

# Toughening of Epoxy Resin Blended with Thermotropic Hydroxyethyl Cellulose Acetate

QIZHOU DAI, JINMING CHEN, YONG HUANG

Laboratory of Cellulose & Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, P.O. Box 1122, Guangzhou 510650, People's Republic of China

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**ABSTRACT:** Thermotropic hydroxyethyl cellulose acetate (HECA) was totally miscible with uncured epoxy resin, and the miscibility was not influenced by the degree of substitution (DS) of HECA. When the epoxy resin was cured with diamine (DDA), HECA became immiscible with the epoxy resin matrix, and a heterogeneous system was formed. Epoxy resin existed as a constant phase, and HECA-rich domains were dispersed in the matrix with dimensions of about 0.2–0.5  $\mu\text{m}$ . Epoxy resin could be toughened by HECA, and the impact strength of the epoxy resin blends with 10 wt % HECA was the maximum. HECA exhibited the highest toughening ability when the epoxy resin was cured at the temperature at which the HECA existed as a liquid crystalline state. The toughening ability was also influenced by the degree of substitution for acetyl of HECA, and the impact strength of the epoxy resin blends decreased with increasing the DS for acetyl of HECA. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1159–1163, 1998

**Key words:** epoxy resin; thermotropic hydroxyethyl cellulose acetate; toughening

## INTRODUCTION

Epoxy resin (ER) are thermosetting polymers for many applications with required high modulus and strength, low creep, and good performance at elevated temperatures. However, their brittleness, low toughness, and poor impact resistance result in the limitation of their applications.

Much research in toughening ER has been reported. One of the most successful methods of increasing the toughness of ER is to incorporate some dispersed particles as the second phase into the crosslinked polymer.<sup>1</sup> According to this procedure, the filler can be rigid particles, such as  $\text{SiO}_2$  or glass spheres, or reactive rubbery particles, such as organosiloxane rubber<sup>2</sup> or butyl nitrile rubber,<sup>3</sup> or both rigid and rubbery

materials. It has been confirmed that the addition of the second phase of dispersed rubbery particles in the thermoset is generally the most effective method for toughening. The impact strength of epoxy resin can be increased by 1–3 times when the rubbery material in the system is lower than 10 wt %.<sup>3,4</sup> The existence of the rubbery phase, however, usually results in lowering some effective properties, such as  $T_g$ , elastic modulus, fracture strength, and high-temperature performance.

Another approach for toughening thermosets is to incorporate some liquid crystalline polymers (LCPs).<sup>5</sup> The LCPs can not only modify the low toughness and poor impact properties of epoxy resins but also have some advantages, such as high mechanical properties, low thermal expansion, and good properties at high temperature, which normally lack in the rubber toughening systems. Therefore, LCPs are good materials for toughening ER.

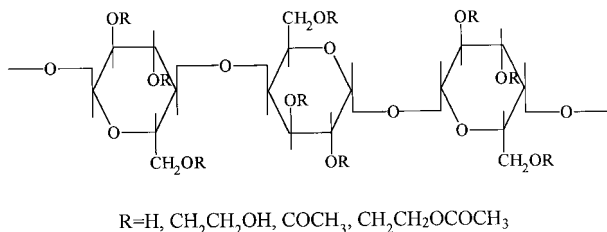
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Correspondence to: Y. Huang.

Cellulose and its derivatives are semirigid chain polymers and can form lyotropic liquid crystals in the appropriate solvents. Some of cellulose derivatives can also form thermotropic liquid crystals.<sup>6</sup> Thermotropic cellulose derivatives have a few of advantages, such as plentiful resources and biodegradability, which can not be substituted by synthetical LCPs. It has been reported that ethyl cellulose, which can form thermotropic liquid crystals, can be blended with thermoplastics and can form microfibers during extrusion. These microfibers can toughen polypropylene efficiently.<sup>7</sup> Hydroxyethyl cellulose acetate (HECA) is a thermotropic material, and the liquid crystalline phase can exist in the temperature region between 130–185°C.<sup>8</sup> In this report, toughening of epoxy resin blended with thermotropic hydroxyethyl cellulose acetate was studied, and the morphology and the mechanical properties of epoxy resin blended with HECA were also discussed.

