Mechanical Properties and Morphology of Blends of Hyperbranched Polymer with Polypropylene and Poly(vinyl chloride)

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A B S T R A C T

Hyperbranched poly(amide-ester) (HBP) has a compact, highly branched, three-dimensional structure, which has a high density of functional end groups and inherently low viscosity. The HBP additives are able to behave as lubricants during processing and as compatibilizing agents in the blend. In this work, polypropylene/poly(vinyl chloride)/hyperbranched poly(amide-ester) (PP/PVC/HBP) blends were prepared by melt mixing; the PP/PVC (80/20 mass ratio) blends were investigated in detail. Mechanical and rheological properties were measured. The tensile strength of the blends reached the maximum value when the content of hyperbranched poly (amide-ester) was 3 phr; the impact strength of the blends was small changed as that of pure PP/PVC. The viscosity of the PP/PVC/HBP blends was higher than that of pure PP/PVC blends, whereas the viscosity of the PP/PVC/HBP blends dropped with added more HBP. The scanning electron microscopy (SEM) showed that a two-phase morphology was characteristic of blends and dual-continuous morphology of PP/PVC/HBP (80/20/3) blend. With more or less HBP, the PVC spherical droplets of the minor phase dispersed in a PP continuous matrix phase, whereas there was a large difference between/among the minor-phase particle size. The SEM photos also confirmed that HBP could enhance the adhesion at the interface and reduce the phase separation of PP/PVC blend. The tensile strength of blends was in accord with morphology and DSC of blends.

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INTRODUCTION

Dendritic polymers are a new class of three-dimensional, man-made molecules by an unusual synthetic route that incorporates repetitive branching sequences to create an unusual architecture. Dendritic polymers include dendrimers and hyper-branched polymers. Dendrimers have a perfectly branched uniform structure and mono-dispersity, hyperbranched polymers with the branching occur in a more random fashion and polydispersity, whereas two classes have a high density of

functional end group and inherently low viscosity. The highly branched structures and numerous end groups in hyperbranched polymers generate the improved solubility and compatibility with other polymers, and reduce the melt viscosity as well as crystallinity [1]. Compared with dendrimers obtained from multistep synthesis [2], hyperbranched polymers are more advantageous because they can be easily synthesized through one-pot polymerization processes [3-4].

Hyperbranched polymers have attracted considerable and increasing interest for many applications in recent years. Although there have been much progress in the structural understanding and the methods of synthesis of hyperbranched polymers, actual application of hyperbranched polymers technology and science is still in its infancy. There have been several studies on mechanical and rheological properties of hyperbranched polymers in limited material conditions. Kim et al. [1] blended hyperbranched polyphenylene with polystyrene; they found a remarkable reduction in melt viscosity (of up to 80%) and shear induced degradation for a blend consisting of polystyrene and five percent of hyperbranched polyphenylene. However, the thermal stability increased while the mechanical blend properties remained unaffected. Schmaljohann et al. [5] used modified hyperbranched polyesters as carriers for organic molecules in polyolefin blends. The resulting materials showed a homogenous distribution of the dye inside the polymer matrix. In contrast, large dye crystals could be observed when neat polyolefin was used as the matrix. Moreover, melt rheology studies showed drastic viscosity reduction as a function of hyperbranched polymer concentration in blends based on hyperbranched polyester and linear polymer [6]. Jannerfeldt et al. [7-8] studied the influences of the addition of hyperbranched polymer grafted polypropylene (PP-HBP) on the interfacial adhesion between fusion-bonded bilayers of PP/PA6 polymer blend. The interfacial adhesion between PP-HBP compatibilised bilayers was ten times compared to maleic anhydride grafted PP (PP-MA) compatibilised bilayers, and PP-HBP show was used as the more effective compatibilizer than the commonly used PP-MA. Mulkern et al. [9] reported that fourth-generation hyperbranched polyols was an excellent processing additive for polystyrene (PS). The hyperbranched polyesters behaved as lubricants during processing, and as self-compatibilizing toughening

agents in the final formation of the blend. A considerable decrease in the blend viscosity of PS or styrene maleic anhydride (SMA) copolymer was effectively investigated with addition of the hyperbranched polymer modifier.

