The Effect of Reactive Aromatic Hyperbranched Polyester on the Properties of Unsaturated Polyester

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Abstract
The aim of this study was to improve the toughness of UPE resin by using an aromatic hyperbranched polyester. The aromatic hyperbranched polyester (HBP) was synthesized and the end-group of the polymer was modified to methacrylate-terminated hyperbranched polyester (MA-HBP). We characterized HBP and the resulting MA-HBP using $^1$H-NMR and DSC. MA-HBP, up to 5 phr, was blended with UPE. The glass transition temperature was not affected by the addition of MA-HBP, but the thermal stabilities of UPE blended with MA-HBP increased. It was found that the fracture toughness of UPE blended with MA-HBP increased by about 25%, as MA-HBP was added up to 3 phr. It slightly decreased with the further addition of MA-HBP to 5 phr.

1. Introduction
Hyperbranched polymers have recently received considerable attention due to their unique highly branched structure.\textsuperscript{1-3} Because of their architecture, these polymers have such attractive properties as low viscosity and excellent solubility. Aliphatic hyperbranched polyester with different degrees of branching and functionality were investigated as tougheners for epoxy resins by Boogh in 1999.\textsuperscript{4} Unsaturated polyester resins (UPE) widely used as thermoset matrix for glass fiber reinforced composites have such advantages as low cost, case of processing, and compatibility with fillers and reinforcements. However, as generally found for thermosetting materials, these matrices are very brittle and susceptible to failure. Moreover, the shrinkage of the UPE during crosslinking with the reactive styrene leads to warpage and cracking. In order to solve these problems, several attempts have been made using various incompatible additives such as carboxylic or hydroxyl-terminated rubbers, either blended or reacted with the resin. The compatible reactive liquid polymers based on flexible polyester resins have been also tried.\textsuperscript{5} In this work, we synthesized aromatic hyperbranched polyester (HBP), modified the end-group of the polymer to reactive end-group, and used the end-group modified HBP to improve the fracture toughness of UPE.

2. Experimental
15g of 5-acetoxyisophthalic acid was placed in a three-neck flask with a mechanical stirrer, a gas inlet and an outlet. The polycondensation was done in two steps. First, the reaction mixture was stirred in a nitrogen stream for 20 min at 250 °C. In second step, vacuum was applied and the reaction proceeded until stirring was not possible. The product was refluxed with THF/H$_2$O mixture for 4 h. The solution was precipitated into methanol, filtered and
dried in an vacuum oven at 60°C. 2g of the carboxylic acid-terminated hyperbranched polymer (CA-HBP) synthesized above was dissolved in 100mL of dry THF. Thionyl chloride (2 ml, ca. 0.02 mol) and 3 drops of DMF were added to the THF solution. The reaction mixture was refluxed for 6 h. After 6 h, the excess of thionyl chloride and solvent were removed by rotary evaporation. The product was redissolved in 70mL of dry THF and placed in the ice-bath of 0°C. Dry THF solution of 2-hydroxyethyl methacrylate (0.02 mol) and triethylamine (0.02mol) was added slowly to the THF solution of product under nitrogen. The precipitation of triethylammonium chloride salt was observed. The mixture was stirred at room temperature overnight, filtered, and then precipitated into petroleum ether. Methacrylate-terminated hyperbranched polyester (MA-HBP) was dried under vacuum at room temperature. Unsaturated polyester (R-280) was purchased from Sewon Chemical Co., Ltd. Unsaturated polyester was mixed with 0, 1, 3, and 5 parts per hundred parts of resin (phr) of MA-HBP. The cure was carried out at this temperature for 2 h and then for an additional 3 h at 120°C.

3. Result and Discussion

Our goal is to investigate to synthesis of the reactive functionalized aromatic hyperbranched polyester and its application to toughening additives of UPE resin. CA-HBP was synthesized with a melt polycondensation of 5-acetoxyisophthalic acid which was prepared by means of acetylation of 5-hydroxyisophthalic acid with an acetic anhydride. To convert the carboxylic acid end group to acid chloride end-group, CA-HBP was reacted with thionyl chloride. The acid chloride end-groups of aromatic hyperbranched polyester were then modified with 2-hydroxyethyl methacrylate to give the reactive functional end-groups. The polymerization and functionalization schemes are described in Scheme 1.

