Reactive Blends of Poly(phenylene sulfide)/Hyperbranched Poly(phenylene sulfide)

Yan Bo, Chen Long, Zhu Meifang, Chen Yanmo**

Summary: Polymer blends consisting of linear poly(phenylene sulfide) (PPS) and hyperbranched PPS (HPPS) were obtained in melt. The solid-state properties of PPS and their blends were investigated by scanning electron microscopy (SEM), thermogravimetric analyzer (TGA), extraction measurement, differential scanning calorimetry (DSC) and dynamical mechanical analysis (DMA). Blends prepared by melt mixing turned out to be reactive as shown by the TGA and extraction measurement. SEM indicated that no phase separation occurs in PPS/HPPS blends. The degree of crystallization of the blends decreased with increasing HPPS content. Both the storage modulus and loss modulus increased as HPPS content increasing.

Keywords: hyperbranched; poly(phenylene sulfide); reactive blend

Introduction

Poly(phenylene sulfide) (PPS) is a very stiff crystalline polymer. It has excellent dimensional stability, high stiffness, high modulus, chemical resistance, and fatigue resistance, which collectively make it comparable to metals.[1,2] For this reason, PPS has been increasingly applied to areas requiring high temperature and chemical resistance as well as to electrical, electronic, and automobile parts.[3,4] However, it should also be mentioned that PPS is brittle with low elongational strain, exhibiting a slow crystallization rate and low impact strength. Furthermore, chemical modification of PPS is extremely difficult. For the practical application of PPS, it is necessary to reduce the brittleness while maintaining its advantageous thermal, mechanical, and chemical properties.

In recent years, dendritic polymers, including dendrimers and hyperbranched polymers, have become an important class of polymeric materials that are currently compared with conventional linear thermoplastics in order to evaluate unusual properties.[5]

In 1992, Kim and Webster firstly reported blending of hyperbranched polyphenylene with linear polystyrene.[6] Enhanced miscibility with linear materials would be expected from these dendritic materials and also additional positive effects on the mechanical, rheological and thermal properties of the polymer blends. In recent years various blends between dendritic polyesters and linear polymers have been described, and advantages for processing of the materials due to the dendritic component have been mentioned.[7–10] Massa et al. surveyed the phase behavior of blends of hyperbranched polyester with linear polymers such as polycarbonates, polyesters and polyamides, found that chemical structure and interaction played a important role in polymer blend miscibility.[7] Schmaljohann et al. used modified hyperbranched polyester as carriers for organic molecules in polyolefin blends. The resulting materials showed a homogeneous distribution of the dye inside the polymer matrix.[8] Jang et al. studies the crystallization behavior of hyperbranched polyester blended with PET, found that the terminal groups and the composition of the hyperbranched

---

State Key Lab for Modification of Polymer Materials and Chemical Fibers, College of Material Sci. & Eng., Donghua University, Shanghai 201620, China
Fax: (+86) 021 67792855
E-mail: happyjack@dhu.edu.cn; ymc@dhu.edu.cn

polyesters had influence on the crystallization behaviors of PET.[9]

It was reported that the hyperbranched aramid and polyamide 6 could yield miscible blends. Moreover, when the hyperbranched polymers had a high concentration of active end groups, the blends prepared by melt mixing turned out to be somewhat reactive.[10–12]

In this work, we attempted to prepare blends of hyperbranched poly(phenylene sulfide)(HPPS) with a commercially available linear poly(phenylene sulfide) (PPS), which some structural similarity and had a high concentration of chlorine end group, that able to promote strong interactions with the linear polymer.

Experimental Part

Materials

The PPS used was a commercial grade (Mw about 50000) manufactured by Sicuan Huatuo Co. HPPS was synthesized in our laboratory (Mw about 22100, MD about 3.1). The molecular masses and molecular mass distribution of polymer were determined by GPC against polystyrene standards. DSC analysis of the above synthesized HPPS samples. The HPPS samples were found to be complete lack of crystalliniy: if the polymer samples were heated to 350 °C, no T_m was observed; then were slowly cooled back to room temperature, no crystallization was observed.

