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Preparation of functionalized polystyrene by reactive extrusion and its blend with polyamide 6

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Maleic anhydride (MAH) was grafted to polystyrene (PS) by reactive extrusion in the presence of a free-radical initiator. The grafting reaction was confirmed by spectroscopic analyses. The amount of MAH grafted on PS was evaluated by a titration method. The polystyrenes functionalized with MAH (MPSs) were blended with polyamide 6 (PA6), and the effect of MAH units incorporated in PS on the compatibility with PA6 was examined by measuring the morphology, rheological and tensile properties. Although the content of MAH in MPS prepared in this study was much less than 1 wt%, a significant change in the morphology and rheological and tensile properties of PA6/MPS blends was observed. The formation of PS-*g*-PA6 copolymers during melt mixing of PA6 and MPS was evaluated using spectroscopic analyses and also confirmed from the high stability of the suspension obtained by dissolving the blend in formic acid. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyamide 6; polystyrene; reactive extrusion)

INTRODUCTION

Immiscible polymer blends are characterized by a two-phase morphology, a thin interface, and poor physical and chemical interactions across the phase boundaries. Therefore immiscible blends often exhibit poor mechanical properties if these problems are not alleviated by appropriate methods. Block or graft copolymers of appropriate chemical structure have been utilized for modifying the interfacial properties of immiscible polymer blends[1,2]. The copolymers segregate at the interface and thus act as an emulsifier, reducing interfacial tension. However, although the addition of copolymers provides an effective method to alleviate the problems of immiscible polymer blends, block or graft copolymers have disadvantages such as difficulty in their synthesis.

As an alternative to replace the method of adding block or graft copolymers separately, compatibilization through the *in situ* formation of compatibilizer in polymer blends has become increasingly important. *In situ* formed compatibilizers are obtained by blending suitable functionalized polymers capable of enhancing specific interactions and/or chemical reactions. The procedure of reactive processing offers a number of advantages over the separate addition type[3]. Details of the compatibilization method, the compatibilization mechanism, and the types of chemical reactions have been well reviewed in the literature[4].

Both polyamide 6 (PA6) and polystyrene (PS) are commodity polymers that possess unique properties individually. A polymer blend of PA6 and PS is expected to be highly desirable because of its commercial potential. In practice, however, it is difficult to obtain good performance because PA6 and PS are immiscible. Therefore, studies aimed at enhancing the compatibility between PA6 and PS have been carried out by various investigators[5–10]. These works have studied the use of functionalized polystyrenes as a compatibilizer: the functional monomers, which can interact with the amine or carboxylic end groups of PA6, are introduced in PS through an appropriate copolymerization method. Various functional monomers such as methacrylic acid[5], maleic anhydride (MAH)[6], acrylic acid[7], glycidyl methacrylate[8] and sulfonic acid[10] have been successfully used in this way to compatibilize PS with PA6. Although many studies on the compatibility of this blend system have been reported, studies on the preparation of functionalized polystyrene via melt extrusion (melt grafting of MAH anhydride on to PS) and its effects on the compatibility of PA6 and PS blends have not been reported to date.

Reactive extrusion has been used to introduce other types of functional groups into polymers and to modify existing functional groups[3]. One of the most common subjects in this field is grafting of MAH, the reaction scheme of which is well known. Polyethylene, ethylene–propylene copolymers and other polymers have been used as base polymers for grafting MAH[11–16]. However, the similar grafting reactions of molten PS with MAH have been rarely reported.

