Compatibility Effect of Radiation-Grafting-Functionalized Styrene–Butadiene–Styrene on Polyamide 6/Styrene–Butadiene–Styrene Blends

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ABSTRACT: Styrene–butadiene–styrene (SBS) was grafted with dibutyl maleate (DBM), methacrylic acid (MAA), or maleic anhydride (MAH) by ^{60}Co γ-rays. The grafted SBS was blended with polyamide 6 (PA6). The compatibility of the PA6/SBS blends was studied with scanning electron microscopy and rheological measurements. The results showed significant improvement in the compatibility of PA6 blended with MAH- or MAA-grafted SBS, with the former being more effective, whereas grafting DBM was ineffective in this respect. Mechanisms of the compatibility enhancement and ineffectiveness are discussed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1029–1036, 2008

Key words: compatibility; graft copolymers; polyamides; radiation

INTRODUCTION

Polymer blending is an effective way of producing new polymeric materials that are attractive, low-cost substitutes for expensive homopolymers or copolymers, even though most polymer pairs are thermodynamically immiscible in nature because of the low entropy of mixing.[1]

Polyamide 6 (PA6), an engineering thermoplastic with good toughness, strength, abrasion resistance, and chemical resistance, is not ideal with its larger water-absorbing capacity, melt-processing instability, and relatively low impact strength. As reported by a number of authors, PA6 can be improved in this respect through blending with other polymers, such as polypropylene (PP),[2] polycarbonate (PC),[3] acrylonitrile–butadiene–styrene (ABS),[4] poly(phenylene oxide) (PPO),[5] ethylene–propylene–diene rubber (EPDM),[6] and ethy- lene-*co*-vinyl acetate (EVA).[7] However, less attention has been paid to blending PA6 with styrene–butadiene–styrene (SBS), an important class of thermoplastic elastomers that possess the superior properties of both plastic and rubber, that is, good elasticity and resistance to low temperatures and wet traction.

To tackle the compatibility problem, polymer blending is performed with a reactive compatibilizer, normally a graft or block copolymer, that is capable of reacting with functional groups of PA6.[8–11] An interfacial reaction between the two polymer phases can help control the morphology and strengthen the interfaces. Wu et al.[12] synthesized maleic anhydride (MAH) grafted EPDM and glycidyl methacrylate (GMA) grafted EPDM as compatibilizers of PA6/poly(phenylene oxide) blends. Wei et al.[13] grafted GMA onto low-density polyethylene (LDPE) and a styrene/ethylene–butene/styrene block copolymer to compatibilize a blend of PA6 and LDPE. Byung Seon Yoon et al.[14] investigated a PP/PA6 blend with PP-*g*-MAH as a compatibilizer. Most of the graft polymers, however, have been synthesized by chemical methods.

In comparison with chemical grafting processes, radiation graft copolymerization can be conducted conveniently in an extended range of reaction temperatures with less harmful residuals and decreased energy consumption. In this study, SBS was grafted by ^{60}Co γ-rays with monomers of dibutyl maleate (DBM), methacrylic acid (MAA), or MAH. In the grafting of MAH, a solution was added with styrene (St) as a second monomer to improve the grafting degree of MAH. The grafted SBS was used as a compatibilizer for the PA6/SBS blend. The surface morphology, rheological behavior, and compatibility of the samples with different amounts of grafted SBS were investigated.

EXPERIMENTAL

Materials

Nylon 6 (1013B) with a number-average molecular weight of 25,000 was supplied by UBE Chemical Co.

(Tokyo, Japan). SBS (product no. 791), from Yueyang Petrochemical Co., Ltd. (Yue yang, China), was used to produce linear SBS, containing 30 wt % St, with a number-average molecular weight of 130,000 by gel permeation chromatography. DBM, MAA, MAH, and St monomers (analytical grade) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Radiation grafting

DBM and MAA monomers of given concentrations were dissolved in an aqueous solution with a surfactant and cyclohexane, whereas MAH and St (in a 1 : 1 molar ratio) were dissolved in toluene. SBS was immersed in the solution, which was stirred to form a uniform mixture that was allowed to cure for 24 h before its transfer to glass ampules for radiation grafting. The ampules were evacuated and irradiated at the ambient temperature by ^{60}Co γ-rays to 10 kGy at a dose rate of 0.606 kGy/h. The grafted SBS was washed with water and acetone to remove the residual monomer and homopolymer and was vacuumdried at 60°C to a constant weight. The experimental conditions were optimized by previous experiments.[15,16]

The degree of grafting (G) was determined by titration and calculated with eq. (1):

$$G = \frac{\frac{C_{KOH}V_{KOH} - C_{HCl}V_{HCl}}{1000(\times 2)} \times M}{w} \times 100\% \qquad (1)$$

where C_{KOH} and C_{HCl} are concentrations (mol/L) of KOH–ethanol and HCl–ethanol, respectively; V_{KOH} and V_{HCl} are volumes (ml) of KOH–ethanol and HCl–ethanol, respectively; M is the molecular weight of the monomer; and w is the weight (g) of the grafted SBS. For DBM or MAH, the difference between molar KOH and molar HCl was divided by 2.

Fourier transform infrared (FTIR) analysis

The grafted SBS was characterized by FTIR spectroscopy in a transmittance mode on a Vatar 370 FTIR spectrometer (Nicolet, Instrument, Madison, Wisconsin, United States). The FTIR spectra were recorded from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} and 32 scans.