Blends Preparation

Three kinds of blends were prepared, all based on weight fraction; the PPS/HPPS ratios were 95/5, 90/10 and 80/20. All polymers were kept in vacuum oven at 80 °C for 12 h before processing. Blends of PPS and HPPS were prepared using a DACA twin-screw extruder. The melt mixing temperature was 300 °C and the screw speed was 75 rpm. The final mixing time was chose to be 10 min for all blends, which was far after the torque had reached a minimum plateau value. All blends were cooled rapidly in air after the extrusion process.

Differential Scanning Calorimetry(DSC)

The measurement of samples was performed using a DSC (Modulated DSC 2910, TA Inc. American). The sample were first heated up to 320 °C, held in the molten state for 5 min to destroy any residual nuclei and later cooled to room temperature, then heated up to 320 °C again under a N_2 atmosphere. The heating and cooling runs were carried out at a rate of 10 °C/min. The crystallization temperature (Tc) and melt temperature (Tm) were determined from the peak maxim of the DSC thermograms.

Dynamic Mechanical Analyser(DMA)

The samples were measured in a dynamic mechanical analyzer (Modulated DMA Q800, TA Inc. American), on bending (double cantilever), at 1 Hz, strain of 64 μm and at heating rate of 5 °C/min.

Thermogravimetric Analyzer (TGA)

TGA was done with a NETZSCH TG-209-F1 thermogravimetric analyzer. Conventional constant heating rate TGA measurements were run at 10 °C/min in nitrogen with the sample size about 8–10 mg to provide a control set of values for thermal decomposition parameters. The nitrogen flow was 30 ml/min.

Scanning Electron Microscopy (SEM)

The morphology and composition of the blends were analyzed using a scanning electron microscopy (JSM-5600LV, JEOL Inc. Japanese). The surfaces were prepared by breaking the samples in a liquid N_2 atmosphere and coating these surfaces with Au.

Synthesis of HPPS

The synthesis procedure of HPPS in this work was similar to that in Hanson's work[5] and Hewen Liu's work.[13] To improve monomer conversion, we decrease reaction temperature and NMP was used as the reaction medium. A 250 ml three-neck flask was charged with NMP 80 ml, 2,4-dichlorbenzenthiol 10 g and KOH 5.6 g. The mixture was stirred under pure N_2 and was heated and maintained 10 h. The reactions were then cooled and diluted with an equal volume of water and poured into 300 ml 10% HCL solution. The resulting precipitate was vacuum-dried at 80 °C and then dissolved with vigorous stirring in a minimal amount of THF. The THF solution was added drop wise to hexanes with vigorous stirring over a period of 2 h. This precipitate was then filtered, washed with hexanes, and dried thoroughly under vacuum. The product obtained as yellow powder. The mechanism of the synthesis of HPPS was illustrated in Figure 1. FTIR(KBr): 3051, 1565, 1449, 1365, 1095, 1029, 868, 810 cm^{-1} and 1HNMR(CD3Cl) 7.47, 7.43, 7.39, 7.37, 7.26, 7.22 ppm, which behave similar characteristics to those obtained in Hanson's work[5] and Hewen Liu's work.[13] In the AB2 systems, the degree of branching determined by NMR is usually about 50%–60%.[2–4] However, for the hyperbranched PPS, the degree of branching could not be determined from its ^{1}H-NMR spectrum because the chemical shifts of the aromatic protons were not well resolved for this determination.[5,6]

Results and Discussion

All the samples were prepared by using a microcompounder. It was observed that the torque value decreased at first, and then reached a minimum plateau value during the mixing process. But the minimum plateau value was higher with increasing hyperbranched polymer concentration in the mixture. This result was a preliminary indication of an enhanced processability of the material.

