Terminal Anhydride Functionalized Polystyrene by Atom Transfer Radical Polymerization Used for the Compatibilization of Nylon 6/PS Blends

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ABSTRACT: Terminal maleic anhydride functionalized polystyrenes were synthesized using atom transfer radical polymerization (ATRP). The functionality of these polymers was determined through their reaction with poly(ethylene glycol methyl ether) (PEGM) followed by gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR). Melt mixing of these reactive polystyrenes with nylon 6 resulted in blends with good mechanical properties attributed to an in situ formation of a copolymer which may be used for the compatibilization of the binary nylon 6/polystyrene. The mechanical properties of the resulting ternary blends were significantly improved with the addition of the modified polystyrene even when the molecular weight of the polystyrene used was higher than that of the respective block in the copolymer. The enhanced mechanical properties, as well as the fine PS dispersion in the nylon 6 matrix revealed by scanning electron microscopy of the compatibilized cryofractured samples, support the hypothesis that an effective compatibilization of nylon 6/PS has been achieved.

Introduction

Terminal functionalization of polymers represents an interesting field of research because of their macromer character and their potential applications in several technological areas, such as surface modification, adhesion, lubrication, and compatibilization of polymer blends.[1] These polymers can undergo chain extension by reaction with other polymers or monomers having proper counterfunctional groups. An in situ formation of a block copolymer consisting of these functionalized polymers and another polymer bearing proper terminal groups is also possible during blending. Of the reactive pairs investigated, the ones based on the reaction of amines with anhydrides exhibit sufficiently fast kinetics in the melt state to provide technologically useful, compatibilized polymer blends.[2−5]

Various approaches for the terminal functionalization of polystyrenes have been published. Among them Takenaka et al. have reported a method for the synthesis of anhydride-terminated polystyrenes and polydienes involving a Diels−Alder addition of maleic anhydride to a diene-terminated polymer.[6] Park et al. reported on the synthesis of hydroxy-terminated PS and subsequent esterification with trimellitic anhydride chloride (TMAC), resulting in polystyrenes having terminal anhydride groups.[7] Most recently Cernohous et al. succeeded in synthesizing polystyrene bearing a single succinic anhydride at the chain end using anionic polymerization techniques.[8]

Radical polymerizations are important for the industrial production of commodity polymers but are still very difficult to control because of the fast, irreversible termination of the growing radicals through coupling and disproportionation reactions. Because of these termination reactions, many attempts have been made to convert radical polymerizations into living ones.[9−14]

Wang and Matyjaszewski reported on a "living"-controlled radical polymerization technique, the atom transfer radical polymerization (ATRP),[15−16] in which a catalytic amount of a Cu(I) coordination complex reversibly abstracts an X atom (X = Cl, Br) from the polymer chain ends, converting them from a dormant to an active propagating state. Of course in this technique as well as in every radical polymerization, complete elimination of termination reactions is not possible, so it is referred to as "living" in quotations.[17] However, well-defined polymers with predetermined molecular weights, low polydispersities, and terminal functionalities as well as block copolymers can be prepared via ATRP.

The blending of polymers for production of new tailor-made materials at low cost and for recycling mixed polymeric materials has gained great interest in recent years. Polyamide 6 (nylon 6) and polystyrene (PS) are commodity polymers each with unique properties. Thus, a nylon 6/PS blend is expected to have commercial interest because it could provide a combination of the useful properties of its constituents. In practice, it is difficult to obtain such blends with good performance because of the immiscibility of the blend components. Therefore, studies aimed at enhancing the compatibility between nylon and PS have been carried out by various research groups. Most of them deal with functionalized styrene copolymers capable of reacting with amine end groups of the polyamide during melt mixing. The result is an in situ formed compatibilizer having nylon grafts or blocks. Reactive styrene copolymers with anhydrides,[18−20] acrylic acid,[21] ethylene oxide,[22] methacrylic acid,[2] glycidyl methacrylate,[23] or sulfonic acid[24] have been investigated.