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Table 1 Properties of polymers

Designation	$\bar{M}_n$ ($\times 10^3$)[a]	$\bar{M}_w$ ($\times 10^3$)[b]	T_g (°C)[c]	MAH content (wt%)
PS	115	306	100	–
PA6	18	–	44	–
MPS-0.08	113	300	100	0.083
MPS-0.11	113	282	99	0.113
MPS-0.18	113	288	97	0.183

[a] Number-average molecular weight measured by gel permeation chromatography (g.p.c.) using THF as eluent

[b] Weight-average molecular weight measured by g.p.c. using THF as eluent

[c] Glass transition temperature determined by differential scanning calorimetry at a heating rate of 20°C min^{-1}

In this work, we attempt to graft MAH on PS through reactive extrusion. The PS-*g*-PA, which is formed during melt mixing of PA6 and PS grafted with MAH (MPS), is examined using spectroscopic analysis and also confirmed from the high stability of the suspension formed by dissolving the blend in formic acid. Also, we investigate the effect of MAH units incorporated in PS on the compatibility with PA6.

EXPERIMENTAL

Materials

Commercial polystyrene and nylon 6 were supplied by Hannam Chemical and Tongyang Nylon Co., respectively. Their properties are listed in *Table 1*. MAH was obtained from Aldrich Chemical Co. and ground to a powder before reaction. 1,3-Bis-(t-butylperoxy isopropyl)benzene (Peradox 14), obtained from Kayaku Noury (Japan), was used as an organic peroxide initiator. Its half-life is about 2.5 min at 180°C.

Functionalization of polystyrene

The functionalization of PS with MAH was carried out in a Brabender twin-screw extruder. The reaction components (pre-dried PS, MAH and initiator) were premixed in a super mixer for 3 min. A temperature gradient was maintained in the barrel of the extruder, with the entrance region being kept at 170°C, the compression zone at 180°C, the metering zone at 190°C and the die at 200°C. The screw speed was set at 20 rev min^{-1}, and the residence time was 5.5 min. The extrudate, obtained in the form of a rod strand, was cooled in ambient air and then pelletized. To control the content of MAH in the MPS, the recipe of the reaction components was varied.

Determination of maleic anhydride content

The amount of MAH grafted on PS was calculated from the acid value. The extruded products were dissolved in tetrahydrofuran (THF) and precipitated into methanol to remove the free MAH. The precipitate was completely dried, dissolved in THF again and two to three drops of distilled water added. The solution was stirred overnight in order to fully hydrolyse the anhydride groups. The acid number was determined by titration with a standardized methanolic NaOH solution (0.001 N) using phenolphthalein as indicator. The acid number was easily converted to the MAH content as follows:

$$\text{MAH [wt\%]} = \frac{\text{acid number [mg KOH/g]} \times 98}{2 \times 400}$$

Blend preparation

The pre-dried polymers were melt-mixed using a Brabender twin-screw extruder operating at a constant speed of 30 rev min^{-1}. The mixing temperature was 230°C, and the residence time was 3 min. Before mixing, the extruder was flushed with nitrogen to avoid potential degradation of the component polymers. The extrudates were pelletized and dried in a vacuum oven at 80°C for 48 h. Only blends containing 80 wt% of PA6 were prepared.

Morphological observations

The morphology of blends was observed with a scanning electron microscope (SEM; Jeol JSM-840A) at an accelerating voltage of 25 kV. The blend samples were fractured at liquid nitrogen temperature, and the cryogenically fractured surface coated with gold. To remove the minor phase in the blends, a solvent extraction method using THF was employed.

Tensile properties

Dumb-bell type specimens were prepared at 230°C using a Mini Max moulder (CS-183MMV, Custom Scientific Instruments). The specimens were tested on a tensile tester (Instron model 1445), all tests being performed at a crosshead speed of 2 mm min^{-1} and a temperature of 20°C. Seven specimens of each blend were tested and average values were taken as experimental data.

Rheological measurements

The dynamic rheological properties of the homopolymers and their blends were measured at 230°C using a rheometer (Rheometrics RMS 800) in the parallel plate mode under a nitrogen atmosphere. The parallel plate geometry has a gap of 2 mm and a radius of 12.5 mm. Strain was maintained at 10%.