## EXPERIMENTAL

HECA was prepared by esterification of hydroxyethyl cellulose (the degree of substitution for hydroxyethyl was about 1.5–1.8) with acetic anhydride catalyzed by  $ZnCl_2$ .<sup>8</sup> The degree of substitution for acetyl was dependent on the reaction time and the amount of catalyst and was measured by elemental analysis. The molecular weight of HECA, was measured by gel permeation chromatography (GPC) and calibrated by standard polystyrene,  $M_n$  was  $6.5 \times 10^4$ , and  $M_w$  was  $15.1 \times 10^4$ . The distribution of molecular weight  $M_w/M_n$  was 2.34. The degree of substitution for acetyl was calculated from the oxygen content of HECA, measured by elemental analysis. The molecular formula of HECA is as follows.



The diglycidyl ether of bisphenol A (DGEBA) with epoxy value of 0.48 (E-51, supplied by Guanhzhou Chemical Material Corporation, China) was used as a matrix material. The chem-

ically pure 4,4'-diaminodiphenylmethane (DDA) was used as the hardener. Other reagents used in this study were chemically pure and used without further purification.

The blends of DGEBA with HECA were prepared by solution casting using acetone as the solvent. The solvent was allowed to evaporate slowly at room temperature. The blends were dried in a vacuum oven at 60°C to remove the residual solvent. The epoxy resin blends were prepared by mixing preweighted HECA–DGEBA mixture and DDA (24 wt % with respect to the DGEBA) in the melted state at the curing temperature. The blends were cast into a polytetrafluoroethylene model to form a bar specimen. The specimen then was cured at a certain temperature for 6 h.

The miscibility of the HECA–DGEBA blends was studied by observing with an optical microscope (Leitz, ORTHOPLAN-POL). The cured bar specimen was polished to  $120 \times 10 \times 4$  mm impact specimen with a  $1 \times 1 \times 1$  mm cross-notch in the middle. The impact strength measurement was carried out on an impact strength test machine. All specimens were annealed for 2 h before measured.

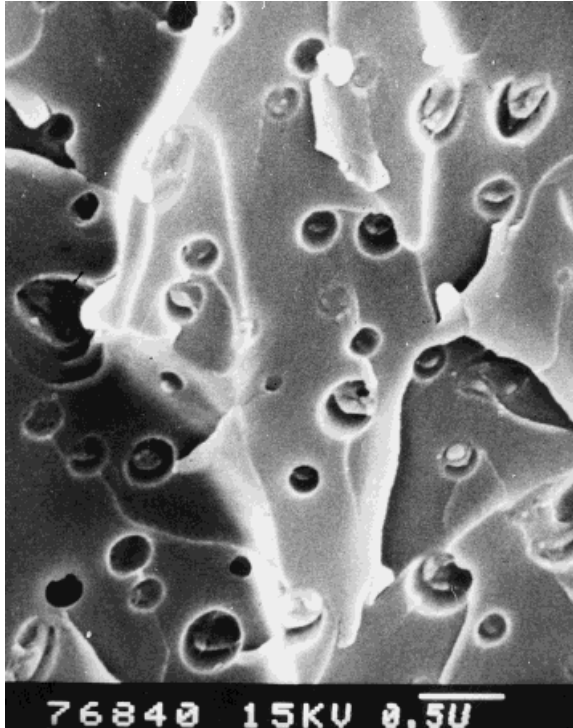
The fracture surface obtained in the impact strength measurements was observed by a scanning electron microscope (S-430, HITACHI, Japan) after being coated with a thin layer of gold.

