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Modification of vinyl ester resin by a new thermoset liquid crystalline diacrylate

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Vinyl ester (VE) resins possess outstanding corrosion resistance and satisfy a critical requirement in fiber-reinforced plastic applications. However, VE resins are also brittle in nature and therefore, toughening has been an important topic for both scientists and engineers. Several techniques have been developed to improve the toughness of VE resins including (1) modifications of network structure via manipulation of VE molecular weight and styrene content, (2) use of reactive and non-reactive rubber modifiers designed for phase separation upon cure, and (3) use of nanostructured thermoplastic fiber mats for interlaminar toughening [1]. However, these techniques still have some limitations, for example, limited improvement of toughness is generally achieved by the first method, while great toughness can be obtained in rubber-toughened systems, but thermal resistance and modulus of original resins are also usually greatly reduced. The third method generally brings complex and difficult processing problems. Therefore, developing new toughening techniques for thermoset resins without sacrificing other positive properties of original thermosets has been an interesting and meaningful academic topic.

During the last decade, the research on liquid crystalline thermosets (LCTs) has accelerated because of the potential combination of the unique properties of liquid crystalline polymers and the excellent performance of thermosets. As compared to ordinary thermosets, crosslinked LCTs have a higher fracture toughness [2, 3]. The potential for using LCTs for toughening ordinary thermosets had been examined by some researchers [4, 5]; their results showed an improvement of fracture toughness, however, this research mainly focused on epoxy resins, and no similar investigation on the toughening of VE has been done so far. In this paper, a new thermoset liquid crystalline diacrylate (its molecular structure is shown in Fig. 1), ME, synthesized by our group [6] was used to modify a commercial VE resin based on bisphenol A epoxy resin, and the properties of the modified resins were studied.

Four ME modified VE systems with different ME contents (Table I) were prepared by mixing the appropriate weight of ME and VE at 90 °C by stirring until a transparent mixture was obtained. The mixture was cooled to about 60 °C, 1.5 phr dicumyl peroxide (DCP) and 0.5 phr benzoyl peroxide (BPO) were added and thoroughly stirred till DCP and BPO were completely dissolved in the mixture. The resultant mixture was cast into a clean pre-heated mold for curing per the procedure of 60 °C/2 hrs + 80 °C/2 hrs + 100 °C/2 hrs + 120 °C/2 hrs + 140 °C/2 hrs + 170 °C/2 hrs.

Fig. 2 is the typical DSC curves of VE and VE/ME2 samples; the addition of ME tends to shift the curing temperatures from 113–197 to 128–203 °C. The reason for this change is that (1) VE has a higher styrene content than VE/ME2, moreover, the molecular weight of ME2 is higher than that of VE, so the reactive double bond content per weight in the VE system is higher than that in the VE/ME2 system, resulting in the former having a lower curing temperature than the latter.

As stated above, the main target of this study is to investigate the toughening effect of ME on VE resin, therefore, the toughness of the modified resins and original VE resin, which can be manifested by the impact strength and plain strain critical-stress intensity factor (K_{IC}), is the first property to be studied. The influences of ME and its content on the impact strength are plotted in Fig. 3. The impact strength of VE/ME initially increases with the increase of the ME content, and reaches the highest value when the ME content is 20%; after that, an increase in the ME content causes the impact strength to decrease. In the case of VE/ME2, the impact strength is 7.1 kJ/m^2, about 71% higher than that of VE. The effect of ME content on K_{IC} of modified resins has a similar trend (Fig. 4), indicating that ME is an effective toughener of VE, and the optimum ME content is again 20%. In the remaining part of this letter, VE/ME2 is chosen as the optimum system for the following evaluations.

