

ELASTOMERIC REACTIVE MICROGELS AS TOUGHENER FOR EPOXY ADHESIVES

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ABSTRACT

Elastomeric reactive microgels were evaluated as toughener for epoxy adhesives. It turned out that elastomeric microgels can improve lap shear strength and peel strength greatly. The glass transition temperature of the resin matrix was not affected by the presence of dispersed microgel particles, and thus the microgel-toughened adhesives have a good bond strength at elevated temperatures.

INTRODUCTION

Epoxy adhesives can be toughened by appropriate amount of elastomeric particles. So far liquid rubbers such as carboxyl-terminated polybutadiene-acrylonitriles (CTBN) are used most successfully^[1]. However, there still exist several disadvantages in the liquid rubber-toughening technique. Firstly, the in situ formed rubber particles are distributed broadly in size, and the morphology and, in turn, the mechanical properties change easily with additives such as reinforcing fibres and the time-temperature schedule of the cure^[2]. Moreover, the phase separation is usually incomplete, and as a result the glass transition temperature T_g of the resin is depressed by incorporation of liquid rubber^[3].

In order to overcome the above mentioned disadvantages efforts have been made to use preformed rubber particles as toughener for epoxy resins. Siebert and Rowe^[4] and Trostyanskaya et al.^[5] have prepared rubber-epoxy resin blends by mixing rubber latices into epoxy resin. Although the toughness of epoxy resins could be improved by rubber latices, the stability of the blends was not good enough, and the contamination of the emulsifier could not be eliminated.

In this paper we describe a new approach to the toughening of epoxy adhesives with preformed rubber particles. We found that elastomeric reactive microgels are effective toughener for epoxy resins. Reactive microgels differ from rubber latices in that they have internally crosslinked structure. They can be prepared through emulsifier-free emulsion polymerization^[6,7], and are easily free from any ionic contaminants by the treatment with ion exchangers. Owing to the shell-core structure of the microgels the blends of microgel and epoxy are extremely stable.

EXPERIMENTAL

1. Preparation of reactive microgels.

Elastomeric reactive microgels used in this work are copolymers of butyl acrylate with unsaturated polyester. In a 1 l 4-necked flask equipped with stirrer, thermometer and gas inlet tube, 16 g carboxylated unsaturated polyester from hexanediol and maleic anhydride ($\bar{M}_n$ 1610, carboxyl number 1.20 meq/g), 8g NaHCO_3 and 400 ml degassed distilled water were introduced. The unsaturated polyester was dissolved by stirring under strict exclusion of oxygen. 64 g n-butyl acrylate was added. After vigorous stirring for 15 min. at 70°C, the polymerization was initiated by injection of 4 ml 10% aqueous solution of $\text{K}_2\text{S}_2\text{O}_8$. The polymerization was carried on at that temperature for 4 h.

The microgel thus prepared was designated as M44. Microgels of different particle size and

carboxyl content were prepared by changing the ratio of unsaturated polyester to n-butyl acrylate. The average diameter of microgel particles in latices was measured using a nanosizer, which is based on quasi-elastic light scattering. The carboxyl number was determined by neutralization titration. The analysis data are given in Table 1.

Table 1 Analysis of reactive microgels

Code	Average diameter (nm)	Carboxyl number (meq/g)
M 44	80	0.18
M 03	51	0.26
M 06	63	0.32

2. Measurement

For the study of the stress-strain properties dumbbell specimens were prepared by casting a mixture of epoxy resin (diglycidyl ether of bisphenol A with an epoxy number 5.1 meq/g from Wuxi Resin Factory) 100 parts (wt.), curing agent 2-ethyl-4-methyl imidazole (EMI-24) 10 parts and microgel 10 parts. The curing was effected at 70°C for 2h and 120°C for 3 h. The thickness of the specimens was 1 mm, gauge length 30 mm and width of the narrow section 6 mm. Stress-strain curves were measured on an Instron testing machine at a crosshead moving rate 2 mm/min.

