

LIQUID CHLOROPRENE-HYDROXYETHYL METHACRYLATE COPOLYMER MODIFIED EPOXY RESIN

II. N,N-DIMETHYL BENZYL AMINE CURING SYSTEM

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ABSTRACT

A series of liquid chloroprene-hydroxyethyl methacrylate copolymer (CP-HEMA) modified epoxy resin were prepared. The effects of CP-HEMA content, curing conditions on physical properties of the modified system were examined. With IR and Viscoelastocuremeter, the curing reaction rate was determined and the mechanism of the curing reaction was discussed. The effects of CP-HEMA content and curing conditions on morphology were mainly observed by scanning electron microscopy.

INTRODUCTION

In recent years, considerable development has been made in the field of liquid rubber modified resins. The researches were mainly focused on the liquid carboxy-terminated butadiene-acrylonitrile copolymer (CTBN) modified system. The thermosets of epoxy resins belong to brittle materials because it has the molecular structure of high crosslinking networks. Therefore, adding a small amount of liquid rubber into epoxy resin will disperse the stress density around brittle cracks and increase its toughness significantly. As a consequence, the mechanical properties are increased and the brittle cracks that may happen below the yield point are suppressed^[1-4].

The effects of several liquid butadiene-acrylonitrile copolymers with different functional groups on the mechanical properties and morphology of modified epoxy resin thermosets cured with tertiary amines were examined^[5]. The result shows that the peel strength of CTBN modified system is twice as much as that of the system modified by the rubbers without active terminal groups. The latest research works in the field stress on the relationship between morphology and physical properties^[6, 7]. Williams^[8] has developed a mathematical model to predict the effects of curing parameter on different modified thermosets under unisothermal conditions.

The CP-HEMA modified epoxy resin has been reported^[9]. The synthesis and characterization of CP-HEMA has also been investigated^[10]. In the present paper, the mechanical

properties, curing reaction and morphology of CP-HEMA modified epoxy resin with N,N-dimethyl benzyl amine as a catalyst are studied through the use of IR, viscoelastocuremeter and scanning electron microscopy. The correlation of curing reaction and morphology with mechanical properties is discussed.

EXPERIMENTAL

Materials

CP-HEMA were synthesized by ourselves with 1500—2500 ($\bar{M}_n$) and 8.0×10^{-4} — 10.9×10^{-4} (hydroxy value, equ./g) and 1.8—2.3 (functionality of hydroxygroup). Epoxy resin (commercial name being 618) is manufactured by Wuxi Resin Factory and N,N-dimethyl benzyl amine used as a catalyst is the product of Shanghai Chemicals Factory.

Preparation of CP-HEMA modified thermosets

Required amount of CP-HEMA was dissolved in the epoxy resin. N,N-dimethyl benzyl amine was added into the mixture, mixed thoroughly, degassed, poured into models, then cured under certain temperature to form the thermosets for measurements.

Techniques

Mechanical properties data were obtained using standard methods with a tensometer. Curing reaction rates were determined with JSR-Viscoelastocuremeter. IR spectrum of absorbing vibration of epoxy groups was obtained with Perkin Elmer IR spectroscope performed by the following procedure. A mixture of CP-HEMA, epoxy resin and catalyst was coated on the surface between two pieces of NaCl salt plates that fixed together so that the thickness of the thermosetting membrane remains unchanged during curing. The thermosets were broken off small fragments with brittle crack surfaces. Then the surfaces were observed by scanning electron microscope.

RESULTS AND DISCUSSION

The effects of CP-HEMA content on mechanical properties: Shear strength obviously increases as CP-HEMA content rises, in the meantime, transition temperature (T_g) drops (Figs. 1 and 2). The shear strength approaches the maximum value as CP-HEMA is up to 30%. In comparison with pure resin system, the shear strength increases by more than 80 kg/cm². When the content is over 30%, the system transforms from tough to flexible one and the strength and T_g decrease.