It is known that the biggest disadvantage of rubber modifiers is that they greatly improve the toughness of brittle resins, but also sharply decrease the thermal property and modulus of original resins, therefore, it is necessary to study the effect of ME on the thermal

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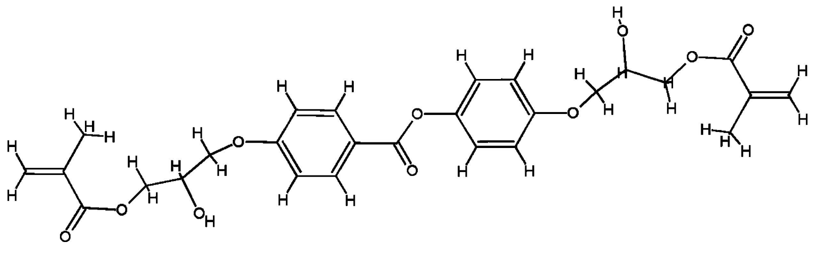

Figure 1 Molecular structure of ME.

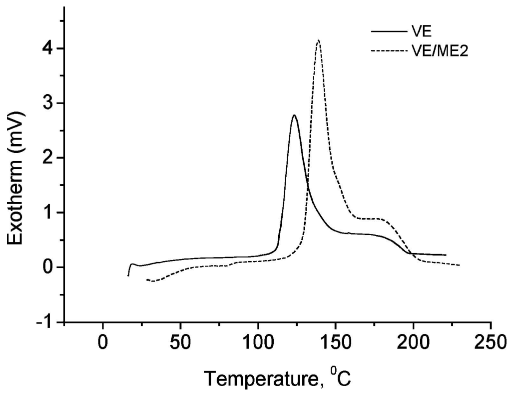

Figure 2 DSC curves of VE and VE/ME2 (at 10 °C/min in nitrogen).

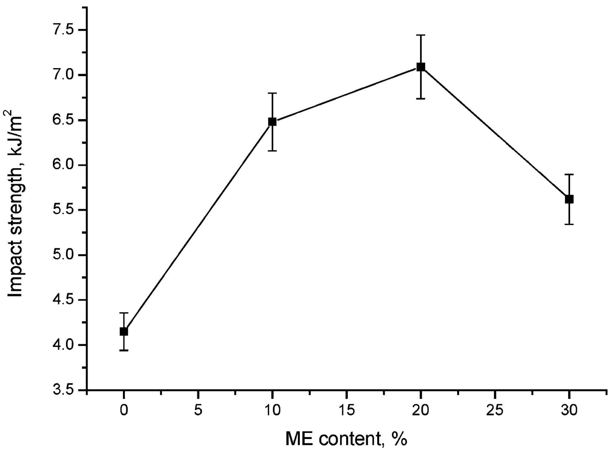

Figure 3 Influence of ME content on the impact strength of modified resins.

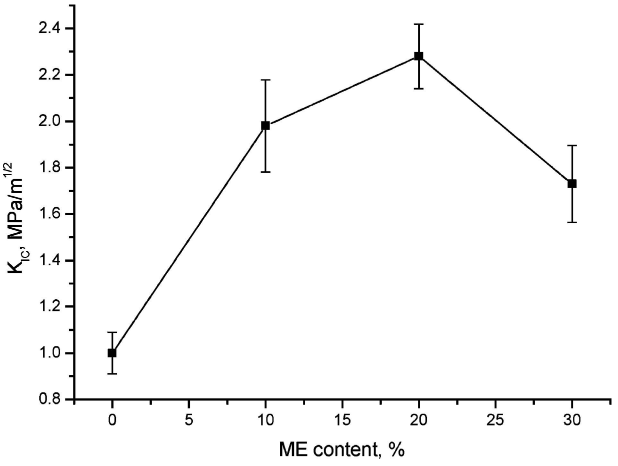

Figure 4 Influence of ME content on K_{IC} of modified resins.

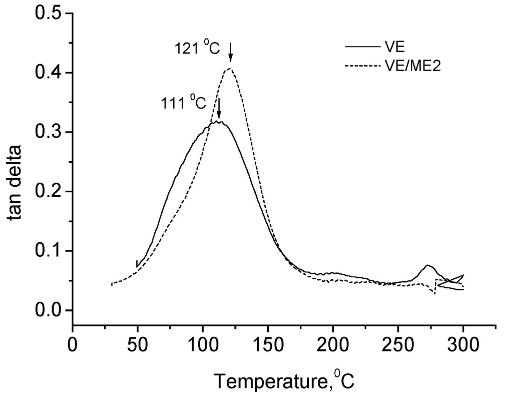

Figure 5 Overlay tan delta as a function of temperature for VE and VE/ME2.

