Free-radical melt grafting of the multi-monomer system of maleic anhydride (MAH)/styrene (St) onto polypropylene (PP) was carried out using a single-screw extruder in the first step. Then melt mixing method was employed to prepare two types of blends, polypropylene(PP)/hyperbranched poly(amide-ester)(HBP) and maleic anhydride grafted polypropylene [PP-g-(MAH-co-St)]/HBP blends. The processability and compatibility of the two blends were investigated as a function of HBP added. Through processing and rheological studies, the results showed that HBP was an effective processing additive. The melt viscosity of the PP/HBP blends dropped in proportion to the amounts of HBP added, and melt viscosity of the PP-g-(MAH-co-St)/HBP blends decreased by the addition of up to 7 %wt HBP, after which the blend viscosity remained essentially constant. Characterization including scanning electron microscopy (SEM), differential scanning calorimetry (DSC,) and Fourier transform infrared spectroscopy (FTIR) data indicated that the HBP formed immiscible blends with PP. A significant degree of compatibilization occurred in the systems of [PP-g-(MAH-co-St)]/HBP, which is evident by shifts in the thermal transitions of the HBP phase and by morphology refinement observed by scanning electron microscopy.

INTRODUCTION

Hyperbranched polymers (HBPs) have attracted considerable and extensive attentions for their potential applications in various fields from drug-delivery to coating in recent years [1]. Compared with dendrimers obtained from multistep synthesis [2], HBPs are more advantageous as they can be easily synthesized through one-pot polymerization process [3,4]. They are highly branched macromolecules with three-dimensional dendritic architecture [1]. Due to their compact and three-dimensional structures, there are two properties of low viscosity and high reactivity which make them to be utilized in improvement of both processability and toughness of thermoset resins.
through a controlled reactive phase separation process [5-8].

There have been several studies on hyperbranched polymer/thermoplastic blends. Kim et al. [9] have blended hyperbranched polyphenylene with polystyrene and found a remarkable reduction in melt viscosity (up to 80%) and the shear induced degradation for a blend consisting of polystyrene and 5 %wt of hyperbranched polyphenylene. However, the thermal stability is improved while the mechanical blend properties have remained unaffected. In the tubular blowing process of linear low-density polyethylene (LLDPE) the Boltorn TM-H30 hyperbranched polyester successfully acted as a processing aid and sharkskin was eliminated with no significant influence on other physical properties of the LLDPE film [10]. The dyeability of PP with CI.Disperse Blue 56 could be markedly enhanced through the incorporation of hyperbranched macromolecules such as the Hybrance PS2550 (hyperbranched polyester-amide) into polypropylene (PP) prior to fibre spinning [11]. The amphiphilic hyperbranched aromatic polyester with end group dodecanoyl chloride could also be used as a dye carrier in blends of PP or high-density polyethylene (HDPE), with similar dynamic-mechanical behaviour of the blends compared to that of the pure polyolefins [12].

In this work, maleic anhydride (MAH)/styrene (St) grafted PP [PP-g-(MAH-co-St)] was first obtained by reactive extrusion, and then the [PP-g-(MAH-co-St)]/HBP and PP/HBP blends were prepared. Using a rheometer was an assessment of the benefits in processability resulting from the addition of hyperbranched poly(amide-ester). Furthermore SEM and DSC were employed to evaluate the extent of compatibilization achieved in the [PP-g-(MAH-co-St)]/HBP blends and its influence on morphology of the blends.

EXPERIMENTAL

Materials
Isotactic polypropylene (i-PP) (Mw = 26000 g/mol), with the MFI (melt flow index) of 3.5 g/10 min was purchased from Daqing Petroleum Chemical Corp. (Daqing, China). MAH/St grafted PP [PP-g-(MAH-co-St)] was prepared in a single-screw extruder (Φ=30 mm, L/D = 25). The PP pellets, monomer maleic anhydride (2.0 %wt), monomer styrene (2.0 %wt), and initiator dicumyl peroxide (0.1 %wt) were blended before they were charged into the extruder. The temperature of the cylinder was set at 180-210°C and the screw speed was fixed at 20 rpm. The grafted PP sample was dissolved in refluxing xylene at a concentration of 1.2 %(wt/vol) and excess acetone was then added to precipitate them. Acetone could precipitate only the grafted and ungrafted PP, while the homo- and copolymer of MAH and St were separated.

Elemental analysis showed that the extrudate after purification process contained 1.19 %wt maleic anhydride (MAH). The reason for adding styrene monomer was the very low grafting degree of MAH in free-radical grafting system of MAH with PP in the absence of St. It is because of the low reactivity of MAH toward radical reaction. When St was added, it reacted with MAH to form St-co-MAH copolymer during the melt-grafting process and the grafting of St-co-MAH led to improving the grafting degree of MAH. The main grafting reaction in the system was the grafting of St-co-MAH to PP as molar ratio of MAH to St was approximately 1:1, and grafting degree of the grafted PP was the highest.