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Scheme 1

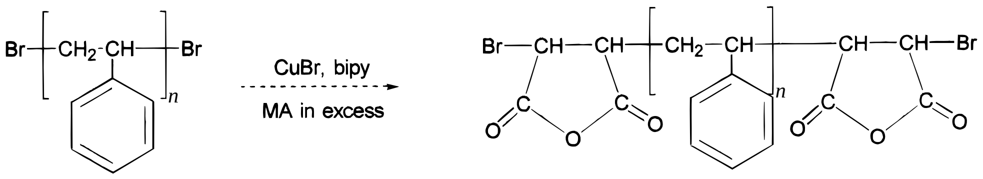


Table 1. GPC Characterization of Synthesized Polystyrenes

sample	M_n	M_w	I (M_w/M_n)
PS-18	18 100	21 300	1.18
PS-15	15 200	17 600	1.16
PS-13	12 700	14 900	1.17
PS-11	11 300	13 400	1.19
PS-6	6000	7000	1.17
PS-3	2500	2800	1.13

In this article, we describe the synthesis of polystyrenes functionalized with maleic anhydride by ATRP and their subsequent reaction with polyamides in the melt, aiming at the formation of a potential compatibilizer for the incompatible nylon 6/PS blends. The effectiveness of the functionalization was determined with GPC and NMR after derivatization with PEGM. Characterization of the blends prepared was performed using dynamic mechanical analysis (dma), tensile testing, differential scanning calorimetry (dsc), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) as well as extraction experiments.

Experimental Section

Materials. Styrene (Merck) was washed with 5% NaOH in order to remove the stabilizers, followed by distillation over finely powdered CaH_2 before polymerization. Diphenyl ether (Merck), used as solvent, was stored over molecular sieves and purged with argon for 30 min before polymerization. Maleic anhydride (Merck) was recrystallized twice from dry chloroform. CuBr (Aldrich) was purified according to the literature procedure.[25] α,α′-Dibromo-*p*-xylene (Acros) was recrystallized from toluene, and 2,2′-bipyridine (bipy) (Merck) was used as received.

Nylons 6 and nylon 11 were obtained from BDH while general-purpose PS (Styron 648) from DOW Plastics. All polymers were dried in a vacuum oven at 80 °C for 48 h to remove sorbed water before processing.

Synthesis of Maleic Anhydride Terminated Polystyrene. Polystyrenes of various molecular weights were synthesized according to the procedure described by Matyjaszewski[15,16] and the results are presented in Table 1. The terminal functionalization of polystyrene was carried out in a previously dried flask equipped with a magnetic stirring bar under argon. Solid compounds, halogen-terminated polystyrene (previously synthesized—Table 1) (1 mmol), CuBr (2 mmol), 2,2′-bipyridine (6 mmol), and maleic anhydride (1 M in solvent) were added into the flask followed by evacuation and flushing with argon three times. Diphenyl ether, degassed and purged with argon for 30 min, was transferred to the flask via syringe, resulting in a 50% v/v solution. The reddish brown styrene solution (in diphenyl ether) was first degassed (three times), sealed tightly with a rubber septum, and heated in a oil bath at 110 °C for 24 h.

After cooling to room temperature, the solution was diluted with THF and the polymer precipitated into *n*-hexane. The precipitation was repeated three times in order to remove the excess maleic anhydride.

Blend Preparation by Melt Mixing. The blends were prepared by melt mixing for 10 min at 230 °C and a rotation speed of 75 rpm in a co-rotating twin-screw microextruder (DSM Research) under an inert atmosphere.

The compositions of the binary blends prepared under these conditions were 95/5, 90/10, 85/15, 80/20, and 75/25 nylon 6/maleic anhydride terminated PS. Ternary blends of 75% nylon 6 with 25% PS and maleic anhydride terminated PS were also prepared. The maleic anhydride terminated PS varied from 0 to 15% in the blends. Since PS had very poor mechanical properties, the selected compositions were those of a high concentration of nylon 6 so as to certify the latter as the matrix. Although these compositions are not typical for studying the compatibilization effect, they were selected in order to explore the limits of the increase of the ultimate properties. Films were made by compression molding between Teflon sheets at 250 °C and 70 kg cm^{-2}, pressure release, and quenching to 0 °C.

