone rubber content = 5 phr).

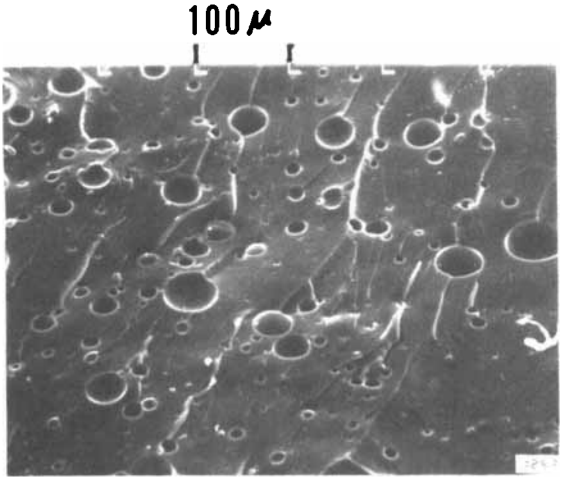


FIGURE 7 Scanning electron micrograph of impact fracture surface for the silicone diamine modified epoxy resin (20 phr).

(SDA), but first we will make mention of the results obtained by McGrath[1,2] in the modification of SDA with silicone oil of the same terminal reactivity. He reports that if the terminals are piperidinated, a preliminary reaction with epoxy resin brought about, and the epoxy resin blended with solubilized polydimethylsiloxane, polytrifluoropropylmethylsiloxane and polydiphenylsiloxane oligomers, then fracture toughness (K_{IC}) increases, micro-order holes appear on the fracture surface, and the same morphology as that which occurs after modification by CTBN and ATBN can be observed. He further reports that SDA has poor

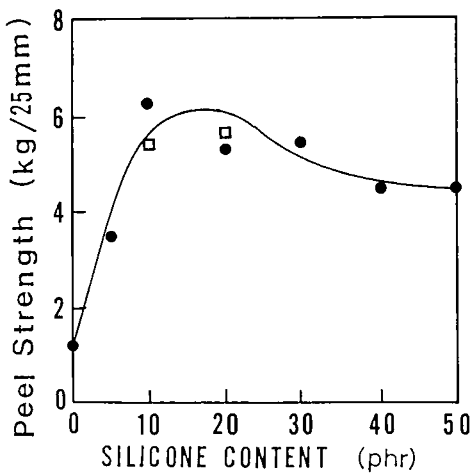


FIGURE 8 Peel strengths for aluminium plates bonded by RTV silicone rubber filled epoxy resin (●) and by silicone diamine filled epoxy resin (□) as a function of silicone content by adhesives.

solubility in epoxy resin and cannot be blended because it causes macro phase separation, and even if an attempt is made to render it soluble by means of a preliminary reaction, because it has bifunctional amino groups, it ends up gelling at the preliminary reaction stage.

We then attempted to disperse SDA into epoxy resin using a compatibilizer. Figure 7 shows a SEM of the Izod impact fracture surface of epoxy resin filled with 15 phr SDA and hardened with PACM (compatibilizer 1 wt%).

A large number of holes can be seen across the surface, which are thought to

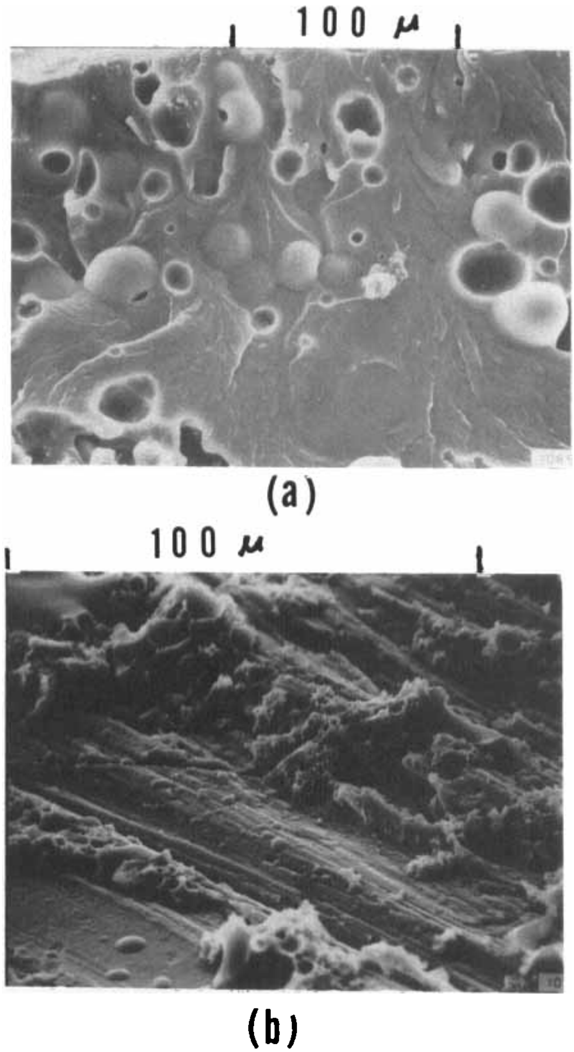
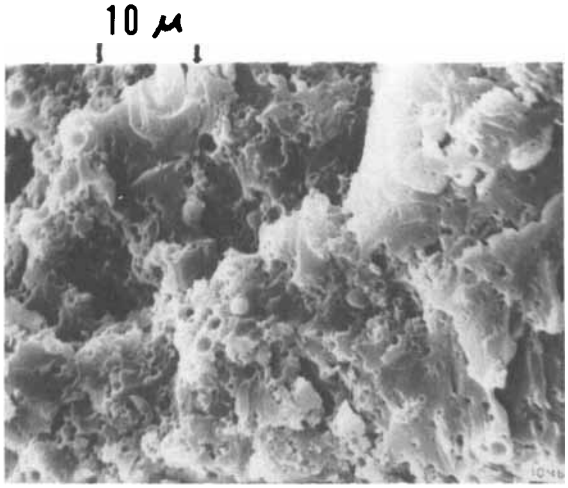


FIGURE 9 Scanning electron micrographs of the fracture surface after the peel test of the aluminium plates bonded with RTV silicone rubber filled epoxy resin. (a) Surface of epoxy resin filled with 20 phr silicone, (b) Surface of Al (silicone 40 phr), (c) Surface of epoxy resin (silicone 50 phr).