Polypropylene (PP) is the fast-growing commodity polymer widely used in various fields because of its excellent performance-processability- price relation. And poly (vinyl chloride) (PVC) is a commodity plastic with many good properties such as nonflammability, relatively low cost and formulating versatility. A major problem in blending PP and PVC is the immiscibility due to the different polarities between two polymers, in which the poor interfacial adhesion and high interfacial tension were existed. The interfacial adhesion between the phases strongly influenced the final properties of the materials. The blend properties of PVC/PP can be improved if a compatibilizer capable of interaction with both PP and PVC is added [10-12].

The focus of our research was to study of the compatibilizing effect of hyperbranched poly(amide-ester) (HBP), as a component, to improve the immiscible property of PP/PVC blends. No studies, to our knowledge, have been reported to aim at the use of HBP as compatibilizer to modify the immiscible PP/PVC blends, and lead to enhance mechanical performance, in which the morphology can be controlled. The results give the promise of hyperbranched poly(amide-ester) for use as compatibilizer and processing aids.

EXPERIMENTAL

Materials

Isotactic polypropylene (i-PP) (M_w 26000 g/mol), with a MFI (melt flow index) of 3.5 g/10min, was purchased from Daqing petroleum chemical Corp. (Daqing, China). Suspension PVC (K=68) with an average polymerization degree of 1000 was supplied by Qilu Petrochemical Corp (Zibo, China). The hyperbranched poly (amide-ester) molecules were synthesized from diethanolamine and succinic anhydride [13], and 24-OH terminated end groups per molecule on average, and the number-average molecular weight (M_n) obtained by vapor pressure osmometry was 7800 g/mol, and the polydispersity was 2.08 measured by size exclusion chromatography. The glass transition temper-

ature (T_g) was 17.3°C and the thermal instability of the HBP began degradation above 200°C, as determined by thermo-gravimetric analysis. Other additives were commercial products. Figure 1 showed schematic illustration of hyperbranched polymer architecture.

Blend Preparation
Prior to blending, PVC with its processing additives was premixed together in a high-speed mixer for 10 min according to the following composition: PVC/tribasic lead sulphate/dibasic lead phosphite/ stearic acid/paraffin (100/2/1/0.4, mass ratio). The blend preparation was carried out at 180°C in a two-roll mill. HBP and PVC were blended for 2 min, and than blended with PP for 6 min. The prepared blends were compressed into sheets with a hydraulic press at 180°C and 10 MPa for 4 min, and than were cooled to room temperature by cool pressing.

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. Charpy impact strength was measured by means of XCJ-40 impact tester according to GB1040. The testing was conducted at room temperature. Values were an average of five testing.

Rheological Measurements
The melt viscosity of all blends under processing conditions was measured using a high- pressure capillary rheometer (model XLY-1) with a capillary die of 1 mm, and L/D ratio of 40. The experimental temperature was fixed at 180°C with experimental loads of 180, 160, 140, 120, 100, and 80 kg/cm^2. Measurements for the correction turned out not to be necessary.