![Scheme 1](image-url)

The structures of synthesized polymers were confirmed by $^1$H-NMR spectroscopy measurements. $^1$H-NMR spectra of CA-HBP and MA-HBP were shown in Figure 2 and 3. In Figure 2, a multiple peak around 7.6–8.8ppm assigned to aromatic protons were observed. Broad proton peaks from carboxylic acid was observed at 13.5ppm The peak at 2.33ppm was attributed to the proton from methyl group at the focal point of HBP. In Figure 3, broad multiple peaks for aromatic protons were observed around 7.5–8.5ppm. The peaks at 4.44 and 4.58ppm were attributed to the protons from ethyl groups of end-groups. The two proton peaks from double bonds and one proton peak from the methyl group on the double bond were observed at 5.68, 6.0 and 1.9ppm respectively.

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Our objective of preparing MA-HBP was to investigate its use as a reactive additive for unsaturated polyester to improve the toughness properties. Since the reactive functional end-groups of MA-HBP can be reacted with UPE resin and styrene, and MA-HBP can be soluble in UPE resin without solvents, they were ideal for blend studies. MA-HBP was found to be able to form homogeneous and transparent solution of UPE resin at room temperature. The glass transition temperature of CA-HBP determined using DSC method was found to be 192.4°C. The DSC scan of MA-HBP showed a $T_g$ at 67.36°C and an exotherm with a peak temperature of 161.52°C. It can be said that this exotherm is attributed to the reaction between the double bonds at the end-groups of HBP. It was found that after DSC measurement, MA-HBP changed into yellow glass-like which is insoluble in THF. $T_g$'s of blends did not change significantly from that of pure UPE. The addition of 5 phr of MA-HBP to UPE resin was found to improve its 10wt.-% weight loss temperature($T_d$) by about 10°C. The thermal properties of UPE with a different amount of MA-HBP were shown in Table 1. The effect of MA-HBP on the mechanical properties of UPE blends was studied using UTM. The tensile strength and Young's moduli of all the cured UPE samples are shown in Figure 4. In figure 5, the fracture toughness properties expressed in terms of the stress intensity factor $K_{IC}$ and elongation at break of UPE blended with MA-HBP were shown. As increasing the content of MA-HBP in UPE resin, the tensile strength was increased but Young's moduli were decreased. The fracture toughness($K_{IC}$) of specimens increased from 19.7 MPa.m$^{1/2}$ to 26.8 MPa.m$^{1/2}$ as the content of MA-HBP increased from 0 phr to 3 phr, and it slightly decreased to 24.6 MPa.m$^{1/2}$ with the further addition of MA-HBP to 5 phr. It is evident from the results that the addition of MA-HBP improved the toughness of the UPE resin.

Table 1. Thermal Properties of UPE blended with HBP

<table>
<thead>
<tr>
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<th>$T_g$ (°C)</th>
<th>$T_d$ (°C)</th>
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<tbody>
<tr>
<td>UPE</td>
<td>134.1</td>
<td>360.7</td>
</tr>
<tr>
<td>MA-HBP-1phr</td>
<td>135.9</td>
<td>363.0</td>
</tr>
<tr>
<td>MA-HBP-3phr</td>
<td>134.6</td>
<td>369.1</td>
</tr>
<tr>
<td>MA-HBP-5phr</td>
<td>137.8</td>
<td>370.0</td>
</tr>
</tbody>
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a. glass transition temperature measured by DMA
b. 10wt.-% weight loss temperature
Figure 5. Young’s modulus and tensile strength of UPE blended with MA–HBP

Figure 4. Toughness properties expressed in terms of the stress intensity factor $K_I$ and the elongation at break of UPE blended with MA–HBP

4. Conclusion
An aromatic hyperbranched polyester (HBP) was synthesized and the carboxylic acid end-group of HBP was modified to methacrylate-terminated hyperbranched polyester (MA–HBP). MA–HBP was blended with UPE to improve the toughness of cured UPE. The tensile strength and fracture toughness increased with the addition of MA–HBP, but the moduli of UPE/MA–HBP blends decreased.

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References