Spectroscopic analysis

The presence of MAH grafted on PS was assessed using a Fourier transform infra-red (*FT*i.r.) spectrometer and ^{1}H nuclear magnetic resonance (n.m.r.) spectroscopy. Compression-moulded thin films, which were placed on potassium bromide windows, were prepared for i.r. measurements. One hundred scans at a resolution of 2 cm^{-1} were signal-averaged. The proton n.m.r. spectra were obtained using a Jeol JNM-EX300 FT-NMR spectrophotometer. The solvent used was dimethylsulfoxide-d$_6$ (DMSO-d$_6$).

RESULTS AND DISCUSSION

Characterization of modified polystyrene

Results of modification of PS through reactive extrusion are summarized in *Table 1*. The molecular weight and molecular weight distribution, estimated by polydispersity ($\bar{M}_w/\bar{M}_n$), of functionalized polystyrene (MPS) are nearly the same as those of PS. This means that significant chain scission of PS does not occur under the reaction conditions used in this study. Degrees of

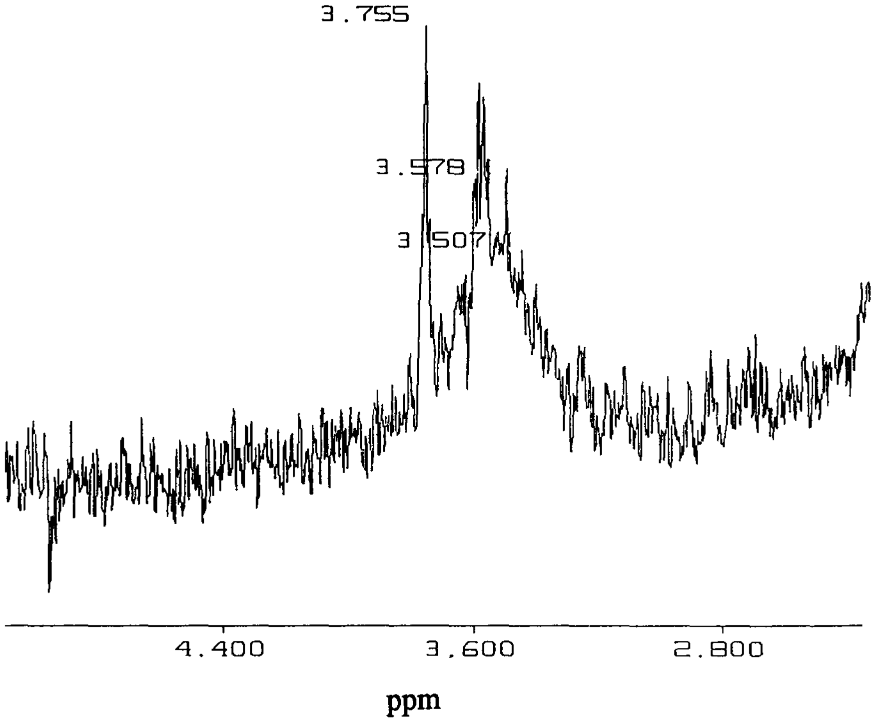

Figure 1 ^{1}H n.m.r. spectrum of MPS-0.18 in DMSO-d_6 solution

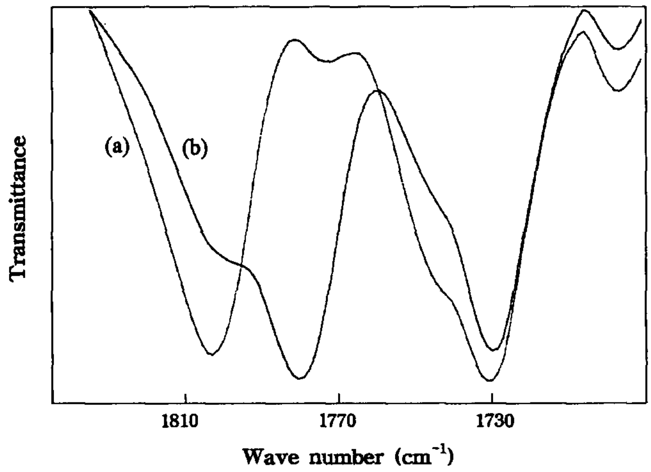

Figure 2 *FT*i.r. spectra of the compression-moulded films of (a) PS and (b) MPS-0.18

grafting obtained here are <0.2 wt% of MAH. MPS-0.18 contains about two MAH units per chain.