The hyperbranched poly(amide-ester) molecules were synthesized from diethanolamine and succinic anhydride [13], with 24-OH terminated end groups per molecule on average. The number average molecular weight (Mn) obtained by vapour pressure osmometry was 7800 g/mol, and the polydispersity was 2.08 measured by size exclusion chromatography. The glass transition temperature (Tg) was 17.3°C and the HBP was thermally unstable above 200°C because of its degradation as determined by thermo-gravimetric analysis. Other additives were commercial products. Figure 1 shows schematic structure of hyperbranched poly(amide-ester).

In blends formation of PP-g-(MAH-co-St)/HBP studied here, a ring opening reaction took place between the PP-g-(MAH-co-St) and the -OH functional groups on the HBP, generating an acid and an ester functionality (Figure 2). Covalent bonds were thus formed between the two polymer molecules generating copolymer compatibilizers.

Blend Preparation
PP and HBP were melt mixed using a twin-roll mill for 10 min at temperature 180°C. The prepared blends were
compressed into sheets with a hydraulic press at 180°C and 10 MPa for 4 min. The content of HBP was set as 0, 3, 7, and 12 %wt and the acquired materials were defined as PP, PP3, PP7, and PP12, respectively. The PP-g-(MAH-co-St) and HBP were melt mixed by the same procedure as above and the corresponding materials were named as PPM, PPM3, PPM7 and PPM12.

For each of the blends prepared, the number of functional groups on the PP, PP-g-(MAH-co-St), and HBP for a given mass of polymer along with the ratio of reactive groups are presented in Table1. There were less MAH functional groups relative to HBP hydroxyl functional groups in PPM7 and PPM12 blends, whereas the MAH/-OH ratio of PPM3 blend was near unity.

Rheological Measurements
The melt viscosity of all blends was measured by using a high-pressure capillary rheometer XLY-1 with a capillary die of 1mm, and L/D ratio of 40. The experimental temperature was fixed at 180°C with experimental loads of 220, 200, 180, 160, 140, and 120 kg/cm². Measurements for the corrections turned out to be unnecessary.

Table1. Estimated ratio of reactive groups in blends.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>HBP(wt%)</th>
<th>MAH/-OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPM</td>
<td>3</td>
<td>1.28</td>
</tr>
<tr>
<td>PPM</td>
<td>7</td>
<td>0.55</td>
</tr>
<tr>
<td>PPM</td>
<td>12</td>
<td>0.32</td>
</tr>
<tr>
<td>PP</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>PP</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>PP</td>
<td>12</td>
<td>0</td>
</tr>
</tbody>
</table>

Morphology
Samples were prepared by freezing the pieces of strands in liquid nitrogen followed by high-speed impact to create fresh fracture surfaces. To improve the contrast for image analysis, the HBP minor phase was extracted using distilled water at room temperature, under continuous stirring for 48 h. The surfaces were covered with gold before observations, using a surface sputter coater model SBC-12. A scanning electron microscopy (SEM) (Tracer Northen Company, KYKY-2800B) operated at an accelerating voltage of 25 kV was used to observe the morphology of the samples.

DSC Measurement
Thermal properties were measured by a differential scanning calorimeter (Mettler TA 4000 Model). Samples were heated to 200°C and cooled down to room temperature at a rate of 20°C/min. The glass transition temperature (T_g) was measured during the subsequent second heating cycle at a heating rate of 10°C/min. The DSC cell was purged with ultra pure nitrogen gas at a constant flow rate 60 mL/min for preventing sample degradation.

FTIR
The pure polymers and blends obtained were hot-pressed under 190°C into a piece of thin film and analyzed by FTIR. The FTIR spectra were recorded on a Nicolet Avatar-330 FTIR spectrometer.

Measurements of Mechanical Properties of Blends
The test specimens were shaped with a universal clipper.
Tensile strength measurements were performed according to GB1843 test method using dumb-bell shaped test specimens on a tensile test machine (LJ-5000N) and a cross-head speed of 10 mm/min. The testing was conducted at room temperature. Values were an average of five tests.