Blending

Blends of different compositions were prepared with a Haake internal mixer. PA6 and SBS were vacuumdried at 80 and 60°C, respectively, for 24 h for 10 min of blending at 210°C and a screw speed of 30 rpm. The compositions (wt %) of the PA6/SBS, PA6/SBS-g-DBM, PA6/SBS-g-MAA, and PA6/SBS-g-MAH were 90/10, 70/30, or 50/50, whereas the PA6/SBS/SBS-g-DBM, PA6/SBS/SBS-g-MAA, and PA6/SBS/SBS-g-MAH compositions were 70/20/10 or 70/10/20.

Scanning electron microscopy (SEM) imaging

The specimens were fractured in liquid nitrogen and etched in boiling toluene to remove the SBS particles. The surfaces of the samples were coated by gold sputtering before they were scanned in a JEOL JSM-6360LV scanning electron microscope (JEOL Ltd., Tokyo, Japan) operated at 15 kV. The number-average diameter of the SBS phase was analyzed with Image-Pro Plus software (Media Cybernetics Co., Bethesda, Wisconsin, United States).

Rheological measurements

Rheological behaviors of the samples were investigated with a strain-controlled rheometer (Advances Rheology Expanded System, TA Instruments, Twin Lakes, Wisconsin, United States). The specimens were processed by a plate vulcanization machine at 225°C to form a layer thickness of about 1 mm.

Dynamic frequency tests from 0.1 to 100 rad/s were performed at 230°C with a strain of 2.0% in a parallel-plate geometry 25 mm in diameter. Dynamic temperature tests were performed over the temperature range of 0–210°C in temperature increments of 3°C under a frequency of 1.0 rad/s and a strain of 0.5% with torsion rectangular geometry. The specimen size was 30 × 12.5 × 1.2 mm^3. The rheological parameters, that is, viscosity, storage modulus (G′), and loss factor (tan δ), were collected automatically by RSI Orchestrator software (TA Instruments, Twin Lakes, Wisconsin, United States).

RESULTS AND DISCUSSION

Grafting of SBS

The graft yields of SBS-g-DBM, SBS-g-MAA, and SBS-g-MAH were 3.68, 3.23, and 3.06, respectively.

SBS-g-MAH was cografted with St because grafting just MAH onto SBS produced a very low grafting yield on account of the lower polymeric activity of the MAH monomer. However, this could be improved by binary-monomer grafting of MAH and St, which, having about the same reactivity ratio, could increase the grafting yield of MAH noticeably. As we reported previously,[16] with a grafting system of 5 wt % MAH and a 1 : 1 molar ratio of MAH to St, the grafting yield (15 kGy of irradiation) of MAH was about 3 times higher than that of a system with just MAH.

Figure 1 shows FTIR spectra of SBS, SBS-g-DBM, SBS-g-MAA, and SBS-g-MAH after the free monomer and homopolymer were completely extracted from the samples. With reference to the virgin SBS spectra, the new peak at 1736 cm^{-1} in the spectra of SBS-g-DBM was attributed to the carbonyl stretching
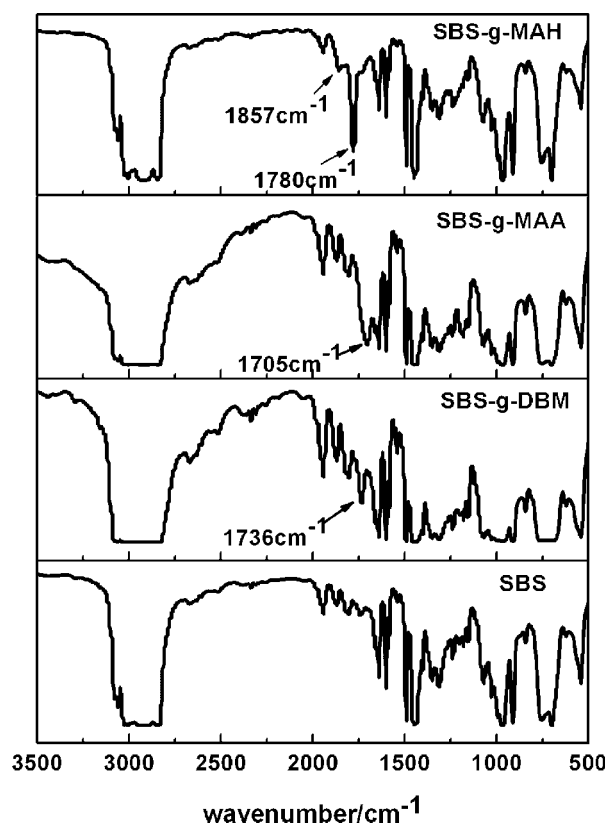
Figure 1 FTIR spectra of SBS, SBS-*g*-DBM, SBS-*g*-MAA, and SBS-*g*-MAH.

vibration. This indicated that DBM had been grafted onto SBS.[17] In the spectra of SBS-*g*-MAA, the new band at 1705 cm^{-1} of the carbonyl stretching vibration implied the grafting reaction of SBS with MAA.[5] In the spectrum of SBS-*g*-MAH, the weak asymmetric and symmetric carbonyl vibration at 1857 and 1780 cm^{-1} indicated that MAH had been grafted onto SBS.[18] In addition, the characteristic peak of SBS did not change before and after grafting.