Figure 1 shows the ^{1}H n.m.r. spectrum of MPS-0.18 in DMSO-d_6 solution. There is a complex multiplet in the 3.5–3.8 ppm region. A similar multiplet in this region has been observed for dodecylsuccinic anhydride and eicosane-*g*-maleic anhydride products although there is some difference[18,19]. According to the results of Russell[18], the ^{1}H n.m.r. spectrum of dodecylsuccinic anhydride shows resonances centred on 3.30, 3.20 and 2.83 ppm, which are assigned to the methine proton and the two methylene protons of the succinic anhydride ring, respectively. However, since virgin PS has no resonances in this region, one can tentatively conclude that the resonances in the 3.5–3.8 ppm region of MPS result from succinic anhydride rings attached at various positions along the polystyrene chain.

The grafting was also confirmed using *FT*i.r. spectroscopy; *Figure 2* shows the spectrum of MPS-0.18 in the range 2000–1600 cm^{-1}. For PS, some weak combination, overtone absorptions and characteristic resonances of aromatic rings are observed in this region. In the spectrum of MPS (*Figure 2b*), a new absorption band at 1786 cm^{-1}, not observed in the spectrum of PS, is found. This characteristic band is assigned to a carbonyl stretching in MAH grafted on PS[16]. From these results, it is clear that MAH units are introduced into the PS backbone via the reactive extrusion process.

*Characterization of PS-*g*-PA6 copolymers*

The *in situ* reaction between MPS and PA6 during melt mixing may form graft copolymers at the interface between the PA6 and MPS. To characterize the copolymer, this must be separated from the mixed product of the following three species: free PA6, unreacted MPS and PS-*g*-PA6 copolymer. These components were separated by a solvent extraction method described elsewhere[20].

Figure 3 shows *FT*i.r. spectra of MPS and PS-*g*-PA6 copolymer separated from the blend of MPS and PA6 (20/80 by weight). Compared with the spectrum of MPS, that of PS-*g*-PA6 copolymer shows the presence of amide groups as evidenced from the carbonyl stretching at 1734 cm^{-1}, the N–H stretching at 3300 cm^{-1} and the N–H bending at 1560 cm^{-1}. Therefore, it is clear that PS-*g*-PA6 copolymer is formed via chemical reaction between MPS and PA6.

More evidence supporting the formation of graft copolymer is observed from Molau's solubility test[21,22]. In our case, the blends were immersed in formic acid, which is a solvent for PA6 and a non-solvent for PS. If there is no graft copolymer, the dispersed phase (PS component) will separate and float on the solution, as observed in the case of PA6/PS blend. On the other hand, when the blends containing MPS are immersed in formic acid, the blends show a persistent turbidity, indicating