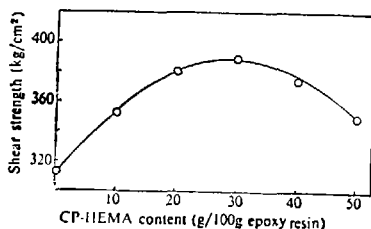


Fig. 1 The effect of CP-HEMA content on shear strength

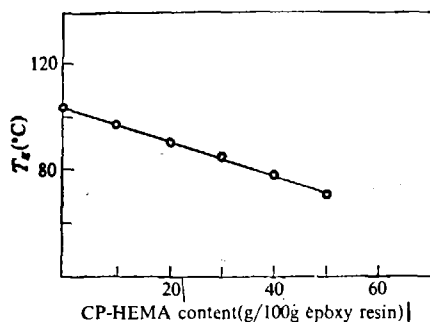


Fig. 2 The effect of CP-HEMA content on transition temperature (T_g)

The peel and impact strengths rise correspondingly with increasing CP-HEMA content. Adding CP-HEMA to the resin causes the modification of the system. This attributes to the flexible long molecular chains of CP-HEMA. In consequence, the physical properties are profoundly improved (Figs. 3 and 4).

Fig. 5 shows the effects of curing temperature on the shear strength. With increasing curing temperature, the shear strength increases prominently and reaches the maximum value at 120°C. On the contrary, the strength is lower than that of pure resin system at 60°C. This implies that the curing reaction between CP-HEMA and resin occurs at certain temperature.

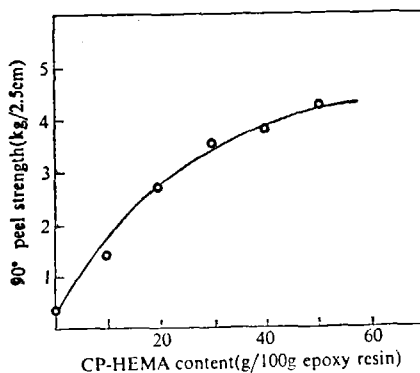


Fig. 3 The effect of CP-HEMA content on peel strength

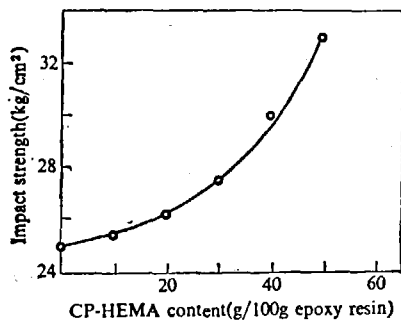


Fig. 4 The effect of CP-HEMA content on impact strength

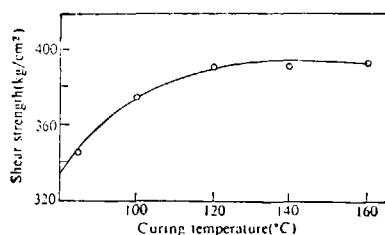


Fig. 5 The effect of curing temperature on shear strength of 30% CP-HEMA system

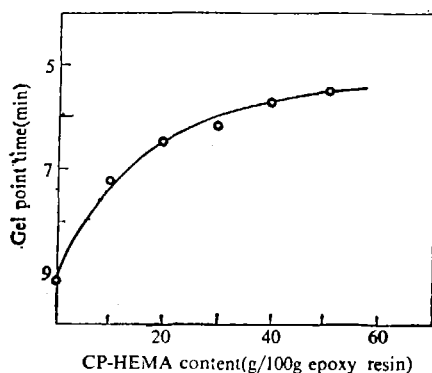


Fig. 6 The effect of CP-HEMA content on curing reaction rate

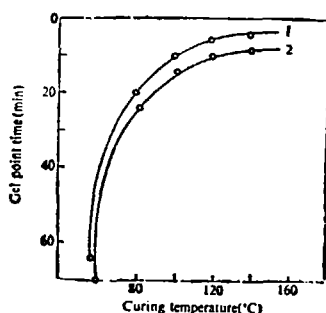


Fig. 7 The effect of curing temperature on the rate of curing reaction
1. 30% CP-HEMA system, 2. pure system.