Morphology of the blends

SEM images of cryogenically fractured and etched surfaces of PA6/SBS blends are shown in Figure 2 (×1000), and larger magnification (×5000) images are given in Figure 3 for better observation of the surface structure. The PA6/SBS ratio of 70/30 was used to ensure the continuous phase of PA6 and prominent effect of the modified polymer alloy. One can see clearly from the PA6/SBS SEM images that it was in a two-phase morphology, with the SBS dispersed phase in spherical domains in the continuous PA6 [Fig. 2(a)]. The SBS dispersed-phase particles of PA6/SBS-*g*-DBM [Fig. 2(b)] were much larger, whereas the particles of PA6/SBS-*g*-MAA [Fig. 2(c)] or PA6/SBS-*g*-MAH [Fig. 2(d)] were much smaller, than those of PA6/SBS. The domain size is often used to indicate the extent of compatibility of multi-
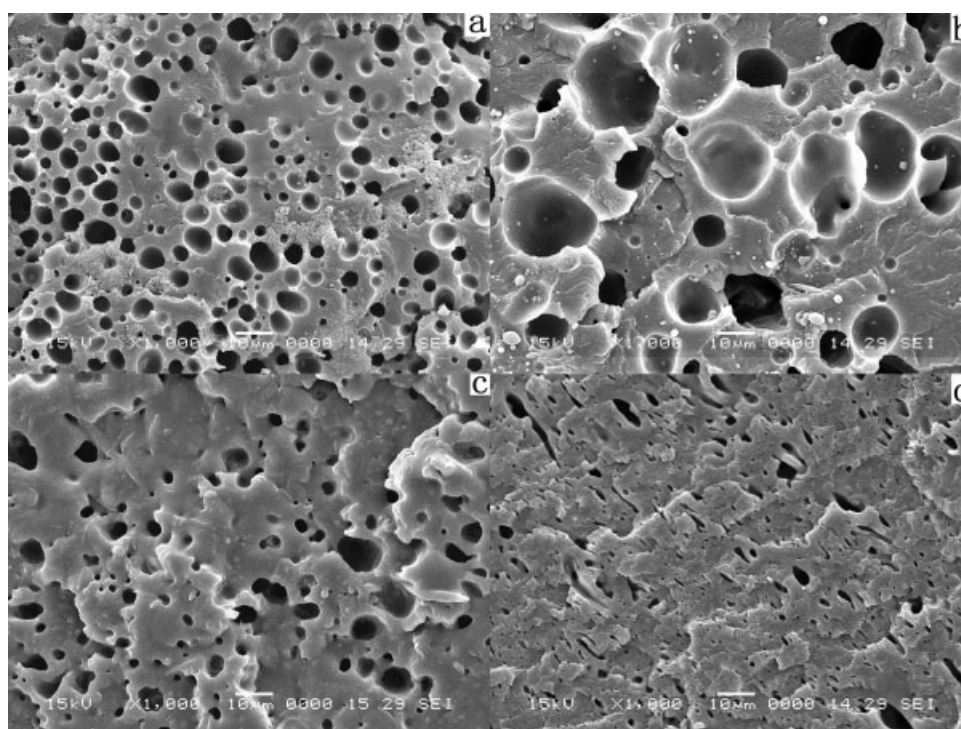

Figure 2 SEM images of fractured and etched surfaces of PA6/SBS (70/30) blends (×1000): (a) PA6/SBS, (b) PA6/SBS-*g*-DBM, (c) PA6/SBS-*g*-MAA, and (d) PA6/SBS-*g*-MAH.
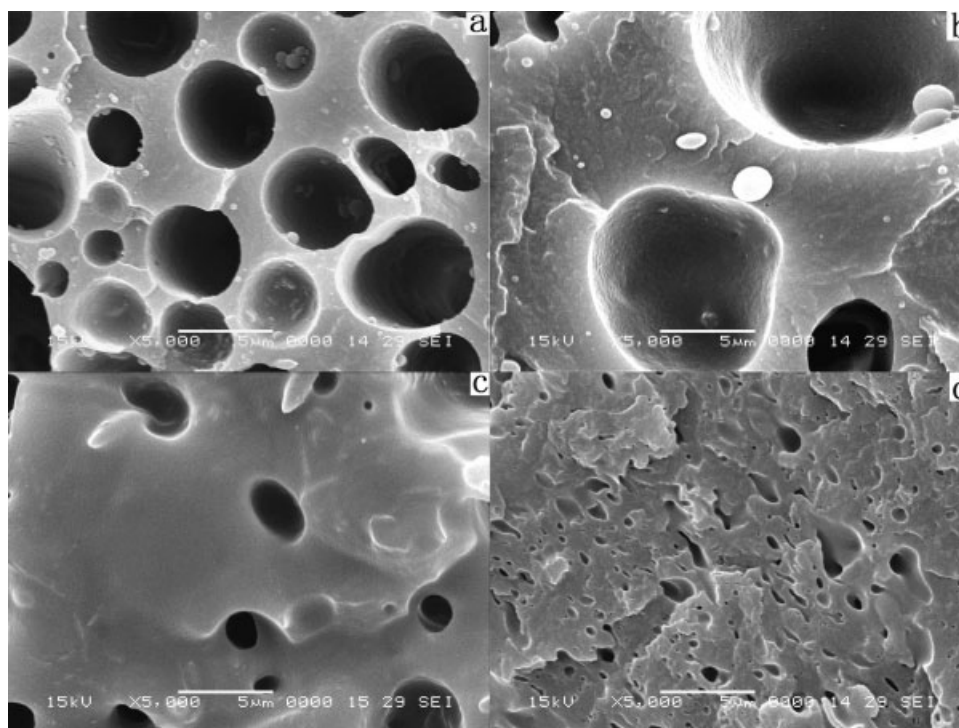
Figure 3 SEM images of fractured and etched surfaces of PA6/SBS (70/30) blends (×5000): (a) PA6/SBS, (b) PA6/SBS-*g*-DBM, (c) PA6/SBS-*g*-MAA, and (d) PA6/SBS-*g*-MAH.