Blends Morphology
Samples were prepared by freezing pieces of the strand in liquid nitrogen followed by high-speed impact to create fresh fracture surfaces, and then were covered with gold using a surface sputter coater, model SBC-12, before observation. To improve the contrast in the PP/PVC blends, the PVC minor phase was extracted
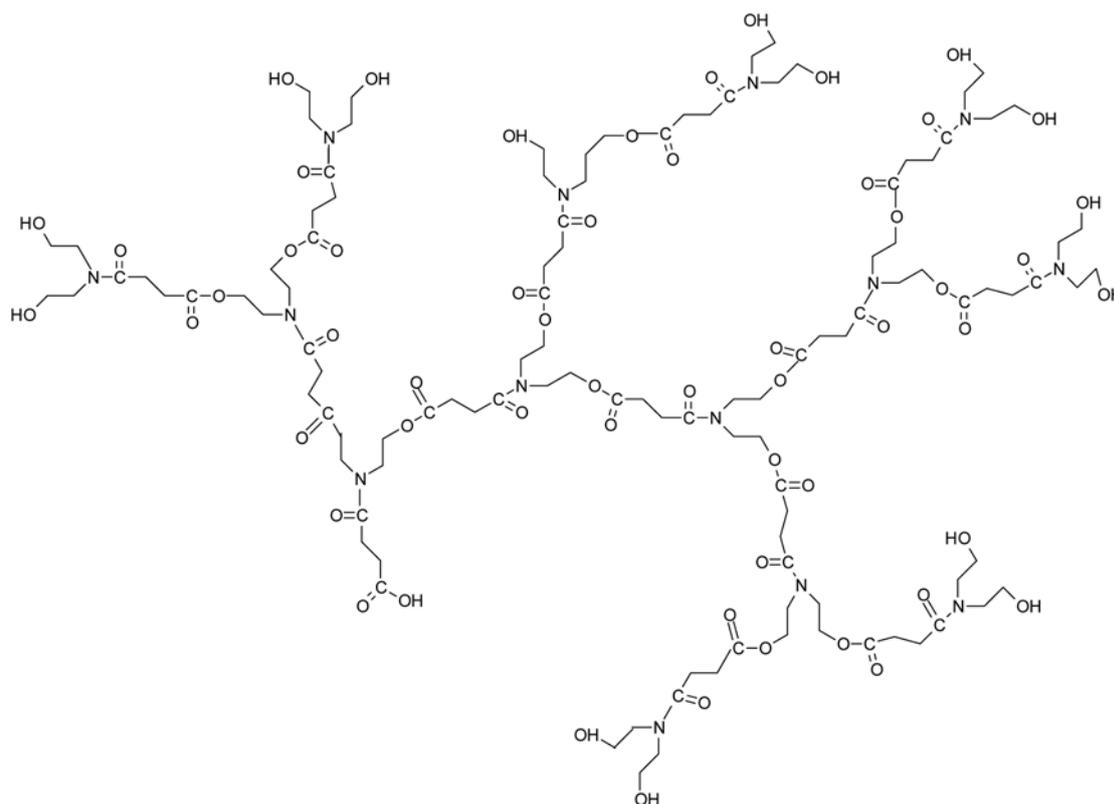

Figure 1. Schematic illustration of hyperbranched poly(amide-ester) architecture.

using tetrahydrofuran (THF) at room temperature, under continuous stirring for 48 h. Thereafter, the samples were dried under vacuum at temperature of 60°C for 24 h. A Scanning Electron Microscopy (SEM) (Tracor Northen Company, KYKY-2800B), operated at an accelerating voltage of 25 KV, was used to observe the morphology of the samples. Image analysis techniques were employed in order to determine the average particle diameter.

DSC Analysis

DSC Thermograms were taken on a Mettler TA 4000 Model apparatus at a heating rate of 10°C/min in the N_2 atmosphere. The glass transition temperature (T_g) was taken at the onset of the corresponding heat capacity jump.

