On polyetherimide modified bismaleimide resins, 1

Effect of the chemical backbone of polyetherimide

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SUMMARY: Four kinds of polyetherimides with different diamines were prepared and used to improve the toughness of bismaleimide resins composed of bis(4-maleimidophenyl)methane and \( \text{o,o} \)-diallyl bisphenol A. Dynamic mechanical analysis and scanning electron microscopy were used to characterize the phase structure of the modified resins. The modified resins display different phase morphologies depending on the polyetherimide backbone structure. The results indicate that the degree of phase separation leads to different morphologies and toughening. The fracture energy \( (G_c) \) was increased by 300% with the PIM modified system.
**Experimental part**

The bismaleimide resin is composed of bis(4-maleimidodiphenyl)methane (BDM) (Hubei fenguang chemical factory) and o,o'-diallyl bisphenol A (DBA) (Jiangyou electric engineering material factory) (Scheme 1).

Four different diamines were used to synthesize the polyetherimide. 2,2-Bis[4-(4-aminophenoxy)phenyl]bisaniline (BAPP) (CHRISKEV CO.) and 4,4'-oxydianiline (ODA) (Shanghai Research Institute of Synthetic Resin) were used without further purification. 4,4'-[1,4-Phenylenebis(1-methylethylidene)]bisaniline (BISP) and 4,4'-[1,3-phenylenebis(1-methylethylidene)]bisaniline (BISM) were synthesized in our laboratory.

Scheme 1: (a) Structure of bis(4-maleimidodiphenyl)methane (BDM), (b) structure for o,o'-diallyl bisphenol A (DBA)

The polyetherimide (PEI) was synthesized by one step from bisphenol A dianhydride (BISA-DA) and four diamines, respectively, in m-cresol at 200°C for 6 h. The calculated mole ratios of diamine and dianhydride were applied in the polyetherimide synthesis in order that the obtained amino-terminated polyetherimides are theoretically equal in the number-average molecular weight. The four polyetherimides with different diamines are designated as PIP, PIM, PIB and PIO corresponding to the different diamines BISP, BISM, BAPP and ODA, respectively (Scheme 2). Although the amino group takes part in the cure reaction, the low amount of end group will have little influence on the chemistry of the network formation. The inherent viscosity is characterized at 0.5 g/dL concentration in 1-methyl-2-pyrrolidone solvent at 30°C. The characteristics of polyetherimides used in this work are listed in Tab. 1.

Each kind of PEI 15 phr (per hundred of BMI resin) was dissolved in DBA by heating at 160°C. Then, the mixture was cooled to 150°C and BDM was added to the mixture. It was kept stirring during the dissolving process. The resulting clean mixture was degassed in vacuo and poured into mould, preheated at 150°C, to obtain 3 mm thick plaque. The ratio of DBA to BDM was kept at 43:57 parts by weight (0.85:1 mole ratio). The curing cycle was 160°C/2 h + 185°C/2 h + 230°C/2 h.

The fracture surface morphology of the blend cured for 5 h at 185°C was observed under the scanning electron microscope (SEM) (HITACHI S-520). The samples were fractured in liquid nitrogen.

The glass transition temperatures of PEIs were determined by SETARAM differential scanning calorimetry (DSC) instrument from room temperature to 350°C at a heating rate of 10°C/min.

The PEIs densities were determined by the water displacement method of ASTM D792.

Dynamic mechanical analysis was made in the dual-cantilever bending mode between 50°C and 350°C using a NETZSC H DMA 242 apparatus at a heating rate of 3°C/min and a frequency of 10 Hz.

Fracture toughness was measured by using the double torsion (DT) method at room temperature in compressive mode with a cross head speed of 0.5 mm/min according to ASTM E-399. The fracture toughness $G_{IC}$ was calculated from the following equation with the assumption of Poisson ratio of BMI resin 0.35.

$$G_{IC} = K_{IC}^2 \times \frac{1 - \nu^2}{E}$$
Results and discussion

Dynamic mechanical analysis

DMA is a sensitive method in exploring the phase structure of polymer blends (13). Dynamic mechanical data of four kinds of pure polyetherimide and the neat BMI resin are given in Fig. 1. The pure polyetherimides give their main loss peak corresponding to their glass transition temperature ($T_g$) with the range from 195°C to 222°C depending on their backbone structures. The glass transition temperatures of the four kinds of PEIs were listed in Tab. 1. Due to the crosslinking of the thermosetting resin, the thermosetting BMI resin has a broader relaxation peak than thermoplastic polyetherimides. After being modified with polyetherimides, the modified BMI resins display complicate tanδ curves in Fig. 2. All modified resins show two relaxation peaks or shoulders corresponding to the $\alpha$ relaxation transition of the two blend components, whereas the unmodified BMI resin gives only one tanδ peak at 292.8°C. One peak is attributed to the BMI rich phase ($\beta$ phase) at higher temperature; the other one is the polyetherimide rich phase ($\alpha$ phase) at lower temperature. Such a result clearly indicates that the phase separation has occurred during the curing process in the modified resin. By the way, DSC measurement was also performed to test the glass transition temperature of the cured resin. However, the $T_g$ of the blend components was calorimetrically undetectable; for PEI it is probably due to its low concentration in the blends; for BMI resin due to its highly crosslink density.