Gel point time is shortened and rate of curing reaction is accelerated with increasing CP-HEMA content at 120°C and the rate of 30% CP-HEMA system is faster than the rate of pure resin system (Figs. 6 and 7). The difference between the two rates tends to enhance with increasing curing temperature.

The curing reaction is investigated by observing the changes of the absorbing peaks of the epoxy groups (915cm^{-1}) in IR spectrum. The intensity of the peak drops markedly with prolonged curing time. It has been seen from above data obtained by viscoelastocuremeter that the gel point time of 30% CP-HEMA modified system is 20.2 min. Consistent data obtained by IR are listed in Table 1. Beyond the gel point time, the curing reaction speeds up and tends to complete for one and half hours. Another consistent fact is that the rate

of curing reaction of modified system is faster than that of the pure resin system. The fact supports such a mechanism of the curing reaction as follows: Tertiary amine promotes the etherification of primary hydroxyl groups with epoxy groups in the meantime of catalyzing the self-polymerization between the epoxy groups. In the pure resin system, the self-polymerization occurs while in modified system, both the etherification and the self-polymerization take place simultaneously. Therefore, the rate of the modified system is faster than that of the pure resin system. To state succinctly, the etherification results in an improvement of the mechanical properties of the modified system.

Table 1 The data of conversion of epoxy groups in curing reaction from IR

Curing time (min)	5	10	15	20	30	40	60	80
Pure resin system (conv. %)	0	4.8	7.7	17.3	39.1	59.3	77.9	82.7
30% CP-HEMA system (conv. %)	0	6.8	10.2	22.9	45.9	67.8	84.4	95.1

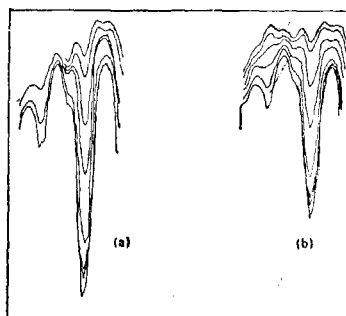


Fig. 8 Changes of epoxy groups (915cm^{-1}) during the process of the curing reaction
(a) pure resin system, (b) 30% CP-HEMA system.

Morphology of the CP-HEMA modified system: In rubber modified systems, it is complicated to say which factor mainly influences the formation of the morphologic two phase microstructure. The formation of the microstructure is not only related to the natures of rubbers and resins, but also concerns kinetics of curing reaction and thermodynamics of the system. In recent years, the formation and development of the two phase microstructure in the rubber modified systems has been an interesting research subject. The correlation of domain sizes of dispersed phase with physical properties has been studied^[7-8].

In CTBN modified system, existence of two phase morphology can be observed by electron microscopy. However, different degree of separation can be created by different curing system and curing condition. The morphology of modified resin system depends largely on the method of the preparation, the compatibility of the resin and the rubber used and the relative rate of the curing reaction of the two components. If curing reaction speeds up, then the degree of the separation inclines to become descending and domain size tends to be smaller^[3]. In other words, the part of the dispersed phase reduces whereas rubber content of domain in dispersed phase increases with increasing curing temperature^[8]. The domain size in CTBN modified system generally is about $0.1\text{--}5\mu$ that depends on system and curing