phase polymer systems; that is, the smaller the domain size is, the more compatible the systems are and the better the mechanical properties are.[19–21] Therefore, grafting DBM decreased the compatibility of PA6/SBS, whereas grafting MAA or MAH enhanced the compatibility.

The two phases of PA/SBS in Fig. 3(a) have clear and sharp interfacial boundaries, and the fractured surface looks smooth and uniform; this implies brittle fracture properties. For SBS grafted with MAA or especially MAH, the surface became rougher, with more dimples and tearing ridges, than that of PA6/SBS. In other words, PA6/SBS-*g*-MAA and PA6/SBS-*g*-MAH had ductile fracture properties. The changes may be a manifestation of lower interfacial tension, higher adhesion at phase boundaries, and enhanced compatibility of the blend.

The three kinds of grafted SBSs with different contents were blended with PA6. The cryogenically fractured and etched samples were scanned by SEM (Fig. 4), and the number-average diameter of the SBS dispersed phase was analyzed with Image-Pro Plus software (Fig. 5). From the figures, one finds that as the SBS content increased from 0 to 30%, the SBS dispersed phase of different blends changed differently in its dimensions. For PA6/SBS-*g*-DBM, the size of the SBS dispersed phase grew markedly and the fracture surface changed inconspicuously, whereas the size decreased and the surface became less smooth for PA6/SBS-*g*-MAA or PA6/SBS-*g*-

MAH. This suggests that the compatibility of PA6/SBS-*g*-DBM may be worsened with a larger amount of grafted DBM, whereas the compatibility of PA6/SBS-*g*-MAA or PA6/SBS-*g*-MAH may be enhanced with more grafted MAA or MAH. In addition, the decrease in the number-average diameter of the SBS dispersed phase in PA6/SBS-*g*-MAH was sharper than that of PA6/SBS-*g*-MAA. This indicated better compatibility of PA6/SBS-*g*-MAH.

Rheological behavior of the blends

Dynamic frequency sweep

The PA6/SBS blends in a 70/30 ratio showed a monotonous decrease in the viscosity for every system as the shear rate increased (Fig. 6); this indicated the pseudoplastic nature of the blends. In comparison with PA6/SBS, the viscosity of PA6/SBS-*g*-MAA and PA6/SBS-*g*-MAH increased apparently, whereas the viscosity of PA6/SBS-*g*-DBM remained unchanged basically. Figure 7(a,b) shows viscosity curves of PA6/SBS-*g*-MAA and PA6/SBS-*g*-MAH with different ratios. With reference to PA6/SBS, the viscosity of the blends with grafted SBS increased with the SBS content as SBS had a higher viscosity than PA6. For the blends of the same ratio, the viscosity of the PA6/SBS-*g*-MAA or PA6/SBS-*g*-MAH was higher than that of PA6/SBS. With a lower content (10%) of grafted SBS, the viscosity increase was
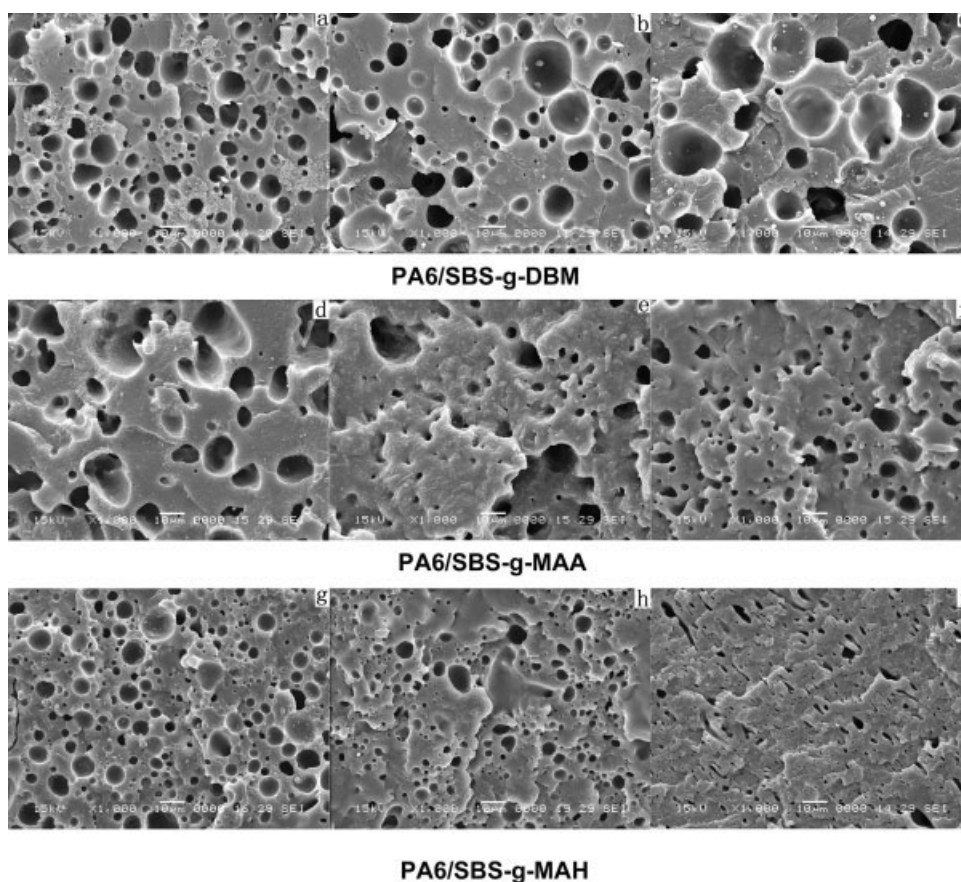
Figure 4 SEM images of fractured and etched surfaces of PA6/SBS blends (×1000): (a) 70/20/10 PA6/SBS/SBS-*g*-DBM, (b) 70/10/20 PA6/SBS/SBS-*g*-DBM, (c) 70/0/30 PA6/SBS/SBS-*g*-DBM, (d) 70/20/10 PA6/SBS/SBS-*g*-MAA, (e) 70/10/20 PA6/SBS/SBS-*g*-MAA, (f) 70/0/30 PA6/SBS/SBS-*g*-MAA, (g) 70/20/10 PA6/SBS/SBS-*g*-MAH, (h) 70/10/20 PA6/SBS/SBS-*g*-MAH, and (i) 70/0/30 PA6/SBS/SBS-*g*-MAH.