## RESULTS AND DISCUSSION

HECA is a thermotropic material and can form liquid crystalline phase in the temperature region between 135–185°C. Uncured DGEBA is miscible with HECA over the whole composition range. All HECA–DGEBA blends are transparent and homogeneous by observing with an optical microscope. No phase separation is observed, and the miscibility of the DGEBA with HECA is not influenced by the variation of the DS for acetyl of HECA.

HECA becomes immiscible with epoxy resin after the DGEBA is cured. HECA is separated from the epoxy resin matrix during the curation and forms a second dispersing phase (as shown in Fig. 1). All cured epoxy resin–HECA blends are untransparent.

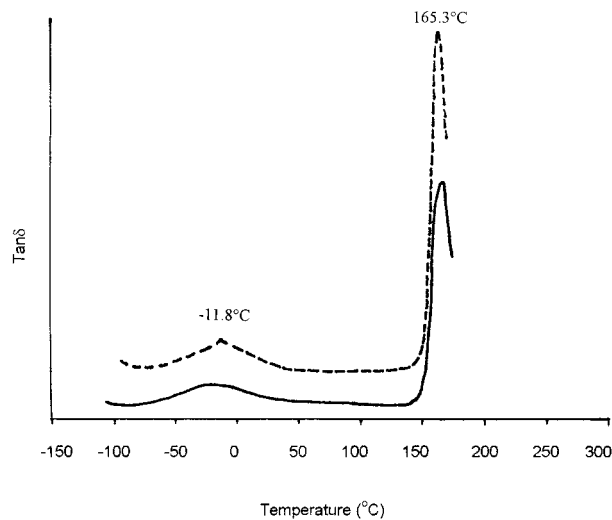
Figure 1 is a SEM micrograph of the fracture surface of epoxy resin–HECA blend. It clearly demonstrates that the HECA is immiscible with epoxy resin matrix after the epoxy resin–HECA



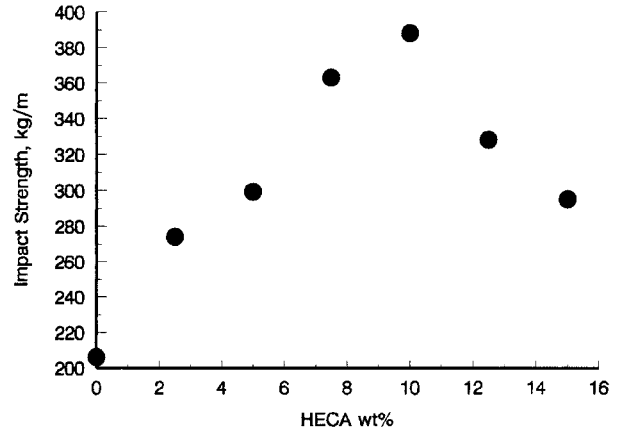
**Figure 1** Scanning electron microscopy micrograph of the fracture surface of epoxy resin-HECA blend (with 10 wt % HECA and cured at 150°C).

blend is cured and forms a second separated phase in the form of particles. The dimensions of the HECA particles that are dispersed in the epoxy resin matrix are in the range of 0.2–0.5  $\mu\text{m}$ .