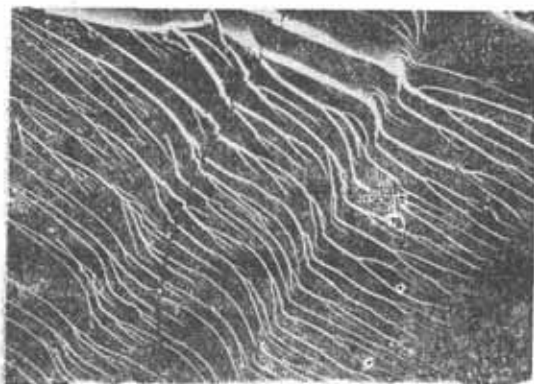


Fig. 9 Pure resin system ESM, 200 ×

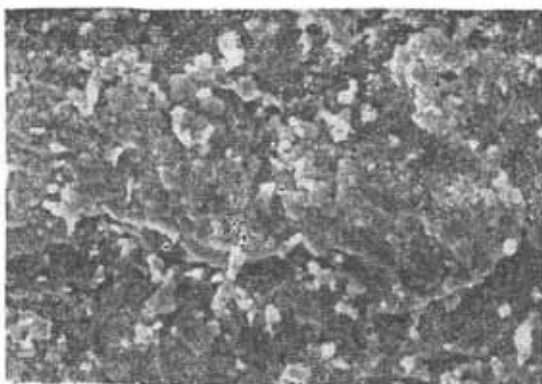
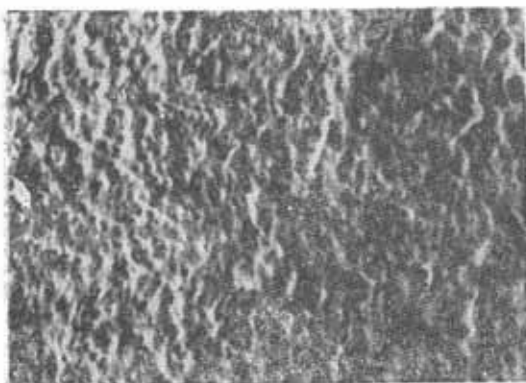
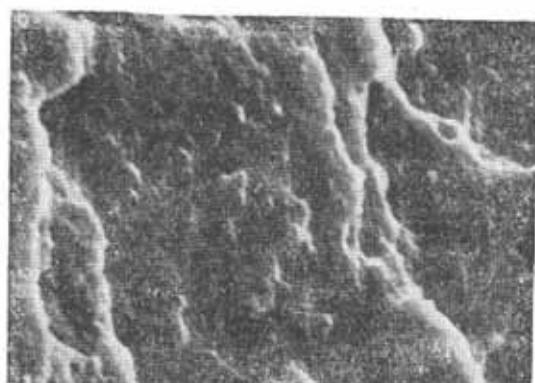


Fig. 10 30% CP-HEMA modified system ESM, 1000 ×

Fig. 11 40% CP-HEMA modified system
ESM, 1000 ×Fig. 12 50% CP-HEMA modified system
ESM, 1000 ×

condition.

Fig. 9 is the electron scanning micrograph (ESM) of the pure resin system, in which scars of broken surfaces can be solely caught sight of. The scanning micrographs of the CP-HEMA modified systems are shown in Figs. 10–12. The concentration of the rubber particles heightens, then the particles disappear and the system transforms into continuous phase with increasing CP-HEMA content. In 30% CP-HEMA modified system, although the rubber particles conceal in the resin phase, the resin component is indistinct in the rubber particles. This can be explained that the two components partially mix with each other. The rubber particles still are visible and their sizes are about $0.3\text{--}1.0\ \mu$. In 40% CP-HEMA modified system, the rubber particles are no longer the domains as independent units, but continuously distribute in the resin phase. It is difficult to measure the size of the particle because the boundaries between the two phases are not clear. In fact, inversion of phase has occurred. In 50% CP-HEMA modified system, the rubber and the resin exist in the system with their own continuities locally although the resin phase has been dispersed phase.

Figs. 13–15 are the ESM of 30% CP-HEMA modified system cured in different conditions. The tendency of development of the separation and the effect of curing condition on the morphology can be followed. With increasing curing temperature and rate of curing reaction, the rubber particles are getting larger, the degree of the separation is increasing.