Dynamic mechanical dissipation spectra were obtained using an automatic torsion braid analysis apparatus (type XHS-1) over a temperature range from -140 to +160°C at 4°C/min.

The morphology of the microgel-modified epoxy resins was studied by electron micrograph of microsections stained with uranium acetate using a JEM-100 electron microscope.

The adhesive bond strength was determined using aluminum alloy LY12CZ adherent etched in a $K_2Cr_2O_7-H_2SO_4$ bath. For lap shear tests panels of 2mm × 20mm × 60mm were used, and the overlap was 15mm. For T-peel tests 130mm × 260mm sheets of 0.5 mm thickness were used. The specimen was cut into stripes of 25mm width after curing of the adhesive. The T-peel strength was recorded on an Instron machine at a crosshead rate 50 mm/min.

RESULTS AND DISCUSSION

1. Morphology and transitions of microgel-modified epoxy resins

Microgel-modified epoxy resins were prepared by dissolving the resin (DGEBA) into a microgel solution in acetone. After removal of the solvent in vacuum stable blends were formed, which were likely real solutions of microgel in epoxy resin. No change in average particle size and polydispersity was found after the blends were stored for months and redissolved in acetone.

When a microgel MO3-DGEBA blend was cured with EMI-24, discrete microgel particles were dispersed in the resin matrix. The diameter of the particles was about 75nm, which is in agreement with the particle size of MO3 in latex. During the cure of M44-DGEBA blends, increase in opacity was apparent. This is due to the clustering of the microgel particles as demonstrated by electron micrograph. We believe that the stability of the microgel particles in epoxy resins is controlled by the carboxyl number of the microgel.

Microgels are macromolecular particles (M_w ca. 10^7). They do bond to the epoxy resin matrix through carboxyl groups, but do not build into the network of the resin. Therefore the glass transition temperature of the resin is not lowered by incorporation of microgels at a level over 40 phr (see Table 2).

Table 2 Transitions of microgel-modified epoxy resins*

Modifier	T_g epoxy resin (°C)	T_g microgel (°C)
neat resin	142	
M 44	150	-69
M 03	144	-60
M 06	146	-61

* Epoxy resin E 51 was cured with 10 phr EMI-24 at 120°C for 3 h, microgels were added at a level 40 phr.

The TBA diagram of microgel-modified epoxy resins is given in Figure 1. On the low temperature side of the mechanical damping curves there are loss peaks corresponding to the β -transition of epoxy resin (ca. -80°C) and the glass transition of microgels (-60 to -70°C) respectively. For the microgel-modified resins there is an increase in mechanical damping over the whole range from -80 to $+80^\circ\text{C}$. This reflects the strong interaction between the matrix resin and the dispersed phase in the boundary layer.

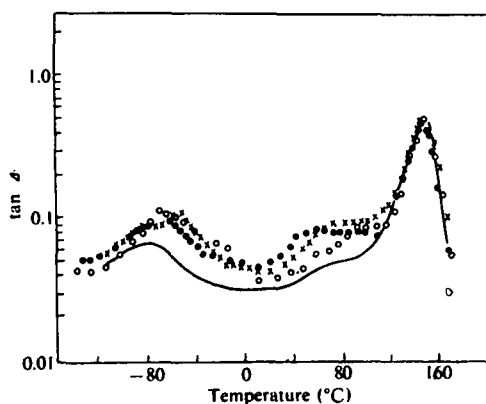


Fig. 1 TBA diagram of microgel toughened epoxy resins
(-- neat resin, ○ M 44, × M 03, ● M 06)

2. Mechanical properties

Mechanical properties of the bulk resins modified with microgels and cured with EMI-24 are given in Table 3. Tensile strength and Young's modulus of the modified resins are lower than that of the control while the ultimate elongation is higher.

There is no correlations between the strength of the bulk resin and the tensile lap shear strength of the adhesive bond. All of the microgel modifiers make an increase in lap shear strength as shown in Table 4 and 5. The bond strength tends to increase with carboxyl number of the microgel modifier (see Table 4). Likely a decrease in modulus and increase in ultimate elongation have made the adhesive more deformable and therefore a more even stress distribution in the bond line.

