

# PREPARATION AND PROPERTIES OF EPOXY RESIN MODIFIED BY LIQUID CHLOROPRENE- HYDROXYETHYLMETHACRYLATE COPOLYMER\*

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## ABSTRACT

The epoxy resin modified by liquid chloroprene-hydroxyethylmethacrylate copolymer (CP-HEMA) is a new kind of structural adhesives with good mechanical properties. By changing its molecular structure, it may also have such desirable properties as retardation of combustion, enduring weather aging, inert oils and chemicals. A series of the thermosets of the epoxy resin modified by CP-HEMA used as a toughener were prepared. The effects of CP-HEMA content, catalyst content and curing temperature on the mechanical properties of modified epoxy resin system were studied. The thermal weight-loss curves were examined. The two-phase morphology was observed and discussed.

## INTRODUCTION

There has been considerable development in the subject on the effects of liquid rubbers on epoxy resin and other thermosetting resins in the past decade. The researches were mainly focused on the system modified by liquid carboxyl-terminated butadiene-acrylonitrile copolymer (CTBN). Adding a small amount of liquid rubber into the epoxy resin will increase its toughness considerably. Therefore, the adhesive modulus is increased, and the brittle cracks that might happen below the yield point<sup>[1,2,3]</sup> are suppressed, CP-HEMA toughened epoxy resin is a new kind of structural adhesives<sup>[4]</sup>, which has not been well documented in the literature.

A series of thermosets of CP-HEMA modified epoxy resin were prepared with varying CP-HEMA content. The effects of CP-HEMA content and curing temperature on mechanical properties were studied. The curves of thermal weight-loss were examined. The microstructure morphology was discussed.

## EXPERIMENTAL

### 1. Materials

(1) CP-HEMA: Number average molecular weight ( $\bar{M}_n$ ): 1500—2100, Functionality

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of hydroxyl group: 1.5—2.3, prepared by ourselves<sup>[5]</sup>.

(2) Epoxy resin 618 manufactured by Wuxi Resin Factory.

(3) 2,4,6-tri (dimethylaminomethyl) phenol (DMP-30) from Shanghai Chemicals Factory, repacked from imported product.

## 2. Modification procedure

Into a glass flask weighed epoxy resin and CP-HEMA were mixed thoroughly, then a given quantity catalyst was added, stirred degassed, finally cured at a certain temperature.

## 3. Measurements

(1) Mechanical properties: The mixture of epoxy resin and CP-HEMA was painted between two steel sheets and their surfaces had been treated by either chemical or physical method. Then the shear strength were determined by an electronic tensile tester. Other strength tests were done by standard methods.

(2) Curing rate: The rate was determined by a viscoelastocuremeter (JSR type made in Japan)

(3) Microstructure analysis: Morphology analysis was performed by transmission electron microscopy (H-500 type). The ultrathin samples were prepared by an ultramicrotome, and stained by exposing the samples to the vapor of aqueous osmium tetroxide solution at room temperature for 2 days.

(4) Thermal stability: The curves of weight loss were drawn by a thermal balance.

## RESULTS AND DISCUSSION

The effects of CP-HEMA content on mechanical properties: Shear strength profoundly increases with increasing CP-HEMA content, whereas the transition temperature ( $T_g$ ) drops a little at the same time. The strength reaches the maximum value at 30% CP-HEMA. As compared with pure resin system the shear strength increases by more than 100 kg/cm<sup>2</sup>. These indicate that the toughening effect of CP-HEMA is apparent (see Table 1).

Table 1 The effect of CP-HEMA content on shear strength

| CP-HEMA (wt. %) | Shear strength (kg/cm <sup>2</sup> ) | $T_g$ (°C) |
|-----------------|--------------------------------------|------------|
| 0               | 217                                  | 114        |
| 10              | 248                                  | —          |
| 20              | 310                                  | 114        |
| 30              | 330                                  | 112        |
| 40              | 327                                  | 110        |
| 50              | 310                                  | 107        |

Peel strength (Fig. 1) and impact strength (Fig. 2) are improved as CP-HEMA content rises. Adding CP-HEMA that possesses molecular structure of flexible main chain into resin can contribute the toughness to the modified system and improve the brittleness of

the resin. Consequently, these strengths are higher in the modified system than in pure resin system.

Bending strength is improved as CP-HEMA content increases with the maximum value at about 30% CP-HEMA beyond which the strength begins to drop. The bending amount rises with increasing CP-HEMA, particularly, beyond the point of 30% CP-HEMA. This indicates that the system transforms from a tough one into a flexible one when the CP-HEMA content increases over 30% (see Table 2).