RESULTS AND DISCUSSION

Tensile and Impact Strength

Figure 2a showed the tensile strength of the PP/PVC dependence on the mass of the HBP. PP and PVC formed highly incompatible mixtures because of the poor interphase adhesion and high interfacial tension between the two phases. The mechanical properties of these mixtures were poor and could be improved by the addition of HBP compatibilizer. The tensile strength with addition of HBP compatibilizer increased as shown in Figure 2a, and the tensile strength of the PP/PVC blends reached a maximum value when HBP content rose to 3phr, and then dropped down quickly. The result came from the change of compatibility between PP and PVC from the better to the worse, and also came from the poor the mechanical properties of the HBP. Blends of immiscible polymers exhibited different properties that depended on composition, viscosity ratio and elasticity ratio between the components, interfacial tension, and process conditions etc. From theoretical point of view, the component polymers with similar viscosity should have the behavior to be mixing well as the other conditions were unchanged. Moreover, It was shown that a change in the viscosity ratio for the blend composition had a significant effect on mechanical property and on the blend phase morphology [14]. The viscosity of PVC was much higher than that of PP, and whereas HBP has a lower viscosity. It
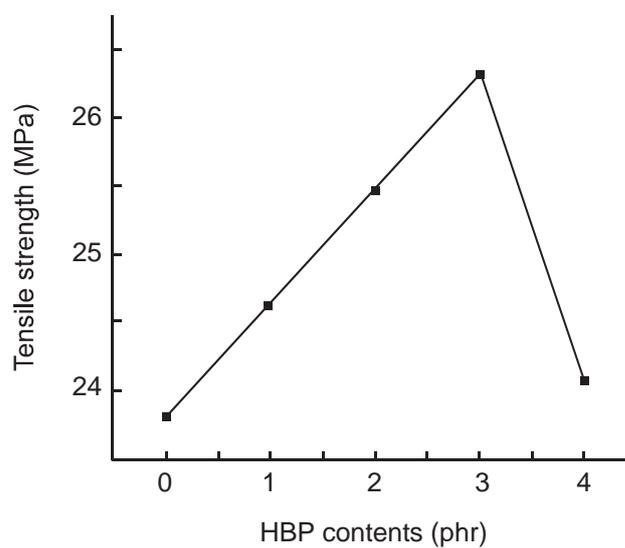

(a)
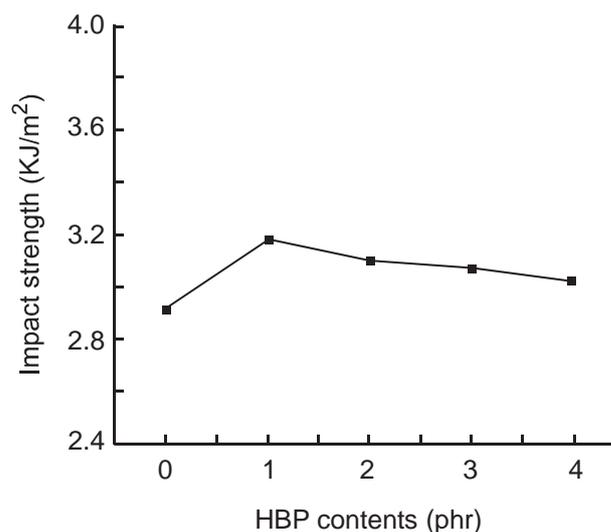
(b)

Figure 2. The tensile strength and impact strength of PP/PVC (80/20, mass ratio) blends as a function of HBP (phr) contents.

should be point out that the viscosity of PVC with addition of HBP decreased drastically compared to that of pure PVC. On the other hand, methenyl hydrogen atom of PVC should interact with the ester carbonyl and amido group of HBP, and then form weak hydrogen band [15]. These two effects have the abilities to improve compatibility of PP and PVC, and deduce the increasing of the tensile strength of the blends. However, the less lack of entanglements in HBP resulted in the brittle material and poor mechanical properties. The addition of excessive HBP was not favorable to

increase the tensile strength of the blends, and so the tensile strength of the blends should be decreasing, as the mass of the HBP is over 4 phr. Therefore, HBP can be used to improve the poor inter-phase adhesion and high interfacial tension between the two phases of PP/PVC blends and the tensile strength of blends reach the maximum value when the blends contained 3 phr HBP. The more HBP should be unfavorable to increase the mechanical property due to the reason mentioned above. Figure 2b showed the curve of impact strength vs HBP content. It was given that the impact strength of the blends had a small increase when HBP content was 1phr, and then the impact strength of the blends decreased a little. The impact strength remained almost unchanged in the experiments. Differing from the tensile strength, the impact strength had maximum value that HBP was 1phr and tensile strength attained maximum value that was 3 phr. It seemed that HBP affected impact and tensile strength in different ways. When the synergism of impact and tensile strength occurred, their ultimate values could not occur at the same composition because of the difference impact and tensile procedures. The impact stress acted quickly so that there was not enough time left to allow the macromolecules to move. On the contrary, macromolecular motion was easier in the tensile procedure. It should be stress that morphology was a key to determine the tensile strength and the impact strength of blends. The final morphology was strongly dependent on the amounts and molecular weights of the HBP and the composition of the blends. The effects of HBP on the final morphologies of the PP/PVC blends were discussed in the other section.