(c)

FIGURE 9—(continued)

be where there was silicone. This closely resembles the pattern demonstrated by McGrath[1,2] with terminally reactive silicone oil, and it shows that if a compatibilizer is used, then epoxy resin can be modified even by SDA. However, under Izod impact fracture testing, *E* hardly increased at all. This is thought to be because the molecular weight of silicone is too low for it to be used as a modifying agent for impact resistance.

3.3 Effect of the addition of silicone rubber on peel strength

Figure 8 shows the relationship between the peel strength of aluminium plates bonded using silicone rubber-filled epoxy resin as the adhesive, and the silicone content.

Peel strength increases as the rubber content increases, with its maximum at 10 phr. Figure 9 shows scanning electron microscope photographs of the fracture surfaces. In the system with a silicone content of 20 phr (Figure 9(a)), the distribution of rubber particles of $1 \sim 20\,\mu\text{m}$ and their matching holes can be seen. Figure 9(b) shows the peel surface of the aluminium plate in the system with a silicone rubber content of 40 phr. Figure 9(c) is the SEM photograph of the surface of the epoxy resin in the system with 50 phr content. In both of these a large number of rubber particles of several micrometers in size can be seen.

Next, the relationship between SDA content and peel strength of aluminium plates joined using SDA-modified epoxy resin as the adhesive is shown in Figure 8 by the hollow squares. The peel strength increased greatly when the SDA content was 10 phr ~ 20 phr. Figure 10 shows SEM photographs of these fracture surfaces.

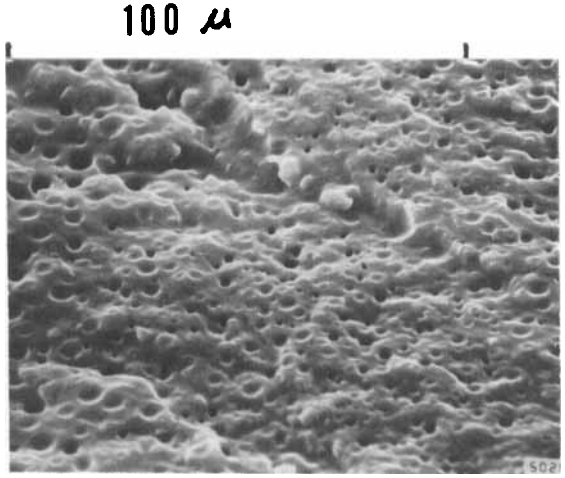


FIGURE 10 Scanning electron micrograph of the fracture surface of epoxy resin filled with 15 phr silicone diamine.

In this case too, a large number of holes can be seen across the surface. From this it can be seen that SDA too is effective as a modifier for peel strength.

4 CONCLUSIONS

In order to find material with strong interfacial activity (compatibilizer) for the epoxy resin/silicone rubber interface, epoxy resin was mixed with silicone oil modified by the introduction of atomic groups having strong compatibility with epoxy resin, and the concentration dependency of this mixture's interfacial tension against silicone oil was investigated. The results show that polyether modified silicone oil containing propylene oxide (EtMPS(3)) has strong interfacial activity, and can be used effectively as a compatibilizer. Following on from this, silicone rubber was dispersed in epoxy resin using EtMPS(3) as a compatibilizer, and the effect of the rubber content was investigated by conducting Izod impact testing and peel testing.

The impact fracture energy (E) of RTV silicone-rubber-filled epoxy resin increased greatly in proportion to the rubber content. Furthermore, rubber particles of $1 \sim 20\ \mu$m were observed across the whole of the fracture surface. The existence was also noted of a certain amount of bonding force between the epoxy resin and the surface of the rubber particles, and it was confirmed that polyether-modified silicone oil is quite effective as a compatibilizer. The peel strength of aluminium plates bonded together using RTV silicone-rubber-filled epoxy resin as adhesive increased in proportion to the silicone rubber content.

On the Izod impact fracture surface of silicone diamine (SDA)-modified epoxy resin, numerous holes were observed, which are thought to indicate the existence of silicone, and which suggest the possibility of modifying epoxy resin with SDA also, but impact energy (E) hardly increased at all. However, peel strength increased greatly at SDA contents of 10 phr ~ 20 phr.

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References

1. J. S. Riffle, I. Yilgor, C. Tran, G. L. Wilkes, J. E. McGrath and A. K. Banthia in *Epoxy Resin Chemistry II*, R. S. Bauer, Ed., *ACS SYMPOSIUM SERIES No 221* (American Chemical Society, Washington, D.C., 1982), p. 21.
2. E. M. Yorkgitis, N. S. Eiss, C. Tran, I. Yilgor, G. L. Wilkes and J. E. McGrath, in *Rubber-Modified Thermoset Resins*, C. K. Riew, Ed., *ADVANCES IN CHEMISTRY SERIES 208* (American Chemical Society, Washington D.C., 1984), p. 137.
3. R. Hata, *Kōbunshi Jikkengaku* (Polymer Experimental Science) *Vol. 12* "Thermodynamic, Electrical and Optical Properties," (Kyoritsu Publishing, Tokyo, 1984), p. 148.