smaller because of the limited amount of the graft monomer, whereas with a 50% concentration of the grafted SBS, the number of graft chains was large enough to make a marked viscosity contribution to the blend.

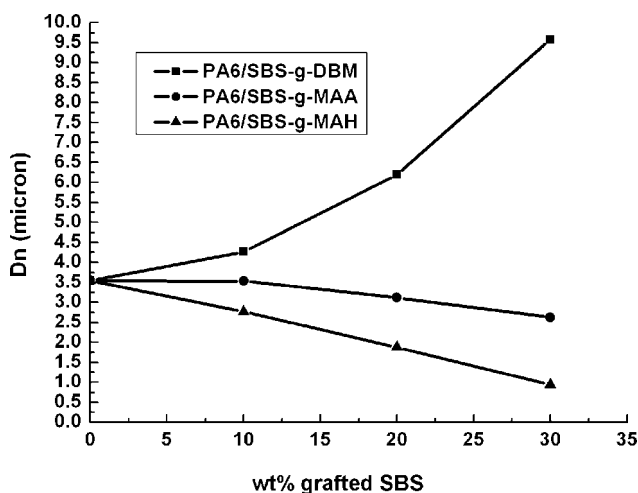The rheology behavior of viscosity is generally a reflection of the inner friction among the molecules.

Figure 5 Average diameter (D_n) of the SBS dispersed phase of PA6/SBS with different amounts of grafted SBS.
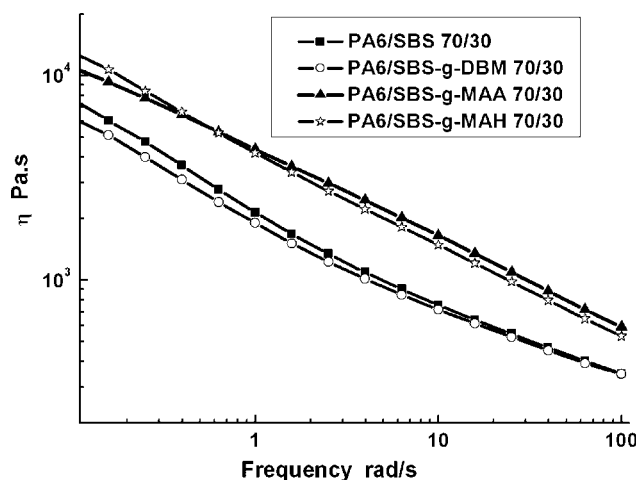

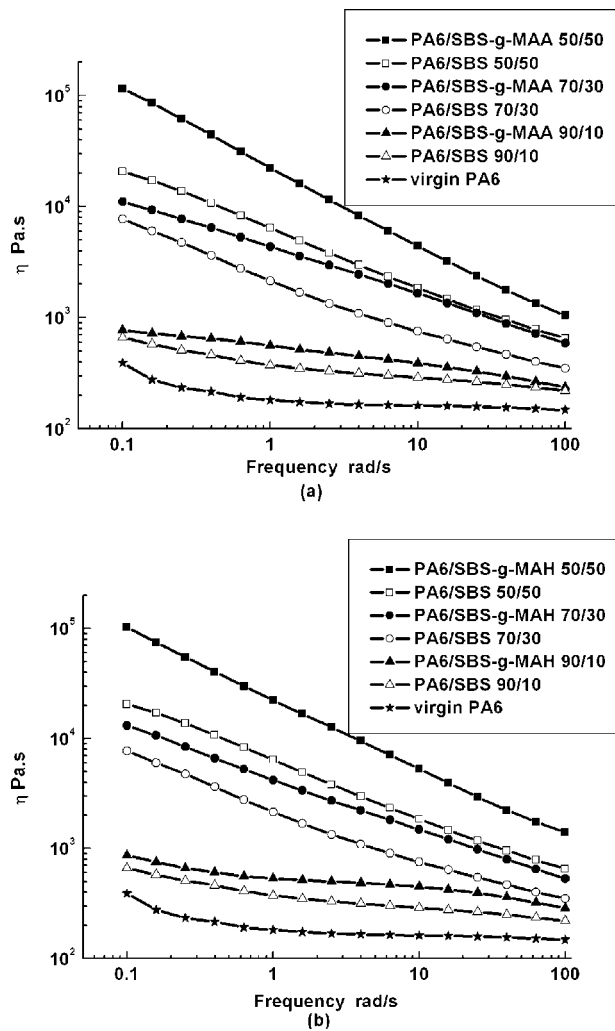**Figure 6** Viscosity (η) versus the shear rate for PA6/SBS blends in a 70/30 ratio at 230°C.