Processing Characteristics
The complex viscosities of PP/PVC (80/20 mass ratio) blends were shown in Figure 3. The rheological properties of all the blends were found to be changing dramatically with the addition of HBP components. In all cases, the viscosity of PP/PVC/HBP blends was higher than the viscosity of PP/PVC blend, indicating that an improvement in compatibility resulted from HBP compatibilizer capable of interaction with both PP and PVC. In the PP/PVC/HBP blends, the viscosity of PP/PVC blend reached a maximum value with the addition of 1 phr HBP, and decreased as the more HBP was added. The drop in viscosity of the PP/PVC/HBP
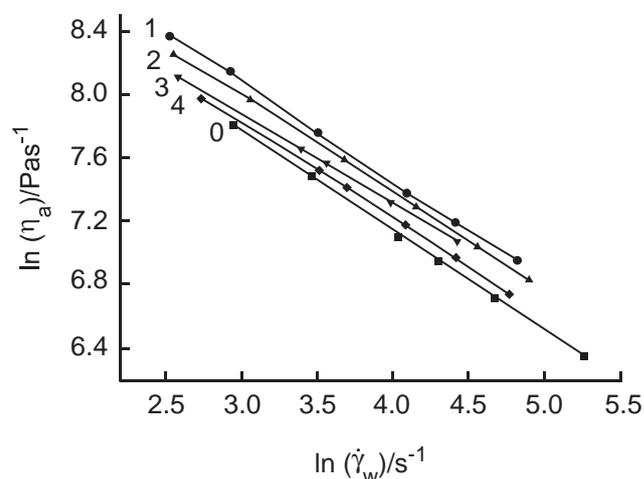

Figure 3. Rheological behaviour of PP/PVC (80/20 mass ratio) with varying addition of HBP 0 phr (0), 1 phr (1), 2 phr (2), 3 phr (3), 4 phr (4).

blends seemed to be an additive effect, and was dependent on the amount of HBP components. The effect could be interpreted by the competing mechanisms taking place in the blends. The HBP behaved as a processing aid because of its molecular structure and low viscosity in melt and solution compare to their linear analogous. At the same time, as above mentioned, hydrogen band should be formed between HBP and PVC associated with the compatibilization combination in the PP/PVC blend. When the amount of HBP was 1 phr, the compatibilizing effect of HBP larger than lubricant effect of HBP, therefore the viscosity of PP/PVC/HBP (80/20/+1 phr) blends was highest. As the more HBP was added (>1 phr), the propensity for the lubricant effect of the HBP should increase, over counterbalancing the compatibilization combination of PP/PVC/HBP, so the viscosity of PP/PVC/HBP blends decreased gradually. With expectation, as the more and more HBP was added, the viscosity of PP/PVC/HBP blends was lower than that of PP/PVC blend.