Figure 2 shows the dynamic mechanical spec-



**Figure 2** Dynamic mechanical spectra of the HECA and the epoxy resin-HECA blend with 15 wt % HECA.

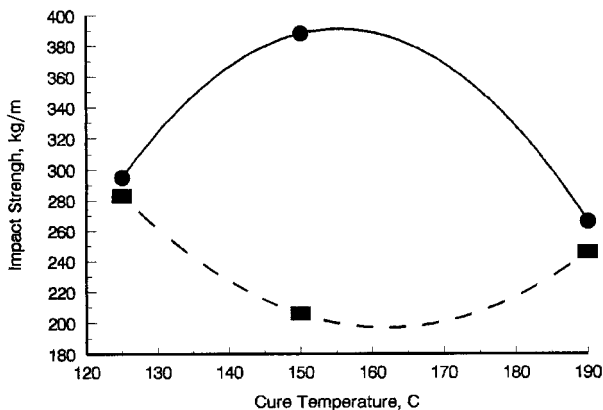


**Figure 3** The variation of the impact strength of the epoxy resin-HECA blends with the HECA composition in blends.

tra of epoxy resin-HECA blends. There are 2 peaks on the curves of  $\tan \delta$  versus temperature. The peak at 165°C is the  $\alpha$  transition of epoxy resin, which is the glass transition. The peak at -11.8°C is the  $\beta$  transition of epoxy resin. When HECA exists in the blends, 2 transition peaks of epoxy resin are unchanged in both position and shape. This indicates that the HECA is immiscible with epoxy resin.

Impact strength is one of important parameters to evaluate the mechanical properties of toughened materials. Figure 3 shows the impact strength of epoxy resin-HECA blends versus HECA composition. It shows that epoxy resin can be efficiently toughened by HECA. When the HECA composition is very small (2.5 wt %), the impact strength of the blend is increased by 33%, and it increases with an increase in the HECA composition. The impact strength of the blend becomes the maximum when the HECA composition is 10 wt % and then it decreases with a further increase in the HECA composition.

HECA can form the liquid crystalline state in the temperature region between 135–185°C, and, therefore, the HECA in blends may have different structures when the blends are cured at different temperatures. The toughening effect may be influenced by the structure of the dispersed phase. Figure 4 gives the curves of the impact strength versus the curing temperature for the epoxy resin-HECA blends and pure epoxy resin. It can be found that the variation of the impact strength for the blends with the curing temperature is different from that for pure epoxy resin. The impact strength increases first with increasing curing



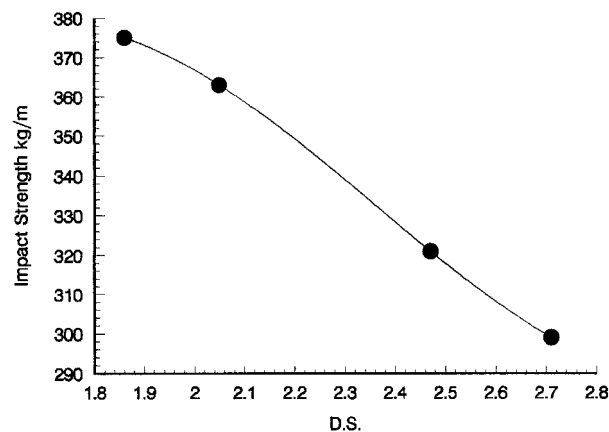
**Figure 4** The curves of the impact strength of the epoxy resin-HECA blends and of pure epoxy resin versus curing temperature.

temperature and then decreases when it reaches to the maximum value for the blends. For the pure epoxy resin, the impact strength decreases first with increasing curing temperature and then increases when it reaches to the minimum value. HECA exhibits the maximum toughening ability when the blend is cured at 150°C. HECA forms the liquid crystalline state at 150°C, and it is the solid state and the isotropic state at 120 and 190°C, respectively. When the liquid crystalline molecules are dissolved in DGEBA, phase separation occurs during the process of curing, and the liquid crystalline molecules can self-arrange and form the liquid crystalline phase in a certain way.<sup>9</sup> In the blends, the HECA is separated from the epoxy resin matrix and forms the particles with liquid crystalline structure when the blends are cured at 150°C. But the HECA can only form the isotropic phase particles when the blends are cured at 120 and 190°C. Consequently, the curves in Figure 4 suggest that HECA with the liquid crystalline state shows the best toughening behavior.