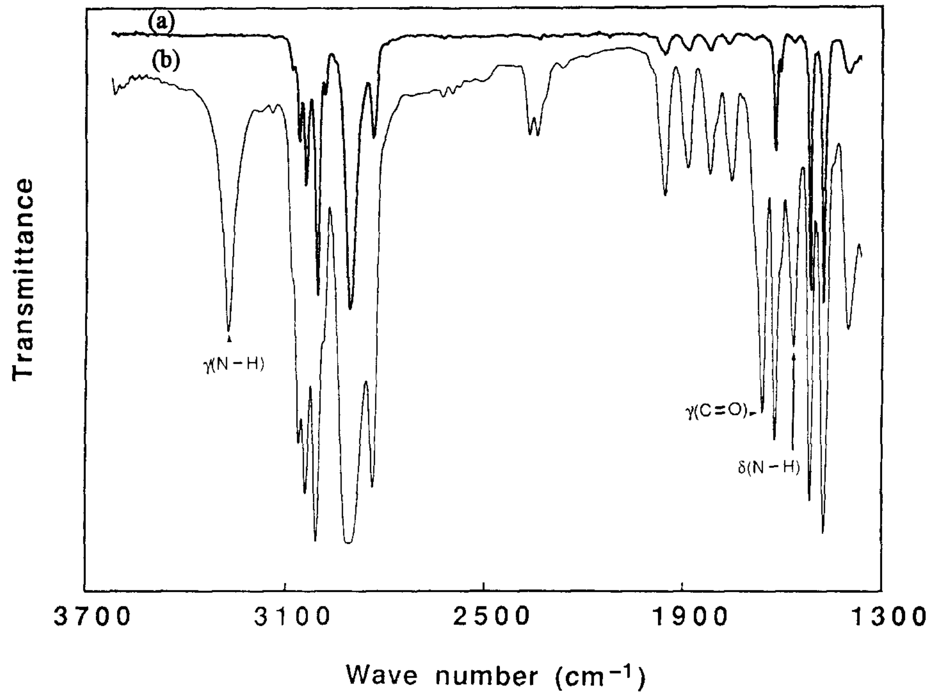

Figure 3 *FT*i.r. spectra of (a) PS and (b) PS-*g*-PA6, separated by centrifuging from the blend of MPS and PA6