The rheological behavior observed for the PP/PVC/HBP blends was not consistent with the most hydrogen bond blending schemes whereby there was typically a significant increase in the viscosity as compatibilization combination took place. A lowered viscosity was, however, consistent with the melt viscosity behavior of hyperbranched molecules and was attributed to the compact molecular structure of the HBP. In addition, the HBP/PVC blends, which resulted from the
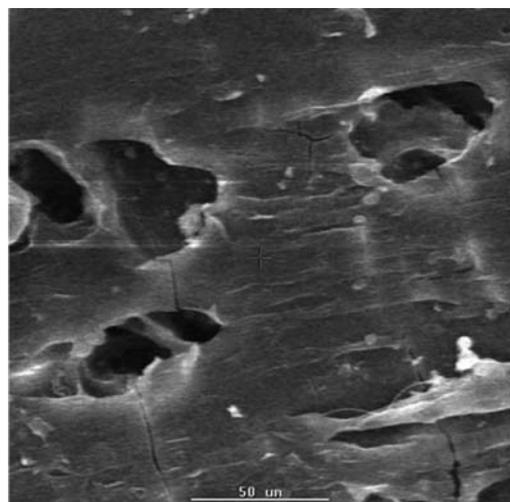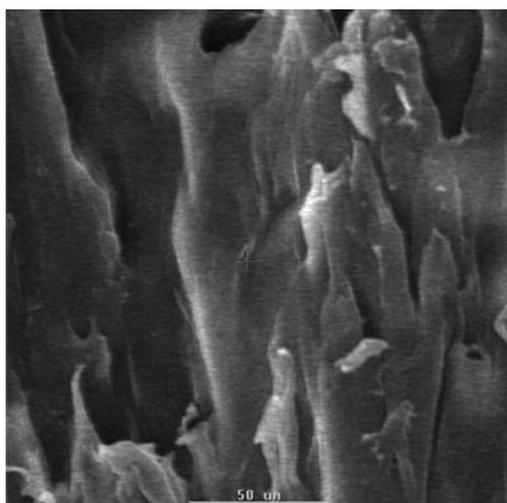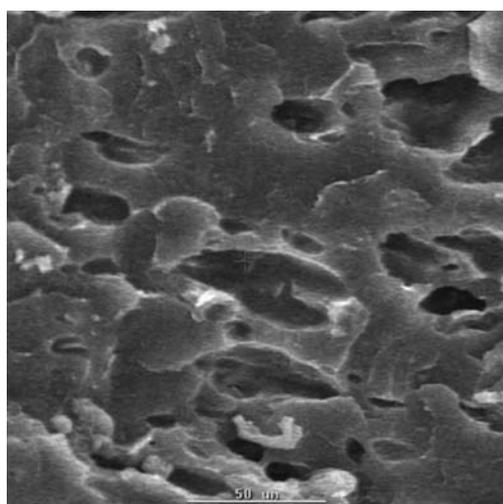
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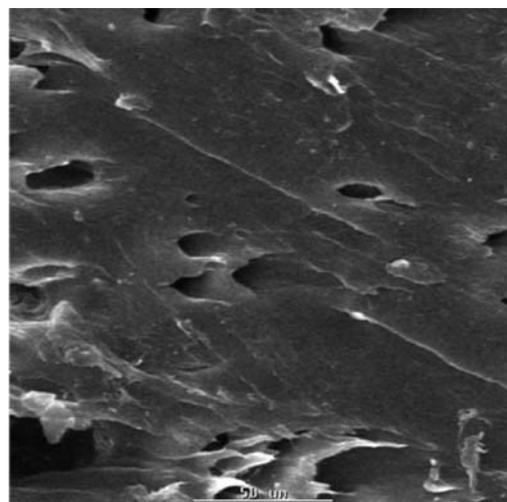
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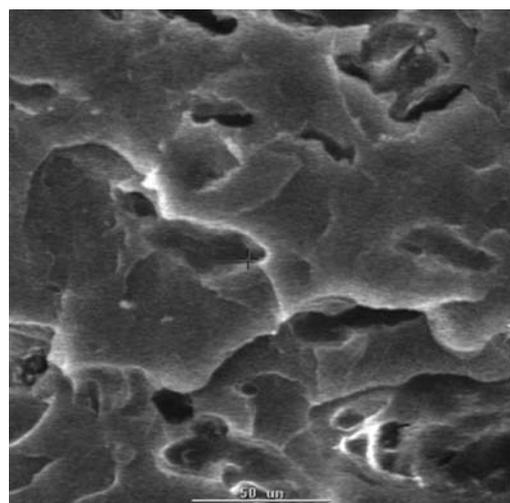
(b)

(d)

(e)

Figure 4. SEM Micrographs of blends PP/PVC (mass ratio)/HBP (phr) (a) 80/20/0, (b) 80/20/1, (c) 80/20/2, (d) 80/20/3, (e) 80/20/4, after extraction of PVC phase.

Table 1. PP/PVC (80/20 mass ratio) blends; second-phase particle diameter distribution.