Polymer and Blend Characterization. Molecular weights of the polymers were determined by GPC with a refractive index detector using chloroform as eluent and PS standards for calibration.

SEM was carried out with a JEOL 6320 F field emission scanning electron microscope on cryofractured and etched specimens.

Dsc measurements were carried out in an inert atmosphere using the DSC plus of Rheometrics Scientific. Sample weight was ca. 10 mg and heating rate 10 °C min^{-1}. Samples were heated to 250 °C and quenched to −50 °C, followed by heating to 250 °C. The second heating run was recorded.

Tensile tests were performed according to ASTM D882 at 23 °C using a J.J. Tensile Tester type T5001 and film strips with dimensions 4.0 cm × 0.65 cm × 0.025 cm. Data reported were obtained at a cross-head speed of 10 cm.min^{-1}.

Dynamic mechanical analysis was performed with a solid-state analyzer RSA II, Rheometrics, at 10 Hz. Specimen dimensions were $3.0 \times 0.5 \times 0.01$ cm^3.

FTIR spectra were obtained using a Perkin-Elmer 1600 spectrometer.

Extraction experiments were performed in chloroform at room temperature for 24 h.

Results and Discussion

Synthesis and Characterization of the Maleic Anhydride Terminated Polystyrene. The polystyrenes obtained by the ATRP polymerization had molecular weights up to 2×10^4 and polydispersities ranging from 1.13 to 1.19 as shown in Table 1. These polystyrenes were further used in order to introduce one molecule of maleic anhydride (MA) at every chain end. To ensure the reactivity of the macroinitiator, Br microanalysis was performed, and the results showed that one bromine atom corresponded to every polystyrene chain end. Having Br−PS−Br as initiator and taking into account that MA can hardly be homopolymerized under normal conditions,[26] atom transfer radical polymerization in the presence of an excess of MA was performed so as to yield one molecule residing at every chain end; see Scheme 1.

The existence of MA at the polymeric chain was confirmed by FTIR in the range of 1700−1900 cm^{-1} (Figure 1). For PS, some weak combination of overtone absorptions and characteristic resonances of aromatic rings are observed in this region. In the spectrum of MA−PS−MA (Figure 1b), a new absorption band at 1775 cm^{-1} was found. This characteristic band is

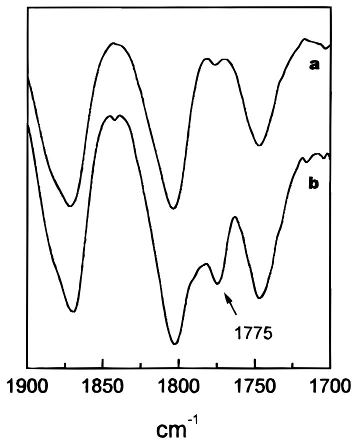


Figure 1. FTIR spectra of unmodified PS-18 (a) and maleic terminated PS-18 (b).

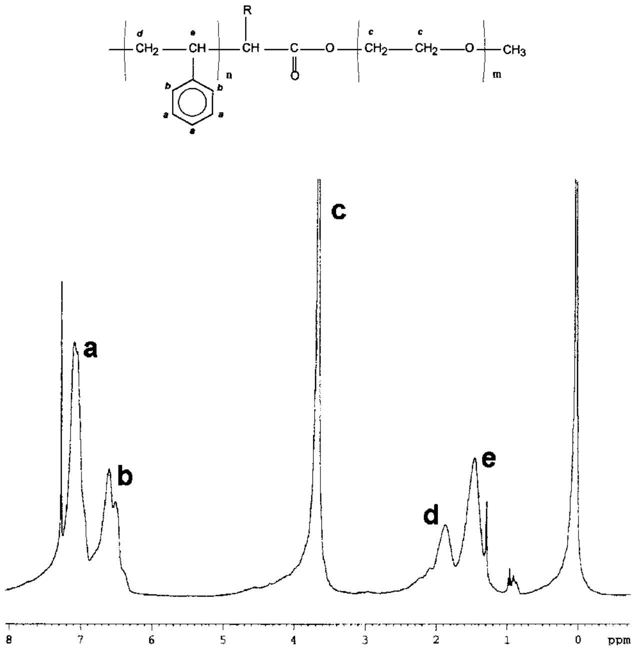


Figure 2. ^{1}H NMR spectrum of MA−(PS-15)−MA after derivatization with PEGM in CDCl$_3$/DMSO 1/1.