It is surprising that the bond strength of microgel-modified epoxy adhesives is not sensitive to the level of the modifier (see Table 5). The lap shear strength remain very high even if the content of the microgel modifier increase to 100 phr. This is quite different from liquid rubber-modified

Table 3 Mechanical properties of epoxy resins*

Modifier	Tensile strength (MPa)	Young's modulus (GPa)	Ultimate elongation (%)
neat resin	81.0	1.41	7.9
M 44 (10phr)	67.3	1.39	8.4
M 03 (10phr)	70.2	1.27	9.3
M 06 (10phr)	63.1	1.11	8.5

* Cured with 10 phr EMI-24 at 70°C for 2 h, 120°C for 3 h.

Table 4 Lap shear strength of epoxy adhesives* modified with 15 phr microgels

Modifier	Control	M 44	M 03	M 06
lap shear strength (MPa)	22.4	25.9	26.7	27.0

* Epoxy resin E51 cured with 10 phr EMI-24 at 120°C for 3 h

Table 5 Influence of the microgel M 06 level on lap shear strength of epoxy adhesives*

level of M 06 (phr)	0	5	10	20	40	60	100
lap shear strength (MPa)	22.4	25.5	26.9	26.7	29.9	24.7	28.2

* Epoxy resin E 51 cured with 10 phr EMI-24 at 120°C for 3 h

systems. In a CTBN-epoxy resin system, the rubber phase is formed during the cure as discrete particles when the liquid rubber is a minor component. As the rubber content increases to ca. 30 phr a phase inversion takes place, and the system becomes "flexible" rather than "toughened". However, no phase inversion occurs in microgel-epoxy resin systems.

Another remarkable aspect of the microgel-modified epoxy adhesives is the high retention of the bond strength at moderate high temperatures (Figure 2). This is in harmony with the fact that the T_g of the resin matrix is not be affected by the presence of microgels.

T - peel strength of epoxy adhesives can be improved greatly with microgel tougheners. The elastomeric microgel particles are crack stopper in the modified adhesives. The fracture of microgel toughened epoxy adhesives shows characteristic start-stop bands. In the T - peel test a crack forms as the peel force rises to a peak value. The fracture plane propagates only a short distance before being stopped. A new crack forms as the peel force reaches a new peak value. Thus the microgel-toughened epoxy adhesives are very crack-resistant.

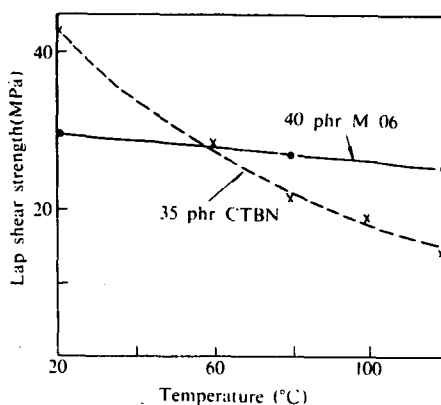


Fig. 2 Influence of temperature on bond strength of epoxy adhesives modified with microgel and CTBN

Table 6 gives a comparison of an elastomeric reactive microgel with a liquid rubber toughener. The reactive microgel modifier has combined the advantages of excellent lap shear strength, good bond strength at elevated temperatures and good peel strength.

Table 6 Mechanical properties of toughened epoxy adhesives*

Toughener		Control	Microgel (20 phr)	CTBN** (20 phr)
lap shear strength (MPa)	RT	25.9	36.1	39.4
	100°C	25.3	31.1	23.3
	120°C	17.1	22.1	14.3
T - peel strength (KN/m)				
		RT	0.5	2.0

* Epoxy resin E 51 cured with 9 phr Dicy at 170°C for 1 h.

** acrylonitrile content 30%, $\bar{M}_n$ 2500.

Keywords:

Microgels; Toughener; Epoxy resin

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