Figure 8 G' versus the shear rate for PA6/SBS blends in a 70/30 ratio at 230°C.

ure 9 shows changes in tan δ with the temperature. In the curve, the tan δ peak represents the glass transition temperature (T_g) of the polymer. For the blends of two polymers with a tremendous difference in T_g, one single tan δ peak exists when the two polymers are compatible. With incompatibility, the blends have two tan δ peaks corresponding to the original T_g values, whereas with partial compatibility, the blends have two tan δ peaks, which are located more closely between the two original tan δ peaks.

For all the blends but PA6/SBS-g-DBM, the tan δ curves exhibit two peaks, which represent T_g of PA6 and SBS, with the former being lower than the latter. It deserves mention that the two peaks are close to each other with MAA- or MAH-grafted SBS. This suggests the better compatibility of the PA6/SBS-g-MAA and PA6/SBS-g-MAH blends. The introduction of MAA or MAH enforced the interfacial adhe-

Figure 7 Viscosity (η) versus the shear rate for (a) PA6/SBS-g-MAA and (b) PA6/SBS-g-MAH with different SBS contents at 230°C.

Introducing MAA or MAH into the blends made them more resistant to flow. Because of the inner friction increase, the interfacial adhesion between PA6 and SBS was improved, and hence the compatibility was enhanced.[19,20] Introducing DBM into the blends, however, did not affect the viscosity.

The rheological tests also revealed the relationship of G' and the shear rate (Fig. 8). G' of PA6/SBS-g-MAA and PA6/SBS-g-MAH was much greater than that of PA6/SBS over the entire frequency range, and this implied a flow property change to a more solid-like type because of stronger adhesion between PA6 and SBS.[19,22] No significant change in G' of PA6/SBS-g-DBM, however, was observed.

Dynamic temperature sweep

The dynamic temperature sweep was performed from 0 to 210°C with the blends in a 70/30 ratio. Fig-
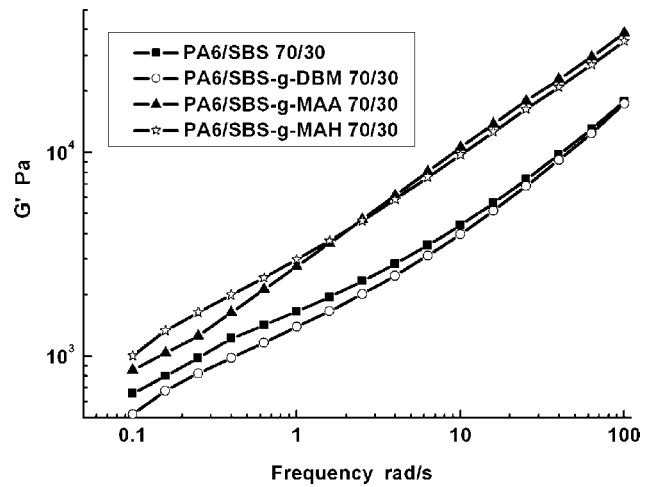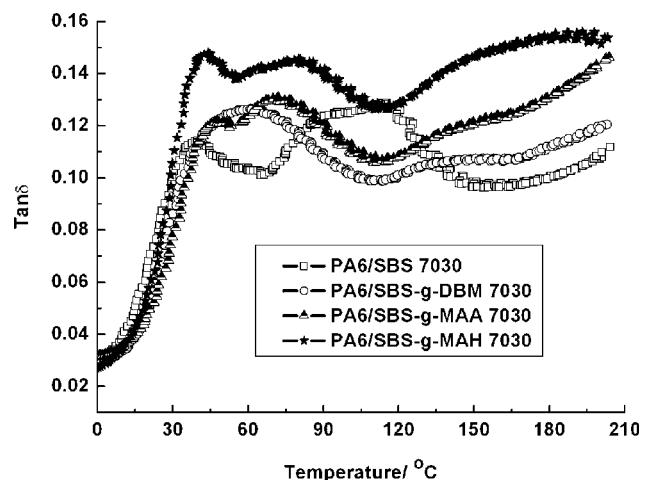