TGA Investigations

The TGA curves of the HPPS and PPS/HPPS blends in nitrogen at heating rates of 10 °C/min were shown in Figure 2. From the Figure 2, it was shown that the thermal degradation temperature (Td) of PPS is 510 °C and the Td of HPPS is 450 °C. But the Td of blends were similar to the PPS and the weight loss occurred in a single stage. The char yield at 700 °C increases significantly with increasing the HPPS

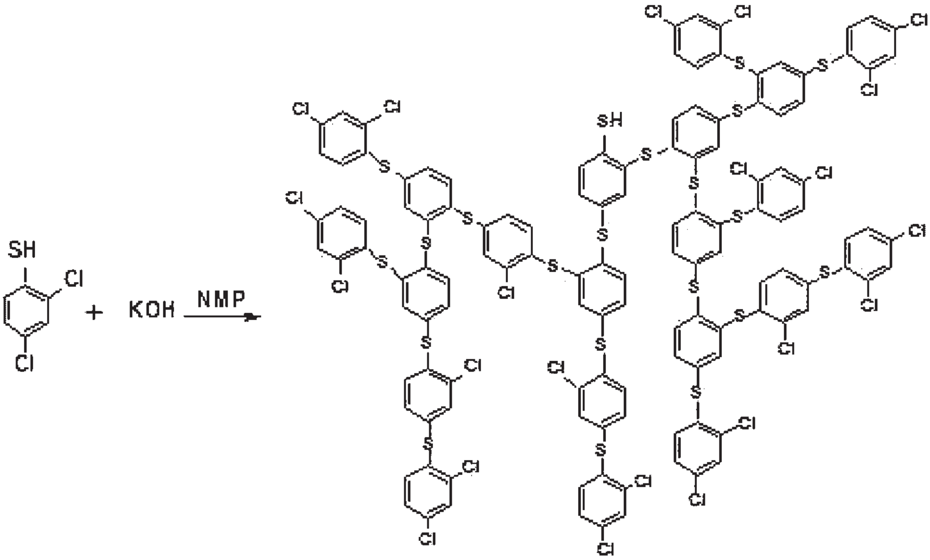


Figure 1.
The synthesis of HPPS.

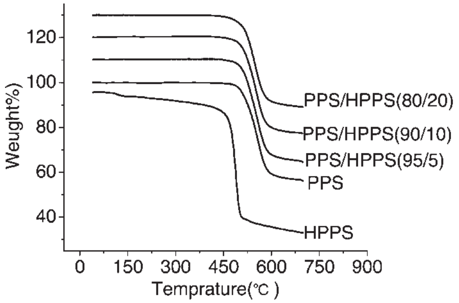


Figure 2.
TGA cures of HPPS and PPS blends.

content. All those strongly indicated that there might be somewhat reaction between PPS and HPPS.

THF is good solvent of HPPS, while the PPS is basically in soluble in this case. Another TGA was taken: the HPPS was kept in N_2 at 300 °C for 30 min. As in Figure 3, the weight loss was no more than 3%. While the residue obtained in this measurement was still solved in THF. These mean that the HPPS neither cross-linked nor volatilized during the melt mixing. Thus using THF to extract HPPS from the blend power, the reactive information between PPS and HPPS can be obtained. The blend was Soxhlet extracted in THF for 24 h then was vacuum-dried at 50 °C for 20 h. The blend sample was tested the weight loss. The weight loss near to zero indicted the HPPS had reacted with PPS so the HPPS could not extracted from the blend.

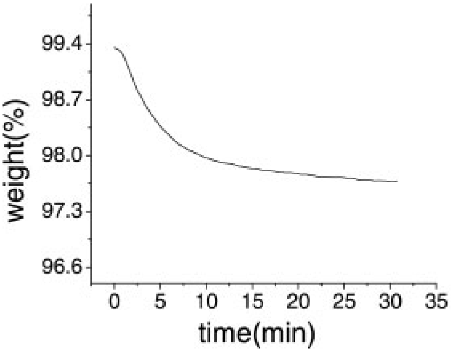
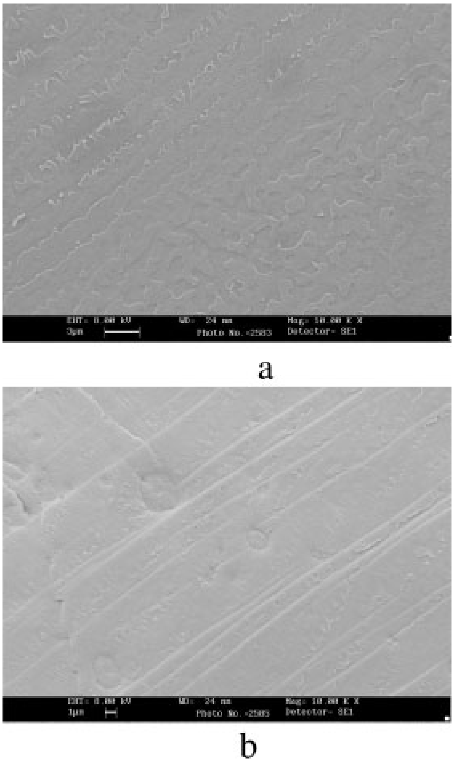