It has been reported that the composites with both the liquid crystalline order and the isotropic structure are more tough than those with only the isotropic structure and only the liquid crystalline order.<sup>10</sup> The HECA can transform from the liquid crystalline state to the isotropic fluid from 135 to 185°C, which is dependent on the molecular weight of HECA.<sup>8</sup> Those with low molecular weight transform to the isotropic phase at the lower temperature, and those with high molecular weight transform the isotropic fluid at the higher temperature. In the epoxy resin-HECA blends, when the curing temperature is 150°C,

the HECA separates from the epoxy resin matrix in the form of particles with 0.2–0.5  $\mu\text{m}$  in diameter during curing. In the HECA particles, the part with high molecular weight forms the liquid crystalline state, and the part with low molecular weight forms the isotropic structure. Consequently, there is a biphasic state in the HECA particles, which have a good toughening ability and act as crack stoppers and improve toughness of the material.

HECA with different DS for acetyl has different polarity and different liquid crystalline behavior. Therefore, the toughening ability of the HECA in blends is also influenced by the variation of the DS for acetyl of HECA. Figure 5 shows the influence of the DS for acetyl of HECA on the impact strength of epoxy resin-HECA blends and it demonstrates that the impact strength of epoxy resin-HECA blends decreases with increasing the DS for acetyl of HECA. The variation of the impact strength with the DS for acetyl of HECA may be due to the variation of molecular interactions and the variation of the chemical bonding between HECA chains and epoxy resin in blends with the DS for acetyl. As we know, the hydroxyl groups —OH can form hydrogen bonding with the carbonyl groups of C=O on polymer chains. There are 3 hydroxyl groups on polymer chains before esterification, and there is the strongest hydrogen bonding when the DS for acetyl is about 1.5 because one carbonyl group can form the strongest hydrogen bonding with one hydroxyl group. For the material of HECA, the degree of substitution for acetyl is changed from 1.8 to 2.8, and, consequently, the strength of hydrogen



**Figure 5** A plot of the impact strength of the epoxy resin-HECA blends (with 5 wt % HECA and cured at 150°C) versus the DS for acetyl of HECA.

bonding,  $—O—H \cdots O=C$ , decreases with increasing the DS for acetyl of HECA from 1.8 to 2.8. The stronger molecular interactions are of benefit to the formation of liquid crystalline phases.<sup>11</sup> It has been mentioned above that the HECA with the liquid crystalline state in blends has the maximum toughening ability. Therefore, the ability of the formation of the liquid crystalline phase decreases with increasing the DS for acetyl of HECA, which results in the decrease of the impact strength of the epoxy resin–HECA blends.

On the other hand, the free hydroxyl group  $—OH$  on HECA polymer chains may react with the epoxy groups on epoxy resin. More  $—OH$  groups can create more chemical linkages between HECA phase and epoxy resin matrix in their blends. Consequently, the impact strength of epoxy resin–HECA blends decreases with increasing the DS for acetyl of HECA because the number of the free hydroxyl group on HECA polymer chains decreases.

## CONCLUSIONS

Thermotropic HECA is totally miscible with epoxy resin before it is cured, and the miscibility is not influenced by the degree of substitution (DS) for acetyl of HECA. But HECA becomes immiscible with the epoxy resin matrix when it is cured with diamine (DDM), and the epoxy resin–HECA is a heterogeneous system after being cured, in which the HECA phase with the dimension of 0.2–0.5  $\mu\text{m}$  is dispersed in the epoxy resin phase. HECA can toughen epoxy resin efficiently and the impact strength of the epoxy resin/HECA blends is the maximum when the HECA composition is 10 wt %. The HECA with the liquid crystalline state has the better toughening ability

than that with the isotropic structure, and the impact strength is changed with the variation of the curing temperature. The toughening ability of the HECA in the blends is also influenced by the variation of the DS for acetyl of HECA, and the impact strength of epoxy resin–HECA blends decreases with an increase in the DS for acetyl of HECA.

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