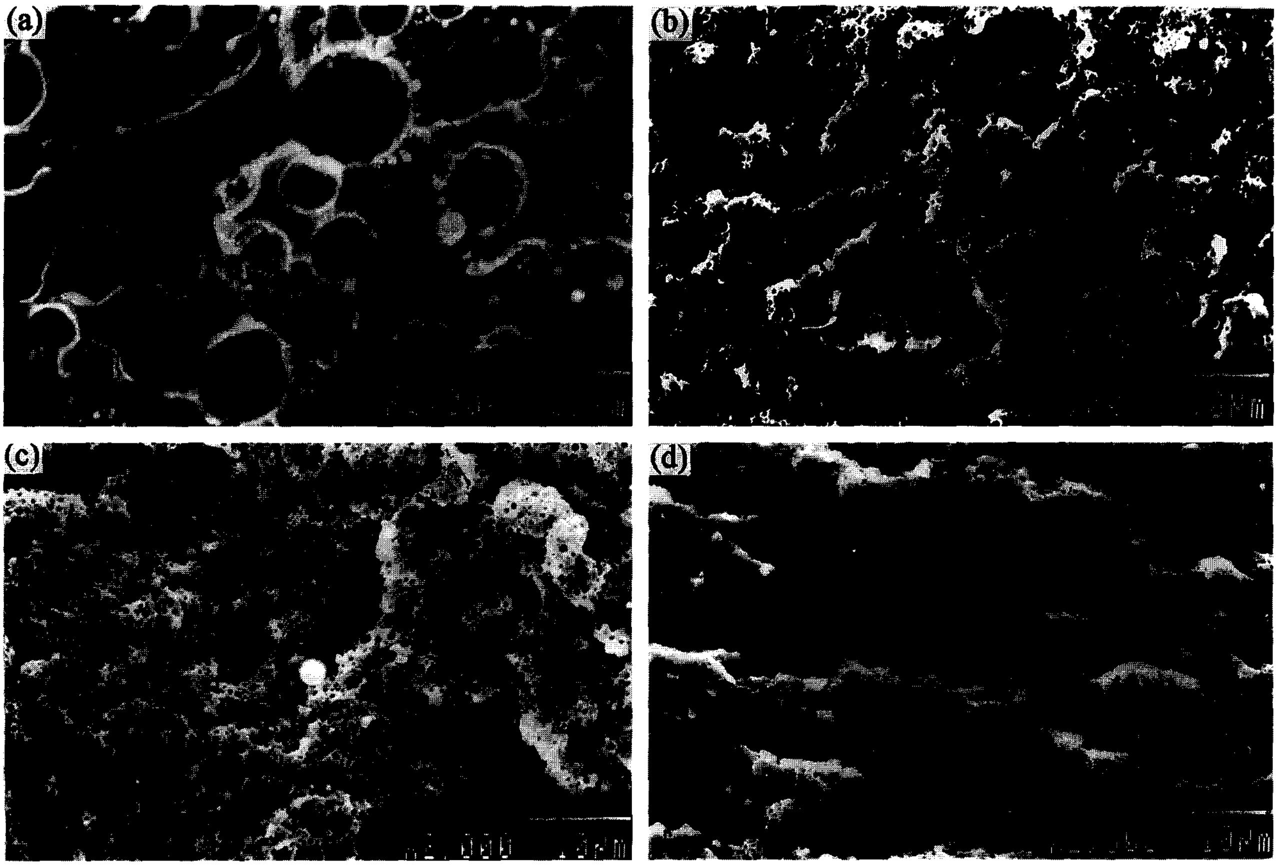

Figure 4 Scanning electron micrographs of 80/20 PA6/MPS blends: (a) PA6/PS; (b) PA6/MPS-0.08; (c) PA6/MPS-0.11; (d) PA6/MPS-0.18

the presence of PA-*g*-PA6 graft copolymer. The results of *Figure 3* and the Molau test indicate that chemical reaction between the anhydride groups of MPS and the amine groups of PA6 takes place during melt mixing.

Blend morphology

In the previous section it was shown that a graft copolymer of PA6 and PS is formed during melt mixing. It is expected that the *in situ* graft copolymer plays a role as an interfacial agent, resulting in the reduction of domain size. The fracture surfaces of blends of PA6 with PS and MPS are shown in *Figure 4*. In the SEM micrograph of the 80/20 PA6/PS blend, PS domains have a well-defined spherical shape and a very broad size distribution. Also, the fracture surface of this blend appears to be very smooth. This is a typical morphology of an incompatible blend. When, instead of PS, MPSs are blended with PA6, the domain size of the dispersed phase is significantly reduced and its distribution becomes more sharp. It is also observed that the domain size decreases with increasing MAH content in MPS.

Interfacial tension, the shear rate of mixing and the viscosity ratio of the blend components are key parameters governing the degree of dispersion[23]. When the shear rate of mixing and the viscosity ratio of the blended polymers are constant, the interfacial tension of the blend plays an important role in reducing the domain size. Therefore, the dramatic effect of the MAH units in MPS on the morphology of PA6/MPS binary blends is due to the interfacial activity of the PS-*g*-PA6 graft copolymers, formed at the interface between PA6 and MPS.

Rheological properties of PA6/MPS blends

The frequency dependence of the complex viscosity for the PA6/MPS blends is shown in *Figure 5*. PA6 shows Newtonian viscosity behaviour over the entire range of frequency examined, while PS shows typical non-Newtonian viscosity behaviour. The viscosity of the PA6/PS blend is lower than those of the two pure components, a typical characteristic of incompatible blends. This behaviour is related to the interlayer slip associated with the repulsive forces between immiscible polymers leading to a reduction of density at the interface[2]. However, as the MAH content in MPS increases, the viscosities of the PA6/MPS blends gradually move to higher values while the blends still show the non-Newtonian behaviour. This observation seems to be attributable to the presence of long branching formed by chemical reaction between the amine groups of PA6 and the MAH units of MPS during melt mixing.

The use of $\log G'$ *versus* $\log G''$ plots is a useful method for rheological characterization. Han and Chuang[24] reported that such plots are very slightly affected by temperature and molecular weight, but strongly dependent upon the molecular weight distribution and side-chain branching. In this plot, data on the upper left side of the equi-modulus line ($G' = G''$) indicate that the rheological properties of the samples are dominated by the viscous response (G'') component, while those on the lower right-hand side are related to the rheological properties dominated by the elastic response (G') component. Shida and Shoroff[25] also suggested that broadening of the molecular weight distribution can result in lower G'' values and increase the slope of the plot.