HBP(phr)	0	1	2	4
Average diameter (m × 10⁻⁶)	9.02	6.32	3.78	6.15
Standard deviation (m × 10⁻⁶)	3.50	2.92	2.38	2.81
Population	52	63	78	65

weak hydrogen bond had a linear/hyperbranched hybrid architecture, was also compact relative to linear architectures of equivalent molecular weight, and had a tendency to reduce chain entanglement promoting a lower viscosity.

Morphology

Figure 4 showed that the morphology observed by SEM for different contents of HBP blended with the same ratio of PP/PVC (80/20 mass ratio). The average minor-phase particle size in the PP/PVC/HBP blends was given in Table1. The PP/PVC blend exhibited spherical phase domains of PVC and weak interfacial adhesion, surrounded by the continuous PP phase as shown in Figure 4a. The SEM micrographs of PP/PVC/HBP blends suggested that the minor-phase particle size of the dispersed phase decreased when compatibilizer concentration increased up to 2 phr [Figures 4b-4c and Table 1], and a co-continuous morphology in Figure 4d when addition of the amount of HBP was 3 phr. This change of morphology could improve the mechanical properties of the PP/PVC blends due to the decrease particle size (phase PVC) and the increase of compatibilization at the polymer/polymer interface. A further increase in compatibilizer concentration did not decrease the size of dispersed particles, and indicated that 3phr compatibilizer was sufficient to occupy the interface between PP and PVC [Figure 4d]. As a result, an excess of compat-

Table 2. DSC results of PP/PVC/HBP blends.

No.	Composite of blends	T_g of PVC (°C)
1	PP/PVC (mass ratio)/HBP (phr)= 80/20/0	88.7
2	PP/PVC/HBP=80/20/1	87.6
3	PP/PVC/HBP=80/20/2	87.0
4	PP/PVC/HBP=80/20/3	85.6
5	PP/PVC/HBP=80/20/4	85.9

ibilizer remained in the bulk and did not contribute to the reduction of interfacial tension, which would not cause further reduction in minor-phase particle size [Figure 4e and Table1]. The change of the average minor-phase particle size was in accordance with the compatibility of PP/PVC blends. The mixing thermodynamics and the kinetics controlled the decrease in the average minor-phase particle size, in which the miscibility was increasing, and did not further discussed in the paper. The compatibility property can be induced by the third component that interacted physically with both phases or had specific interaction with one phase and physical contact with the other. The SEM micrographs demonstrated that the addition of the compatibilizer suppress coalescence, and was in accordance with the mechanical and rheological result, suggesting the formation of an interfacial compatibilizer.

DSC

The DSC analysis results were given in Table 2. It was observed that the glass transition temperature (T_g) of PVC decreased from 88.7 to 85.6°C, and then increase 85.9°C. The changed glass transition temperature of PVC indicated the degree of compatibility of PVC/PP blend, the higher compatibility of PVC/PP blend, the lower the glass transition temperature of PVC.

CONCLUSION

Hyperbranched polymer molecules have a unique, highly branched, three-dimensional structure, which has a high density of functional end groups and inherently low viscosity. These factors make these new polymers attractive for use in blends. The HBP additives are able to behave as lubricants during processing and as compatibilizing agents in the blend.

In this study, it had been demonstrated that hyperbranched poly(amide-ester) could be used successfully to produce partly compatibilised thermoplastic blends with enhanced tensile strength and processing characteristics. The tensile strength of the blends reached the maximum value when the content of hyperbranched poly(amide-ester) was 3phr and then dropped on the increase of HBP. The viscosity of the PP/PVC/HBP blends is higher than that of pure PP/PVC blends, and the viscosity of the PP/PVC/HBP blends dropped added more HBP, indicating that the HBP was acting as

a compatibilizer and lubricant.

Morphology showed that a two-phase morphology was characteristic of all blends except for added 3phr HBP in the PP/PVC (80/20 mass ratio) blends. With more or less HBP, the PVC spherical droplets of the minor phase dispersed in a PP continuous matrix phase, whereas there was a large difference between/among the minor-phase particle size. The morphology of PP/PVC blends exhibits a coarser than that of PP/PVC/HBP blends in diameter in the different blend composition of PP/PVC.

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