assigned to a carbonyl stretching in maleic anhydride units of the modified PS. Maleic anhydride terminated polystyrenes were analyzed by derivatization with a 50% molar excess of a commercial 5 kg/mol Poly(ethylene glycol methyl ether) (PEGM) for the 17 kg/mol modified PS.[8] After reaction for 12 h in DMF at 90 °C, water was added in order to dissolve the unreacted PEGM, the mixture was filtered, and the reaction product was dried in a vacuum oven for 24 h. GPC analysis performed excluded the existence of both unreacted PS and PEGM and showed that the copolymer formed had a polydispersity of 1.21. Its molecular weight was not taken into account because of the existence of the PEGM block in the copolymer. The functionality of the derivatized polymer sample was determined using ^{1}H NMR spectroscopy (Figure 2). More specifically, comparison of the integral ratio of the modified PS aromatic protons H$_a$ and H$_b$ (δ 6.3−7.3 ppm) to the PEGM backbone protons H^c (δ 3.54 ppm) could give the percent functionality of the copolymer PEGM−PS−PEGM. Moreover, the theoretical integral ratio $(H_a + H_b)/H_c$ for the resulting triblock copolymer (PEGM−PS−PEGM) is 0.897. The observed integral ratio was 1.094, indicating the formation of 82% triblock copolymer and certifying the effectiveness of the method. Such amphiphilic block copolymers are of considerable interest for various applications, e.g., as emulsifiers, dispersion stabilizers, and compatibilizers, due to their combined hydrophilic−hydrophobic character.[27−29]

Table 2. Ultimate Properties of the Binary Blends of Nylon/Maleic Anhydride Terminated PS

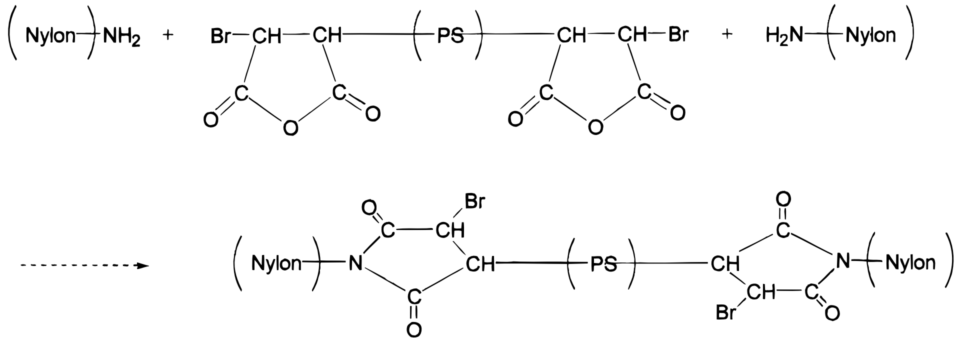
sample	σ_y (MPa)	σ_b (MPa)	ϵ_b (%)
nylon 6	35 ± 4	72 ± 7	583 ± 72
nylon 6/PS-18 (unmodified) 90/10 (6/1 equiv)		46 ± 5	10 ± 1
nylon 6/MA−(PS-18)−MA 90/10 (6/1 equiv)	44 ± 2	50 ± 5	387 ± 35
nylon 6/MA−(PS-11)−MA 90/10 (3/1 equiv)	42 ± 3	48 ± 8	325 ± 34
nylon 11	29 ± 2	41 ± 2	477 ± 72
nylon 11/MA−(PS-18)−MA 90/10 (6/1 equiv)	33 ± 2	40 ± 5	386 ± 39

Beside the above reaction, which has been performed in solution, the possibility that MA−PS−MA could react with other polymers in the melt enhances its utility in polymer blending. Since reactive blending is an issue of increasing interest in practical applications, the possibility of the synthesized end-functionalized polystyrenes participating in such reactions has also been examined. In that respect, blends of nylon 6 with MA−PS−MA have been prepared under reactive conditions and characterized first by studying their mechanical properties.