Tab. 2 gives the comparison of the main loss peak of the PEI modified systems. The $\alpha$ relaxation temperature ($T_\alpha$) of the BMI rich phase all shifted to higher temperature compared with the unmodified system except the PIM system. Whereas, for the $\alpha$ relaxation temperature ($T_\alpha$) of the PEI rich phase, there exists a different change in the four blends. In the PIP and PIB modified systems, the $\alpha$ relaxation temperature ($T_\alpha$) of the PEI rich phase shifts to lower temperature compared with pure PIP and PIB. In the PIM system, the main loss peak of the PIM rich phase doesn’t change much compared with pure PIM. The tanδ peak corresponding to the PIO rich phase is so broad that it is difficult to distinguish the peak position. The decrease of the relaxation temperature of the PEI rich phase can be attributed to the remaining low
molar mass DBA dissolved in the PEI rich phase, acting, therefore, as plasticizer.

Comparing the tanδ peak of these four kinds of the PEI modified systems (Fig. 2, Tab. 2), it is clearly shown that both the peak magnitude of the PEI rich phase (H98) and BMI rich phase (H97) in the PIP and PIM modified systems are higher than that of the PIB and PIO modified systems. The higher magnitude of the α relaxation would be due to the higher mobility of the matrices (α and β phase). On the other hand, the α relaxation peaks corresponding to the PIP and PIM modified systems are broader than that of the neat BMI resin. The broadness of the α relaxation indicates the complexity of the matrix structure existing in the phase separated systems. Contrarily, the α relaxation peaks of the BMI rich phases in the PIO and PIB modified systems are lower and sharper than that of the neat BMI resin. This means that the BMI rich matrix has a lower mobility and relatively simple phase structure. The different α relaxation behavior of four PEI modified BMI resins may associate with the phase separation. The mobility and complexity of the matrix are results of the formation of the different morphologies. From this view, the degree of phase separation in the PIM system and the PIP system is higher than in the PIB and PIO systems. Although the DMA results can give the inference, the scanning electron microscope can identify the morphologies of modified resins.

**Morphology**

Fig. 3a shows the fracture surface of unmodified BMI resin by scanning electron microscopy. The neat resin has only one phase and the fracture surface is smooth and featureless. Fig. 3b–3e provide clear evidence that incorporation of PEI into the BMI resin leads to a two-phase morphology. The morphologies of the cured modified resins change drastically, depending on the PEI backbone chemistry. When using 15 phr of PIM polyetherimide in the BMI resin, full phase inversion was observed (Fig. 3b) with the BMI spherical particles dispersed in the PIM rich matrix. The size of the BMI spherical particle is uniform and is about 15 μm in diameter. In the PIP modified system, two-phase structure was found which corresponds to the BMI rich phase (dark part) and the PIP rich phase (gray white part) (Fig. 3c), respectively. In the
BMI rich phase, the fracture surface is very smooth and PIP domain can be hardly found. In the PIP rich phase, a large amount of BMI matrix is incorporated. This kind of morphology may imply the co-continuous phase structure. To the case of PIB modified systems (Fig. 3d), the morphology is also a co-continuous phase structure. The gray part and dark part corresponds to the PIB rich phase and BMI rich phase, respectively. However, compared with the PIP system, the difference between the two separated phases is not obvious. The morphology of the PIO modified system (Fig. 3e) is not easy to identify. The PIO rich phase is not clear to be observed in the SEM graph.

The above results show that the chemical backbone of polyetherimide strongly affect the phase morphologies of modified BMI resins. The SEM graphs also indicate the difference in the degree of phase separation, where the PIM and PIP polyetherimides cause the phase separation to progress more complete than that of the PIO and PIB modified resins.

**Mechanical properties of modified BMI resins**

From Tab. 3, we can see that the toughening effects in PIM and PIP modified systems are obvious. The $G_{IC}$ values of the PIM and PIP modified systems are nearly three times larger than the neat resin. The modulus of the modified systems are slightly decreased. Obviously, co-continuous or phase-inverted structure is favored to achieve a good toughening effect. It is in good agreement with previous reports. Combining with the DMA and SEM discussions, the phenomenon is observed that the degree of phase separation is associated with the good toughening effect. The high degree of phase separation is a prerequisite to get co-continuous or inverted phase structures, which lead to a good toughening effect.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E$(GPa)</th>
<th>$K_{IC}$/(MPa·m$^{1/2}$)</th>
<th>$G_{IC}$/(J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure BMI resin</td>
<td>3.940</td>
<td>0.970</td>
<td>210.0</td>
</tr>
<tr>
<td>PIM modified</td>
<td>3.567</td>
<td>1.638</td>
<td>667.5</td>
</tr>
<tr>
<td>PIP modified</td>
<td>3.432</td>
<td>1.624</td>
<td>616.3</td>
</tr>
<tr>
<td>PIO modified</td>
<td>3.470</td>
<td>1.110</td>
<td>223.0</td>
</tr>
</tbody>
</table>

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