RESULTS AND DISCUSSION

Analysis of PP-g-(MAH-co-St) by FTIR
The FTIR spectra of pure PP and PP-g-(MAH-co-St) are shown in Figure 3. The absorption band at 2723 cm\(^{-1}\) could be assigned to a PP skeleton characteristic. The absorption bands at 1785 cm\(^{-1}\), 1856 cm\(^{-1}\), and 704 cm\(^{-1}\) in the spectrum of PP-g-(MAH-co-St) were characteristic of the carbonyl group in maleic anhydride and the benzene ring in styrene, respectively. Therefore it was confirmed that both maleic anhydride and styrene were grafted onto polypropylene backbone. It was also assumed that grafted MAH in the samples was in a cyclic form, because no peak was found at 1715 cm\(^{-1}\) which would have been assigned to carboxylic acid.

Processing Characteristics
The apparent viscosities of PP/HBP and PP-g-(MAH-co-St)/HBP blends were shown in Figures 4-6. The rheological properties of all the blends were found to be changing dramatically with the addition of HBP components. In all cases, blend viscosity was lower than the viscosity of the matrix material [PP or PP-g-(MAH-co-St)]. In the PP/HBP blends, the viscosity was dropped with the addition of 3 %wt HBP and continued to be dropping as more HBP was added (Figure 4). In the PP-g-(MAH-co-St)/HBP blends, the viscosity was also dropped significantly with the initial addition of 3 %wt HBP. The viscosity in these blends was successively reduced by further addition of HBP and remained essentially constant when the addition of HBP was over 7 %wt (Figure 5).
The rheological data at a constant shear pressure were plotted and presented in Figure 6 to underline the difference between the behaviours exhibited by the PP-g-(MAH-co-St)/HBP and PP/HBP blends. The continuous drop in the viscosity of PP/HBP blend was an additive effect which was correlated with the amounts of HBP. This had the same effect as BoltronTM-H30 hyperbranched polyester which by adding to LLDPE acted as a processing aid [10]. The viscosity of the PP-g-(MAH-co-St)/HBP blends was stabilized at higher HBP content after the initial drop. This indicated the result of competing mechanisms that take place in the PP-g-(MAH-co-St)/HBP blends.

The HBP acts as a lubricant because of its molecular structure and low molecular weight and it decreases the melt viscosity of the system. At the same time, compatibilization associated with the chemical reaction took place in the blends. As more HBP was added, the favourite condition for reaction was created although, partly counter-balancing the lubrication effect of the HBP.

The rheological behaviour observed in the PP-g-(MAH-co-St)/HBP blends was not consistent with most reactive blending schemes whereby there was typically a significant increase in the viscosity as compatibilization reactions took place. A lowered viscosity attributed to the compact molecular structure of HBP was, however, consistent with the melt viscosity behaviour of hyperbranched molecules. In addition, the PP-g-(MAH-co-St)-g-HBP copolymer compatibilizers which resulted from the reaction formed linear / hyperbranched hybrid architecture. They were also compact relative to a linear architecture of equivalent molecular weight and had a tendency to reduce chain entanglement which would promote lower viscosity.

**Morphology**

The morphologies of PP12 and PPM12 are shown in Figures 7a and 7b, respectively. The PP12 blend exhibits

![Figure 6. Change in viscosity at constant pressure of 1498 MPa.](image)

![Figure 7. SEM Micrographs of (a)PP12 and (b)PPM12 after extraction of HBP phase.](image)
a coarse microstructure with large second-phase particle that is characteristic of an immiscible blend (Figure 7a). The average particle size in the PP12 blend was 11.70 μm in diameter. Large HBP particles remained phase separated in a PP matrix at equilibrium due to the lack of compatibilization at the polymer/polymer interface in the system. Coalescence of the HBP phase might also be taking place as the blend was cooled after processing.

The morphology of the PPM12 blends (Figure 7b) showed a smaller average particle size relative to the PP12 blends. This observed decrease in particle size in the PPM12 might be attributed to a reduction of the interfacial tension and to restriction of particle coalescence during processing which resulted from the formation of a copolymer compatibilizer [14]. The average particle size in the PPM12 was approximately 2 μm. The change of the average minor-phase was in accordance with the compatibility of PP/HBP and PP-g-(MAH-co-St)/HBP. The morphology observed from the fracture surfaces of the PP/HBP and the PP-g-(MAH-co-St)/HBP blends were also consistent with expectations based on past research in the area of polymer blends [15].

DSC Analysis
It was well established that the shifts in the glass transition temperature (T_g) of component polymers could be used to evaluate miscibility and immiscibility in polymer blends. DSC was performed on all the individual polymers as well as the 12% wt HBP polymer blends to determine pure component's T_g's and any subsequent shifts after blending as a result of compatibilization.