Tensile testing of the nylon 6/MA−PS−MA 90/10 blend revealed that the incorporation of MA in the PS chains had a dramatic influence on the ultimate strain ϵ_b values (Table 2). These values are very sensitive to blend component adhesion strength or partial miscibility at the interface of blend components in phase-separated systems and are routinely used to evaluate the degree of compatibilization in polymer alloys.[30−31] More specifically although the stress at break, σ_b, of the nylon 6/MA−PS−MA blend did not differ significantly from that of the respective blend nylon 6/PS, elongation at break shows a great improvement from 10 to ~390%, showing the effect of the reaction between the maleic anhydride terminated polystyrene and the amine end groups of nylon 6. This reaction may lead to the formation of a potential copolymer. Similar results were obtained for the case of the nylon 11/maleic anhydride terminated PS blend (Table 2). The suggested reaction can lead to the formation of a diblock or a triblock copolymer as shown in Scheme 2. Additional reactions which include dehydrobromination of the terminal bromosuccinic anhydrides during reactive blending having as a subsequent the attachment of more than one polyamide chains onto a polystyrene chain end cannot be excluded.

Dynamic mechanical analysis was also performed on blends of nylon 6 with unmodified PS and MA−PS−MA, and the results are presented in Figure 3. These results indicate the existence of two phases for both blends, where in the case of the nylon 6/MA−PS−MA blend there is a small displacement of the T_g of PS in respect to the value obtained for the PS phase in the blend of nylon 6/nonfunctionalized PS.

The successful grafting of the two phases was also confirmed by extraction experiments. Thus, while for the blend with the unmodified PS almost all of the PS seems to be removed by the extraction with chloroform, Scheme 2



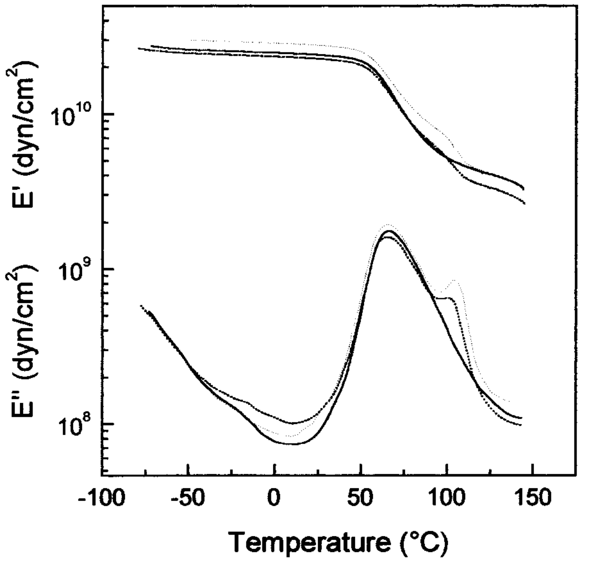


Figure 3. Temperature dependence of the storage (E′) and loss modulii (E″) of pure nylon 6 (—), nylon 6/PS-18 blend (- ○ -), and nylon 6/MA−(PS-18)−MA (-■-).

for the blend with the maleic anhydride terminated PS only 0.5% is removed. Moreover, when the blends were immersed in formic acid, they showed a persistent turbidity, indicating the presence of a copolymer.[19]

Considering the above promising results for the system nylon 6/MA−PS−MA, binary blends of nylon 6 with different amount of MA−PS−MA (0, 5, 10, 15, 20, and 25%) were studied.