Fig. 13 30% CP-HEMA modified system
ESM, 3000 $\times$, cured at 120°C



Fig. 14 30% CP-HEMA modified system
ESM, 3000 $\times$, cured at 80°C

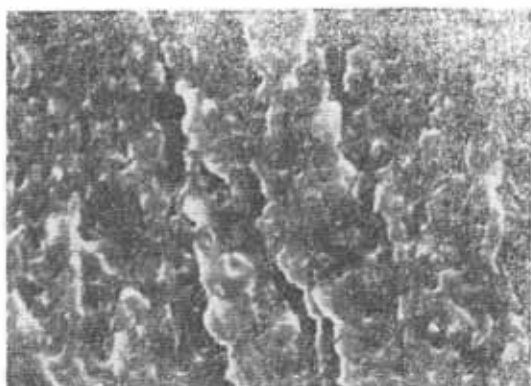


Fig. 15 30% CP-HEMA modified system ESM, cured at 25°C for 1 day and at 80°C

Table 2 shows the solubility parameters (δ), cohesive energy densities ($\delta_1^2 - \delta_2^2$), and interaction parameters (X_{12}) of butadiene-acrylonitrile copolymer (PB-AN) and chloroprene-hydroxyethyl methacrylate copolymer (CP-HEMA) calculated from Krause's method (neglecting the influence of the terminal groups)^[11]. Krause has stated that if $X_{12} > (X_{12})_{cr}$ (interaction parameter at critical point) the two polymers should be incompatible at some compositions. The greater the difference between the two values, the smaller will be the range of compositions over which polymers will be compatible. From Table 2, it can be seen that none of the polymer pairs constituting the modified system are predicted to be compatible before the curing reaction occurs, because all the X_{12} are larger than $(X_{12})_{cr}$. However, the difference between the two values for (A) system is much smaller than that for (B) system. This is a significant proof that the miscible range of composition in (A) system is much more extensive than that in (B) system. In fact, the mixture of CP-HEMA and epoxy resin is a homogeneous solution before the curing reaction occurs^[9]. The turbid phenomenon appears in the process of curing reaction. This is due to formation of two phase microstructure. At elevated temperature, viscosity of system drops and curing reaction speeds up. So the formation of the two phase microstructure depends mainly on kinetics of curing reaction for shorter period. As a result, the rubber particles become larger. At lower curing temperature, the curing reaction slows down and the development of the two phase microstructure

depends largely on thermodynamics of diffusion for longer period. The rubber particles tend to be smaller. On the contrary, in (B) system, at lower curing temperature the development of the two phase microstructure results from unstability of thermodynamics because the difference between X_{12} and $(X_{12})_{cr}$ is larger. In consequence, in extensive compositions the degree of the separation tends to become greater for longer curing period.

Table 2 Interaction parameters calculated by Krause's method

Polymer system	$\delta(\text{cal/cm}^2)^{1/2}$	$\delta_1^2 - \delta_2^2(\text{cal/cm}^2)$	X_{12}	$(X_{12})_{cr}$
PB-AN (88/12)	8.9 ⁽¹²⁾	—	—	—
CP-HEMA (88/12)	9.7 ⁽¹²⁾	—	—	—
Epoxy resin (EP)	10.9 ⁽¹²⁾	—	—	—
EP/CP-HEMA (A)	—	24.7	0.24	0.21
EP/PB-AN (B)	—	39.5	0.66	0.21

CONCLUSION

In CP-HEMA modified epoxy resin system, the physical strengths significantly increase and T_g drops with increasing CP-HEMA content. The system transforms from toughness into flexibility over 30% CP-HEMA content. The data obtained by viscoelastocuremeter and IR spectrum indicate that in the CP-HEMA modified epoxy resin system the etherification of primary hydroxyl groups in the rubber with epoxy groups in the resin occurs in the meanwhile of the self-polymerization between epoxy groups. The improvement of the mechanical properties and the effective toughening to the system attribute to the curing reaction between the rubber and the resin.

There is the two phase morphology in the CP-HEMA modified system. Through electron scanning microscopy, the changes of the morphology are observed with different CP-HEMA content. With increasing curing temperature and accelerating curing reaction, the degree of the separation and the rubber particles tend to become greater. The data of interaction parameters calculated by Krause's method support the following deduction that the formation of the two phase morphology depends mainly on kinetics of the curing reaction between the rubber and the resin at elevated curing temperature for shorter period and it depends largely on thermodynamics of diffusion at lower curing temperature for longer period.

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