The DSC of PP12 and PPM12 blends with those of pure components was examined. The thermal data had been summarized in Table 2. The glass transition temperature (T_g) for pure HBP was 17.3°C whereas that of pure PP corresponded to -9.9°C. The thermal analysis of PP12 showed two T_g's, one corresponding to HBP (17.1°C) and the other to PP (-9.7°C). The results for the PP12 blend showed behaviour typical of an immiscible, uncompatibilized blend in which no significant deviations from the component values were observed for either T_g's exhibited by the blend. The T_g of PP-g-(MAH-co-St) was -7.6°C. The PPM12 blend had also been found to exhibit two T_g's, one corresponding to HBP component (13.7°C) and the other corresponding to PP-g-(MAH-co-St) (-4.6°C). An analysis of DSC (Table2) revealed that on addition of HBP, there were two shifts in the PPM12 blend. T_g shift of PP-g-(MAH-co-St) was 3°C and T_g shift of HBP was -3.6°C. A negative shift of the second-phase T_g was an indication of reaction and the incorporation of PP-g-(MAH-co-St) in the HBP phase. This result from PPM12 blend confirms some degree of compatibilization and is in accordance with SEM micrographs of the fracture surfaces of the blends.

Confirmation of Reaction
Figure 8 represents infrared spectra of HBP and PPM and PPM12 blends. The MAH ring of PP-g-(MAH-co-St) shows strong absorption at 1785 cm⁻¹ (Figure 3). This spectral region had been emphasized for the PPM12 blend along with its pure components in Figure 8. The relative strength of the MAH absorption (1785 cm⁻¹) to the PP-g-(MAH-co-St) reference absorption (1467 cm⁻¹) was significantly less in the blend than that in the pure PP-g-(MAH-co-St). The 1467 cm⁻¹/1781 cm⁻¹ absorption ratio increased from 1.26 in the pure PPM to 2.43 in the PPM12 blend. The decrease in the strength of the MAH absorption (1781 cm⁻¹) and increase in the absorption ratio indicated that ring opening reactions were taken place under the simulated blending conditions. It is the reaction that was responsible for the in situ formation of PP-g-(MAH-co-St)-g-HBP copolymer compatibilizer during processing, which resulted in refinement of the morphology of PPM12 blend.

Tensile Strength
Figure 9 shows the tensile strength of blends as a func-

<table>
<thead>
<tr>
<th>Materials</th>
<th>HBP T_g (°C)</th>
<th>PP T_g (°C)</th>
<th>PP-g-(MAH-co-St) T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure component</td>
<td>17.3</td>
<td>-9.9</td>
<td>-7.6</td>
</tr>
<tr>
<td>PP12</td>
<td>17.1</td>
<td>-9.7</td>
<td>-</td>
</tr>
<tr>
<td>PPM12</td>
<td>13.7</td>
<td>-</td>
<td>-4.6</td>
</tr>
</tbody>
</table>

Table 2. Glass transition temperature of pure components and two-phase blends.
tion of HBP contents. Figure 9a indicates that the tensile strengths of the PP blends are decreasing gradually as higher amount of HBP is added. These results have also shown that PP and HBP are immiscible. Figure 9b shows that tensile strength of PPM is slightly increased when 3 %wt HBP is added, and then it is dropped down as HBP contents increase further. The result is deduced from the increase of compatibility between PPM and HBP, and the lack of entanglements of HBP. The chemical reaction between -COOH groups of PPM and -OH groups of HBP has the ability to improve the compatibility of PPM and HBP, and results in the increase in tensile strength of PPM/HBP. However, the lack of entanglements in HBP results in a brittle material and poor mechanical properties.

The addition of excessive HBP was not favourable in increasing the tensile strength of the blends. Therefore, the tensile strength of the blends should be decreased as the mass of the HBP is beyond 3 %wt.

**CONCLUSION**

This work showed that hyperbranched polymers might be used successfully to produce self-compatibilized thermoplastic blends with enhanced processing characteristics. The viscosity of the PP/HBP blends was dropped down gradually as more HBP was added which is an indication of HBP acting as additive. The viscosity of the PP-g-(MAH-co-St)/HBP blends decreased when HBP was added of up to 7 %wt, and basically it was unchanged as more HBP was added. Morphology showed that PPM12 and PP12 blends are a two-phase morphology with an average second-phase particle size of 11.70 μm and ~ 2μm in diameter, respectively. The thermal analysis showed that PPM12 and PP12 blends have two distinct T_g s, but T_g of PPM12 was changed and T_g of PP12 remained constant. The combined results of the morphology studies and thermal analysis indicated that the occurrence of inter-chain reaction between hydroxyl functional groups of the HBP and the MAH functionalities of the PP-g-(MAH-co-St) formed copolymer compatibilizers in PP-g-(MAH-co-St)/HBP systems during processing. The occurrence of this ring opening reaction in the PPM12 was confirmed by FTIR technique as well.

**REFERENCES**