The effect of curing temperature: The shear strength increases as the curing temperature is elevated, but the shear strength of the system is lower than that of the pure resin system at 50°C, perhaps it means that there is no reaction between epoxy groups on the resin and hydroxyl groups on CP-HEMA at such curing temperature. The maximum value of the

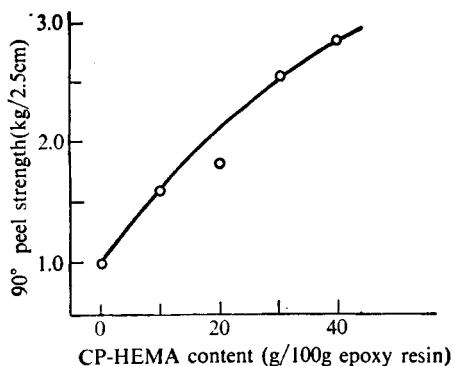


Fig. 1 The effect of CP-HEMA content on peel strength

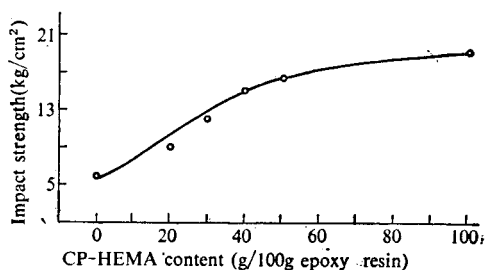


Fig. 2 The effect of CP-HEMA content on impact strength

Table 2 The effect of CP-HEMA content on bending strength

| CP-HEMA (wt.%) | Bending strength (kg/cm <sup>2</sup> ) | Bending amount (mm) |
|----------------|----------------------------------------|---------------------|
| 0              | 577                                    | 4.7                 |
| 20             | 675                                    | 5.6                 |
| 30             | 720                                    | 6.2                 |
| 40             | 702                                    | 13.9                |
| 50             | 606                                    | More than 20        |

shear strength appears at 120°C, beyond this temperature the shear strength approaches constant (see Fig. 3).

Curing rate: The curing rate gradually drops with increase of CP-HEMA content at 60°C. On the contrary, the rate is accelerated with increase of CP-HEMA at 120°C (see Fig. 4). The experimental results are due to that the etherification reaction of epoxy groups of the resin with hydroxyl groups of CP-HEMA proceeds difficultly at lower temperature. Along with the increase of CP-HEMA content, the concentration of epoxy resin decreases, therefore the curing rate correspondingly tends to decrease. At higher curing temperature, the

reactions mentioned above are easy to occur, which lead to an acceleration of curing rate when CP-HEMA content increases. These results can serve to illustrate the relationship between the strength and the curing temperature.

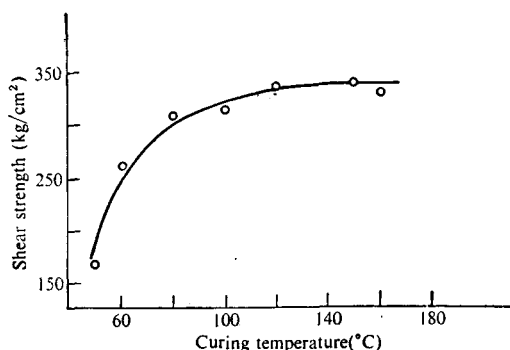


Fig. 3 The effect of curing temperature on shear strength

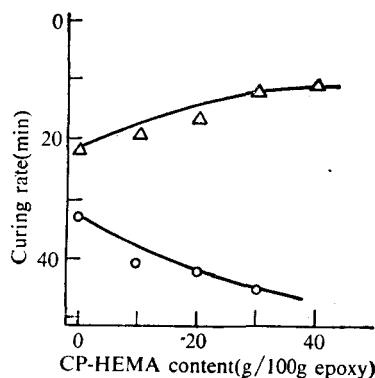


Fig. 4 The relationship between CP-HEMA content and curing rate  
 Δ Cured at 120°C; ○ Cured at 60°C

**Thermal stability:** The curves of thermal weight-loss (Fig.5) shift toward the direction of lower temperatures with increasing CP-HEMA. The decomposition temperature of 30% CP-HEMA system is 241°C, only 9°C lower than that of pure resin system. The decomposition temperature of 100% CP-HEMA system remains as high as 217°C.

Fig. 6 shows that the decomposition temperature and temperature of 20% weight-loss have dropped slightly and the temperature of 100% weight-loss has no apparent change as CP-HEMA content increases. In the system containing 30% CP-HEMA the temperature of 20% weight-loss is 339°C, the temperature of 100% weight-loss is 595°C.