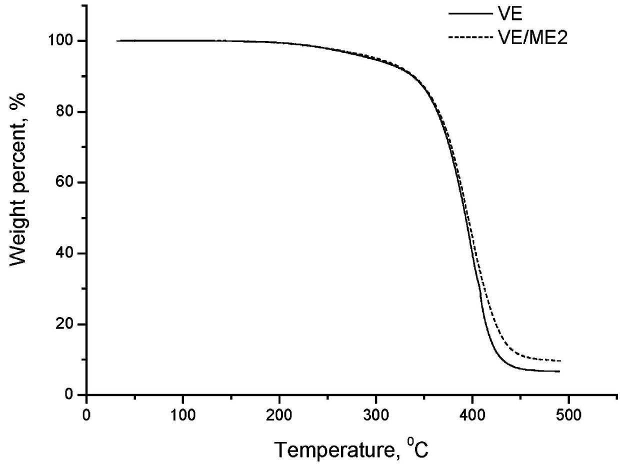

Figure 6 TGA plots of VE and VE/ME2 (at 10 °C/min in nitrogen).

property and modulus of VE resin. Glass transition temperature (T_g) of samples was detected by the dynamic mechanical analysis (DMA) method which can be taken as the maximum of the curve tan delta versus temperature, as shown in Fig. 5. It can be seen that the T_g value of VE/ME2 is 121 °C, which is 10 °C higher than that of pure VE resin. Since the glass transition process is considered to be affected by molecular packing, chain rigidity and linearity [7], the increase in T_g of the modified system in comparison with original VE resin can be attributed to the rigidity of ME2.

TABLE I Formulations of VE/ME systems

	VE	VE/ME1	VE/ME2	VE/ME3
VE content (%)	100	10	20	30
ME content (%)	0	90	80	70

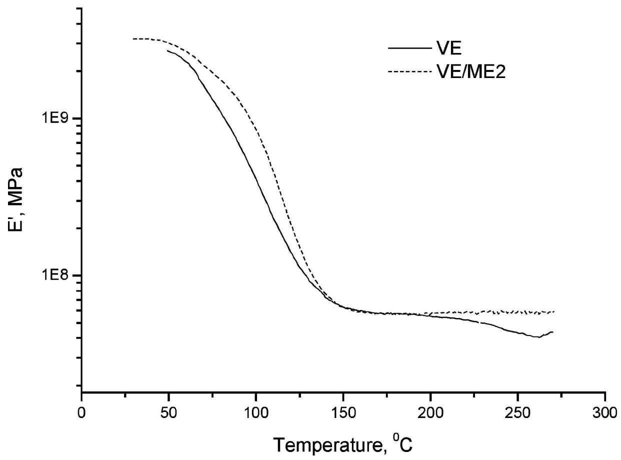

Figure 7 Overlay storage moduli (E') as a function of temperature for VE and VE/ME2.

Fig. 6 shows the thermogravimetric analysis (TGA) curves of VE and VE/ME2, the initial degradation temperature of VE/ME2 is about 4 °C higher than pristine VE resin; moreover, VE has a somewhat higher degradation rate and char yield than VE/ME2, suggesting that VE/ME2 has a slightly better thermal stability.

The overlay storage moduli (E') as a function of temperature for VE and VE/ME2 are plotted in Fig. 7. The VE/ME2 shows higher values of E' over the entire temperature range of study, suggesting that the incorporation of ME into VE does not reduce the modulus of original VE.

From the viewpoint of molecular structure, the intensity of the damping peak reflects the rigidity of materials. The intensity of the damping peak of VE/ME2 is higher than that of VE, meaning that the incorporation of ME tends to increase the rigidity of the cured structure, which is also in accordance with the trends of the increases of T_g and E' in Figs 5 and 7, respectively.

Based on the above investigations, it can be concluded that relatively small amounts of ME can be used as an effective additive to improve the toughness of VE as well as the thermal property and modulus.

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