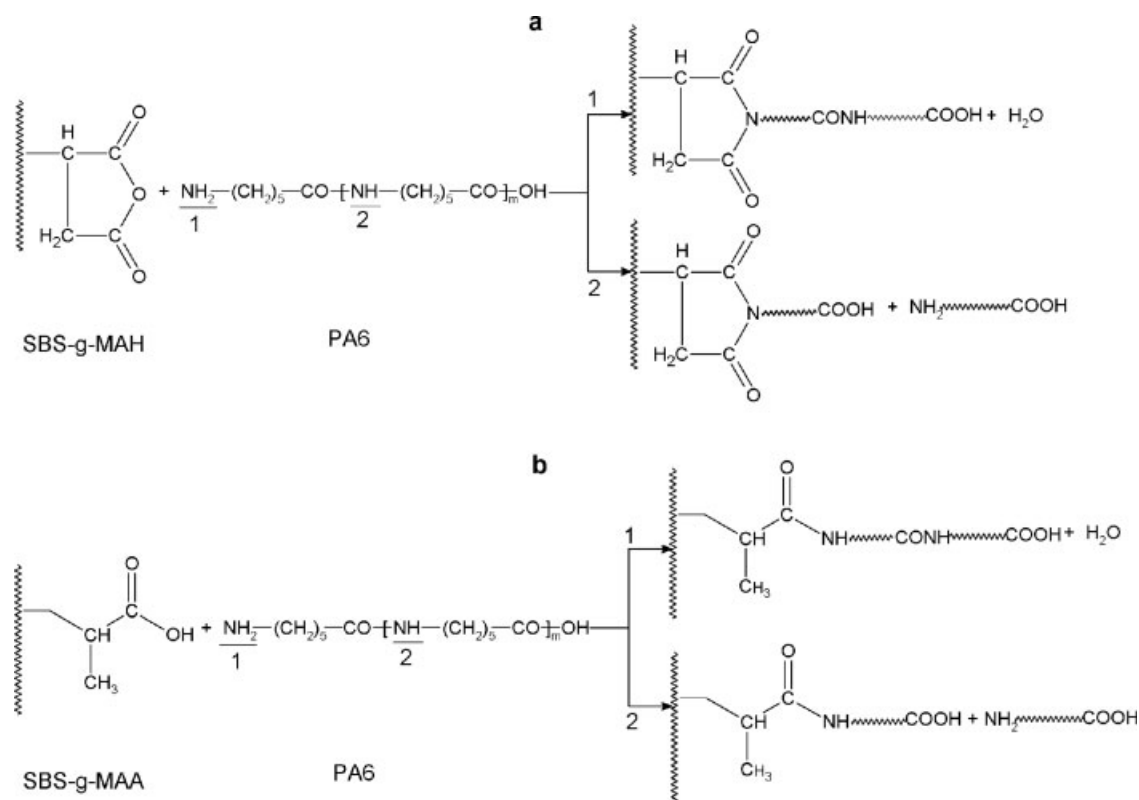**Figure 9** Tan δ of PA6/SBS blends in a 70/30 ratio.

Figure 10 Interfacial reaction between PA6 and (a) MAH and (b) MAA.

sion of PA6 and SBS; as a result, the two immiscible phases were immersed in each other and tended to become the homogeneous phase, which was responsible for the lower T_g of SBS and the higher T_g of PA6.[23] For unknown reasons, tan δ of PA6/SBS-*g*-DBM did not vary as regularly, and further studies are needed to overcome the problem.

Potential reactions between grafted SBS and PA6

From the experimental results, we can conclude that SBS grafted with MAA or MAH can enhance the compatibility of PA6/SBS blends (SBS-*g*-MAH is better). This can be attributed to chemical interactions between MAA or MAH groups and amine groups of PA6, generating bridges between PA6 and SBS and leading to reduced interfacial tension and enhanced interfacial adhesion and viscosity.[3–5,7,12,24–28] With an increasing amount of MAA or MAH on SBS, the dispersion of SBS in the PA6 matrix becomes finer, with increased viscosity and G' of the blends. The sketch maps of the interactions are shown in Figure 10. The amine end groups and the amide links of PA6 can interact with the anhydride or acid groups, but the amine reaction proceeds much faster than the amide reaction.[28–30] Additionally, the number of amine end groups and amide links is in excess to the MAA or MAH units over the entire composition range under investigation. Therefore, the anhydride

or acid/amine (or amide) reaction is dominant. The reaction between the amine (or amide) and anhydride or acid is nucleophilic substitution, and the reaction activity of the acid anhydride is stronger than that of carboxylic acid. Under the same processing conditions, the MAH/amine (or amide) reaction is expected to be more complete than the MAA/amine (or amide) reaction. This is a possible reason for the better compatibility of PA6/SBS-*g*-MAH than PA6/SBS-*g*-MAA. Moreover, some publications have reported that in immiscible PA6/polyolefin blends, MAH is more effective than acrylic acid (AA) as a compatibilizing agent. For example, in an LDPE/PA6 blend, the compatibility effect of PE functionalized by MAH was higher than that of ethylene–acrylic acid copolymers.[31] In an isotactic PP/PA6 blend, MAH was more effective than AA in improving the compatibility.[32] In a blend of PA6 and a poly(methyl methacrylate) grafted shell of core–shell impact modifiers, a styrene–maleic anhydride copolymer was more effective than a styrene–acrylic acid copolymer as the reactive element of compatibilizers.[33] This is consistent with our experimental results.

DBM-functionalized SBS did not affect the compatibility or even morphology of the PA6/SBS blend. Possible reasons include short grafting chains of SBS-*g*-DBM that may have depressed the reaction efficiency of the DBM groups with the amine groups of PA6, steric factors that may have hindered reac-

tivity because of the butyl group linked by an ester group, and fluidity of the blend that may have been worsened by DBM-grafted SBS and may have induced an incomplete DBM/amine reaction. All these resulted in adverse effects on the DBM/amine reaction that helped in strengthening interfacial adhesion between PA6 and SBS. Besides, the DBM grafting increased the molecular branch of SBS; hence, the SBS dispersed phase was larger in the morphology.