Figure 6 shows the $\log G'$ *versus* $\log G''$ plots for PA6/PS and PA6/MPS blends. When MPS is used as a blend component the curve shifts from the viscous-dominant region to the elastic-dominant region, and its slope increases. These results suggest that MPS reacts with PA6, resulting in some branching and molecular weight broadening taking place.

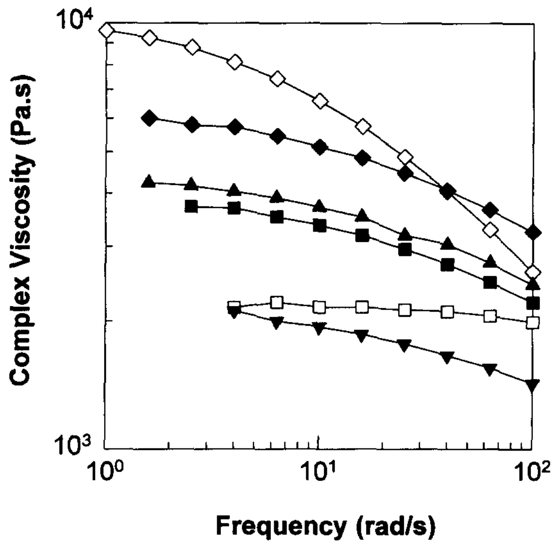

Figure 5 Complex viscosity *versus* frequency for homopolymers and 80/20 PA6/MPS blends: □, PA6; ◇, PS; ▼, PA6/PS; ■, PA6/MPS-0.08; ▲, PA6/MPS-0.11; ◆, PA6/MPS-0.18

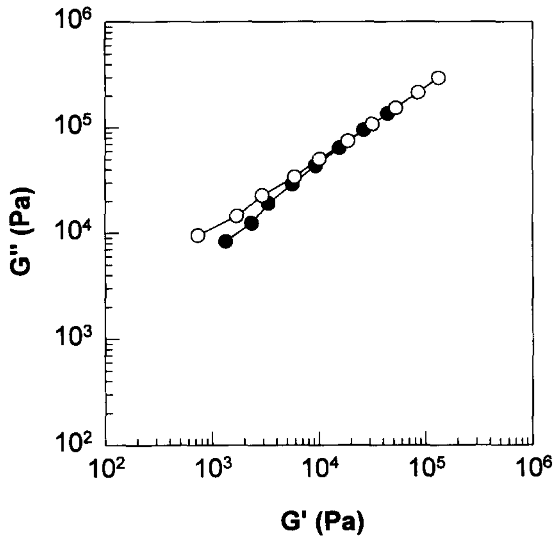

Figure 6 Log–log plot of loss modulus (G'') against storage modulus (G') for 80/20 PA6/PS and PA6/MPS blends: ○, PA6/PS; ●, PA6/MPS-0.11

Table 2 Tensile properties of 80/20 PA6/MPS blends

Blends	Modulus (MPa)	Strength (MPa)	Elongation (%)
PA6/PS	530 ± 30	47.8 ± 1.2	187 ± 13
PA6/MPS-0.08	574 ± 28	54.2 ± 1.4	257 ± 13
PA6/MPS-0.11	594 ± 48	56.8 ± 1.8	243 ± 10
PA6/MPS-0.18	596 ± 47	57.5 ± 2.6	238 ± 11

Tensile properties of PA6/MPS blends

Interfacial adhesion is an important parameter for controlling the mechanical properties of multiphase systems: good adhesion between the matrix and dispersed phase may be essential for proper stress transfer without interfacial debonding. From the morphological observation we realized that the PS-*g*-PA6 copolymer, which is formed during melt mixing, acts as a compatibilizer of the PA6/MPS blends. The mechanical