Figure 3.
TGA cure of HPPS at 300 °C.


a

b

Figure 4.
The SEM photograph of the fracture section for PPS/HPPS (80/20) before (a) and after (b) extracted with THF.

SEM Investigations

Already the results from TGA and the extraction measurement indicated strongly that reactive blends were formed. Further evidence could be obtained by detailed investigation via SEM of THF etched blend samples. Figure 4a and Figure 4b showed the SEM photographs of PPS/HPPS (80/20) blend fracture surfaces from extruded pieces before and after THF etching. The fracture section of the blends leaded to homogenous, i.e. no phase separation in all case studied. The etched sample did not show any indications of HPPS domains. In case of the existence of such domains, THF should dissolve them during etching and visible holes would be the result. Such domains were shown when hyperbranched polyesters were mixed with polyolefins.[8]

Table 1.
Thermal characteristics of PPS/HPPS blends for a heating rate of 10 °C/min with DSC.

PPS/HPPS	T_g (°C)	Tc(°C)	Tm(°C)	ΔH_m(J/g)
100/0	86.2	233.5	282.1	46.2
95/5	86.3	229.2	281.2	39.2
90/10	86.5	228.6	280.4	39.5
80/20	89.2	228.1	278.0	33.8
0/100	98.5	–	–	–

DSC Investigations

All samples were investigated by differential scanning calorimetry (DSC) to see changes in the melting and crystallization behavior of the blends. All the Tg, Tc, and Tm for PPS, HPPS, and PPS/HPPS blends are summarized in Table 1. From Table 1, it could be seen that there was only one Tg in PPS/HPPS blends, and the Tg increased with increasing HPPS content. Both of the Tc and the Tm in blends were a little lower than that of pure PPS. The heat of fusion (ΔHm), normalized to the PPS content of the blends, decreased with increasing HPPS content, indicted that the degree of crystallization of the blends decreased with increasing HPPS content that would be registered due to an increase in the molecular weight.[14–16]

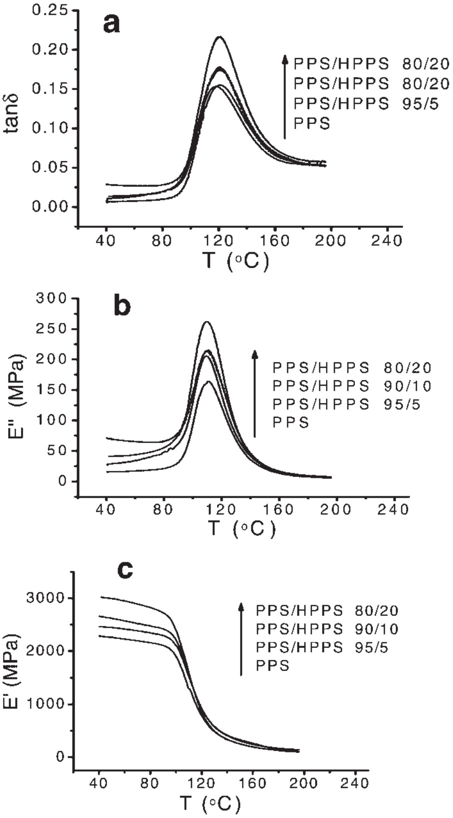


Figure 5.
DMA cures of PPS/HPPS blends, a: tanδ – T cures; b: E″ – T cures; c: E′ – T cures.