CONCLUSIONS

Graft copolymers SBS-*g*-DBM, SBS-*g*-MAA, and SBS-*g*-MAH as compatibilizers of PA6/SBS blends were synthesized by irradiation. The morphology and rheology of the blends were examined. Introducing MAA or especially MAH enhanced the compatibility of PA6/SBS. PA6 blended with MAH- or MAA-grafted SBS had a smaller SBS dispersed phase and increased viscosity and G'. The effects became stronger as the MAA or MAH graft on SBS increased. This can be attributed to chemical interactions between the MAA or MAH groups and the amine groups of PA6, leading to reduced interfacial tension and enhanced interfacial adhesion. The improved compatibility of PA6/SBS blends with radiation-grafted SBS suggests promising engineering applications.

References

1. Paul, D. R.; Newman, S. Polymer Blends; Academic: New York, 1978; Vol. 1.
2. Shi, D.; Ke, Z.; Yang, J. H.; Gao, Y.; Wu, J.; Yin, J. H. Macromolecules 2002, 35, 8005.
3. Horiuchi, S.; Matchariyakul, N.; Yase, K.; Kitano, T.; Choi, H. K.; Lee, Y. M. Polymer 1996, 37, 3065.
4. Jafari, S. H.; Pötschke, P.; Stephan, M.; Warth, H.; Alberts, H. Polymer 2002, 43, 6985.
5. Wu, D. Z.; Wang, X. D.; Jin, R. G. J Appl Polym Sci 2006, 99, 3336.
6. Wang, C.; Su, J. X.; Li, J.; Yang, H.; Zhang, Q.; Du, R. N.; Fu, Q. Polymer 2006, 47, 3197.
7. Bhattacharyya, A. R.; Ghosh, A. K.; Misra, A.; Eichhorn, K. J. Polymer 2005, 46, 1661.
8. Pal, S. K.; Kale, D. D. J Polym Res 2000, 7, 107.
9. Kudva, R. A.; Keskkula, H.; Paul, D. R. Polymer 2000, 41, 225.
10. Okada, O.; Keskkula, H.; Paul, D. R. Polymer 1999, 40, 2699.
11. Araújo, E. M.; Hage, E.; Carvalho, A. J. F. J Mater Sci 2003, 38, 3515.
12. Wu, D. Z.; Wang, X. D.; Jin, R. G. Eur Polym J 2004, 40, 1223.
13. Wei, Q.; Chionna, D.; Pracella, M. Macromol Chem Phys 2005, 206, 777.
14. Yoon, B. S.; Joang, Y.; Suh, M. H.; Lee, Y. M.; Lee, S. H. Polym Compos 1997, 18, 757.
15. Fu, H. Y.; Xie, L. D.; Yu, M.; Li, L. F.; Yao, S. D. J Radiat Res Radiat Process 2005, 23, 179.
16. Zhang, Y.; Xie, L. D. Li, L. F. Fu, H. Y. Sheng, K. L. J Radiat Res Radiat Process 2006, 24, 293.
17. Yang, A. H.; Dan, X. C.; Tong, S. Y.; Zhang, L. J. China Synth Resin Plast 2006, 23, 18.
18. Wilhelm, H. M.; Felisberti, M. I. J Appl Polym Sci 2002, 83, 2953.
19. Hong, S. M.; Hwang, S. S.; Choi, J. J.; Choi, H. J. J Appl Polym Sci 2006, 101, 1188.
20. Wang, X. D.; Li, H. Q. J Mater Sci 2001, 36, 5465.
21. Takeda, Y.; Keskkula, H.; Paul, D. R. Polymer 1992, 33, 3173.
22. Wang, W. J.; Zheng, Q. J Mater Sci 2005, 40, 5545.
23. Gao, J. G.; Li, D. L.; Wang, D. Y.; Yang, L. T. Eur Polym J 2000, 36, 2517.
24. Ide, F.; Hasegawa, A. J Appl Polym Sci 1974, 18, 963.
25. Shariatpanahi, H.; Nazokdast, H.; Hemmati, M. J Appl Polym Sci 2003, 88, 54.
26. Ohlsson, B.; Hassander, H.; Törnell, B. Polymer 1998, 39, 6705.
27. Filippi, S.; Chiono, V.; Polacco, G.; Paci, M.; Minkova, L. I.; Magagnini, P. Macromol Chem Phys 2002, 203, 1512.
28. Kudva, R. A.; Keskkula, H.; Paul, D. R. Polymer 2000, 41, 239.
29. Maréchal, P.; Coppens, G.; Legras, R.; Dekoninck, J. M. J Polym Sci Part A: Polym Chem 1995, 33, 757.
30. De Roover, B.; Devaux, J.; Legras, R. J Polym Sci Part A: Polym Chem 1997, 35, 901.
31. Jiang, C. H.; Filippi, S.; Magagnini, P. Polymer 2003, 44, 2411.
32. Johannes, K. F. Reactive Polymers: Fundamentals and Applications; William Andrew: New York, 2005.
33. Lu, M.; Keskkula, H.; Paul, D. R. Polym Eng Sci 1994, 34, 33.