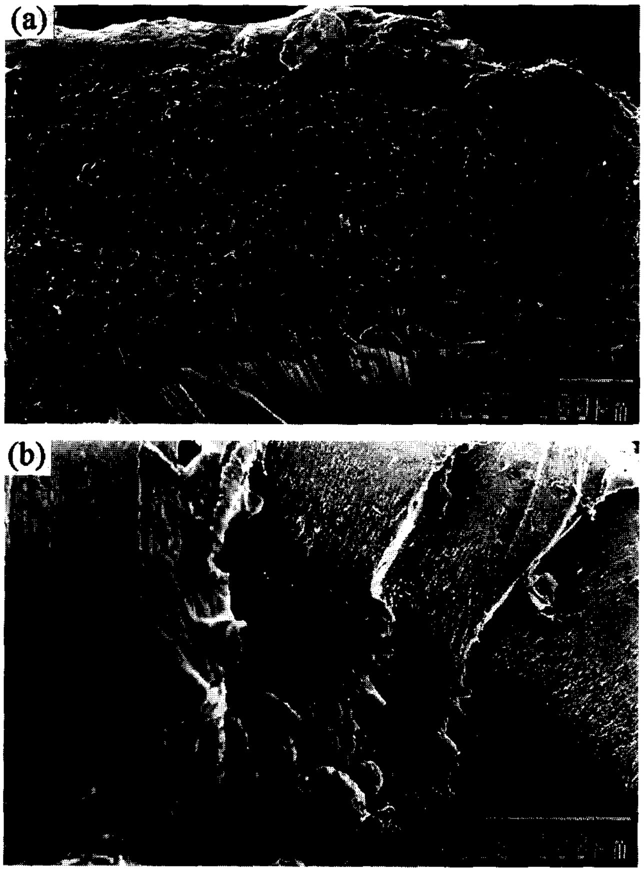

Figure 7 Scanning electron micrographs of fracture surface of 80/20 PA6/PS and PA6/MPS blends after tensile test: (a) PA6/PS; (b) PA6/MPS-0.18

properties of PA6/MPS blends are summarized in *Table 2*; an increase in the tensile properties is observed when MPSs are blended with PA6. The low tensile properties of PA6/PS can be attributed essentially to the larger size of the PS articles with a poor adhesion to the matrix. These domains act as gross material defects, causing premature rupture of the specimen soon after the beginning of yield. On the other hand, in PA6/MPS blends, both particle size reduction and an improvement of interfacial adhesion, caused by the formation of PS-*g*-PA6 copolymer at the interface between PA6 and MPS, seem to lead to the improvement of mechanical properties.

Figure 7 shows SEM micrographs of the fracture surface of PA6/PS and PA6/MPS-0.18 blends after a tensile test. In PA6/PS blends, a sign of the poor adhesion between PA6 and PS is observed from the pull-out of PA6 around PS during the fracture process. However, in PA6/MPS blends, pull-out of the PA6 matrix is not observed, indicating the strong adhesion between PA6 and MPS.

CONCLUSIONS

Polystyrene was grafted with maleic anhydride as a functional modifier in a twin-screw extruder. The results of spectroscopic analysis (n.m.r. and *FT*i.r.) provided evidence that the maleic anhydride units are incorporated in the PS chain. The introduction of MAH units in PS was very effective for controlling the morphology of blends of PA6 with MPS. The domain size of the dispersed phase of 80/20 PA6/MPS blends decreased with increasing MAH content in MPS copolymers, while PA6/PS blends showed morphology typical of an incompatible blend.

The PS-*g*-PA6 copolymers, the reaction products formed during the melt mixing of PA6 and MPS, were separated by a solvent extraction method. The formation of the copolymers was evaluated using both spectroscopic analyses and the Molau test. Also, the rheological properties of the blends provided additional evidence for the formation of long branching between the amine end groups of PA6 and the maleic anhydride unit of MPS during melt mixing. It seems that the formation of the graft copolymers contributes to the compatibility of PA6/MPS binary blends, thus improving mechanical properties.

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