DMA Investigations

Tg was evaluated at the point where the mechanical loss (tanδ) from the DMA cures exhibits a maximum. The HPPS films obtained by compression-molding were very weak, easily breakable and exhibited virtually no tensile strength. Therefore, DMA measurements were done only for the blends and pure PPS. Evaluation of tanδ cures showed clearly that the relaxation peak temperature for pure PPS at 118.2 °C is shifted to higher values with an increase of the content of HPPS component in the blends. Figure 5 shows storage modulus and loss modulus as a function of temperature for the blends and the pure PPS. The modulus increased as HPPS content increasing.

Conclusion

Melt blends of linear poly(phenylene sulfide) with hyperbranched poly(phenylene sulfide), which some structural similarity and has a high concentration of chlorine end group, have been prepared. The solid-state properties of PPS and their blends are investigated by scanning electron microscopy (SEM), thermogravimetric analyzer (TGA), extraction measurement, differential scanning calorimetry (DSC) and (DMA).

The thermal degradation temperature (Td) of PPS is 510 °C and the Td of HPPS is 450 °C, but the Td of blends are similar to the PPS and the weight loss occurred in a single stage. Those indicated that there might be somewhat reaction between PPS and HPPS. The isotherm TGA prove that the HPPS neither crosslinked nor volatilized during the melt mixing. The blend is Soxhlet extracted in THF and the weight loss near to zero. SEM also shows no phase separation occurs in PPS/HPPS blends. All those indicted the HPPS have reacted with PPS in the processing of melt mix. Some properties of PPS/HPPS blends were studied. Only one Tg of blends are obtained by DSC and DMA and the Tg move to high temperature with the HPPS content increasing. The Tc, Tm and the degree of crystallization of the blends decreased with increasing HPPS content. Both the Storage modulus and loss modulus increased as HPPS content increasing.

Acknowledgements: The authors thank National High Tech 863 project (2006AA03Z550) and enterprise funding (2005042) for the Financial support of this project.

[1] J. T. Edmonds, H. W. Hill, US Pat. 3,354,129 (1967).
[2] B. T. Tabor, *Eur. Polymer. J.* **1971**, *7*, 1127.
[3] D. G. Brady, *J. Appl. Polym. Sci.* **1981**, *36*, 231.
[4] L. C. Lopez, G. L. Wilkes, *J. Macromol. Sci. Chem. Phys.* **1989**, *29*, 83.
[5] B. Voit, D. Beyerlein, K.-J. Eichhorn, K. Grundke, D. Schmaljohann, T. Loontjens, *Chem. Eng. Technol.* **2002**, *25*, 704.
[6] Y. H. Kim, O. W. Webster, *Macromolecules* **1992**, *25*, 5561.
[7] D. J. Massa, K. A. Shriner, S. R. Turner, B. I. Voit, *Macromolecules* **1995**, *28*, 3214.
[8] D. Schmaljohann, P. Pötschke, R. Hässler, B. I. Voit, P. E. Froehling, B. Mostert, et al. *Macromolecules* **1999**, *32*, 6333.
[9] J. Jang, J. H. Oh, S. I. Moon, *Macromolecules* **2000**, *33*, 1864.
[10] T. Huber, P. Pötschke, G. Pompe, R. Hässler, B. Voit, S. Grutke, F. Gruber, *Macromol. Mater. Eng.* **2000**, *280/281*, 33.
[11] O. Monticelli, D. Oliva, S. Russo, C. Clausnitzer, P. Pötschke, B. Voit, *Macromol. Mater. Eng.* **2003**, *288*, 318.
[12] O. Monticelli, S. Russo, R. Campagna, B. Voit, *Polymer* **2005**, *46*, 3597.
[13] Xu. Ranglei, Liu. Hewen, Shi. Wenfang, *J. Poly. Sci. Part B: Polymer Physics* **2006**, *44*, 826.
[14] R. T. Hawkins, *Macromolecules* **1976**, *9*, 189.
[15] N. Bulakh, J. P. Jog, *J. Macromol. Sci. -Phys.* **1995**, *B34*, 15.
[16] N. Bulakh, J. P. Jog, V. M. Nadkarni, *J. Macromol. Sci. -Phys.* **1993**, *B32*, 275.