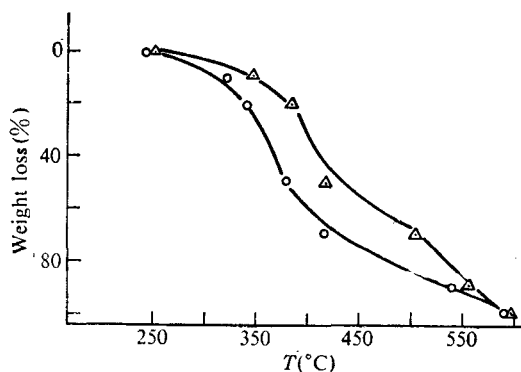


Fig. 5 The curves of thermal weight-loss  
 Δ Unmodified system,  
 ○ 30% CP-HEMA system

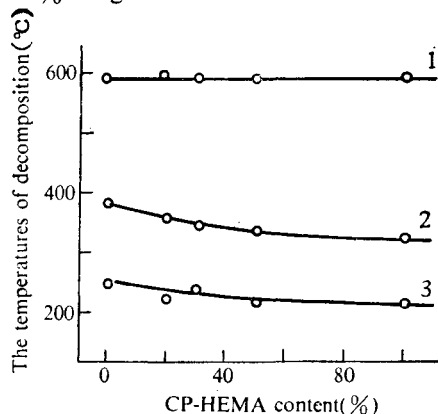


Fig. 6 The effect of CP-HEMA content on weight-loss temperature  
 1 Weight-loss 100%; 2 Weight-loss 20%;  
 3 Decomposition temperature

**Microphase structure:** In the modified system liquid rubbers must be miscible with resin, otherwise they can not react in the curing process, and no toughening effect will be produced. In CTBN toughened system the miscibility mainly depends on nitrile content of CTBN. CP-HEMA dissolves in the resin well because CP-HEMA has the polar groups of ester, hydroxy and chlorine atom.

Table 3 The miscibility of CP-HEMA with epoxy resin

| Liquid rubbers | Active group value       | Miscible state       |
|----------------|--------------------------|----------------------|
| CP-HEMA        | $8.9 \times 10$ (equ./g) | Homogeneous solution |
| CTBN           | CN group 20%             | Opaque solution      |
| HTBN*          | CN group 15%             | Two layers           |

\* Hydroxyl-terminated butadiene-acrylonitrile copolymer

The microstructure was observed by transmission electron microscopy. The rubber particles are partially getting larger and become aggregational domain masses with increase of CP-HEMA content. The two phase microstructure occurs in the curing process. The phase boundary is obscure. It is difficult to measure the sizes of the rubber particles. This indicates that the rubber particles disperse in the resin phase during the curing process, and does not deposit out. This can give enough chances for the rubber to react with resin. The rubber particles disperse in the resin completely and become smaller sizes<sup>[6]</sup>.

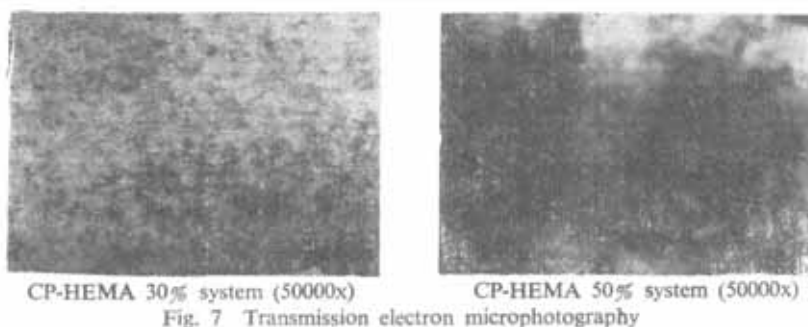


Fig. 7 Transmission electron microphotography

### CONCLUSION

The CP-HEMA used as a toughener improves the mechanical properties of epoxy resin, at the same time  $T_g$  almost does not drop. The system transforms from a tough one into a flexible one when CP-HEMA content is over 30%. The range of the curing temperature is 80–140°C. The curing rate is accelerated with elevating the curing temperature, which will cause good toughening effect.

The curves of thermal weight-loss shift toward lower temperature as CP-HEMA content increases. The decomposition temperature of 30% CP-HEMA system still is 241°C. There is two phase microstructure in the modified system. The rubber particles disperse in the resin phase quite well. The phase boundary is not distinct. The CP-HEMA modified epoxy resin has good mechanical properties. It is suitable for binding metals, glasses and ceramics.

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