Reactive Blending of Nylon 6 with Maleic Anhydride Terminated PS. A more systematic study of the blending behavior of MA−PS−MA with nylon 6 at various compositions has also been performed, and the resulting blends were characterized.

The mechanical properties under large deformation were examined for this binary system, and the results in terms of ultimate stress, σ_b and strain ϵ_b are given in Table 3. The functionalized polystyrene used had a relatively low molecular weight so its mechanical properties were very poor. Therefore, compositions rich in nylon 6 were examined, and although the results show a decrease in σ_b values, the values of ultimate properties obtained (σ_b ca. 40 MPa and $\epsilon_b > 300\%$) are quite satisfactory, implying the effectiveness of the proposed reaction. Furthermore, when mixing was performed for a shorter time, as in the case of the 75/25 blend, the mechanical properties are significantly reduced, supporting the reactive nature of the compatibilization involved.

The dynamic mechanical measurements of the binary blends revealed the T_g's of the pure blend components reported in Table 4. As also shown before, the blends have characteristics of a two-phase system, but they also show the existence of a mixed interface due to the observed small displacement on the T_g's of the pure components. The incompatible binary was considered as a reference for any T_g shift of PS-18 since the pure polymer was too brittle to be studied.

Table 3. Ultimate Properties of Binary Blends Nylon 6/MA−(PS-15)−MA

blend nylon 6/MA−PS−MA	σ_y (MPa)	σ_b (MPa)	ϵ_b (%)
100/0	35 ± 4	72 ± 7	583 ± 72
95/5	24 ± 1	47 ± 3	412 ± 22
90/10	31 ± 3	45 ± 5	397 ± 41
85/15	35 ± 1	40 ± 2	307 ± 47
80/20	26 ± 1	34 ± 1	249 ± 51
75/25	36 ± 1	46 ± 1	403 ± 55
75/25[a]	35 ± 1	33 ± 1	233 ± 26

[a] 5 min mixing time.

Table 4. Viscoelastic and Thermal Properties of the Binary Blends Nylon 6/MA−(PS-15)−MA

blend nylon 6/ MA−PS−MA	T_m[a] of nylon 6 (°C)	crystallinity[a] of nylon 6 (%)	T_g[b] of nylon 6 (°C)	T_g[b] of PS (°C)
100/0	221	48	66	
95/5	221	41	69	*c*
90/10	220	44	70	*c*
85/15	220	43	68	103
80/20	220	38	67	102
75/25	220	37	68	101

[a] Results obtained from dsc measurements. [b] Results obtained from dma measurements. [c] Broad transition.

Table 5. Viscoelastic and Ultimate Properties of Ternary Blends of Nylon 6/PS-15 and of Nylon 6/PS-130 with Various MA−(PS-15)−MA Contents

blend nylon 6/PS/ MA−PS−MA	T_g[c] of nylon 6 (°C)	T_g[c] of PS (°C)	σ_y (MPa)	σ_b (MPa)	ϵ_b (%)
75/25[a]/0	66	104		14 ± 1	23 ± 8
75/20[a]/5	67	103		26 ± 1	82 ± 10
75/15[a]/10	70	101	26 ± 1	28 ± 1	130 ± 29
75/10[a]/15	70	102	29 ± 1	34 ± 4	252 ± 50
75/25[b]/0	66	105	13 ± 1	25 ± 3	291 ± 58
75/20[b]/5	69	104	26 ± 2	29 ± 2	143 ± 73
75/15[b]/10	68	104	26 ± 1	43 ± 2	387 ± 62
75/10[b]/15	69	105	21 ± 1	40 ± 7	392 ± 64

[a] PS-15. [b] PS-130. [c] Results obtained from dma measurements.

The thermal properties of these blends, as obtained by dsc measurements, are presented in Table 4. As shown there, no significant influence of the amorphous polystyrene content on the properties of the crystalline part of nylon 6 can be detected. Only for the compositions of nylon 6 less than 80% is a decrease in crystallinity evident, probably due to dilution effects.

Reactive Compatibilization of the Binary Blends of Nylon 6/PS Using Maleic Anhydride Termi-

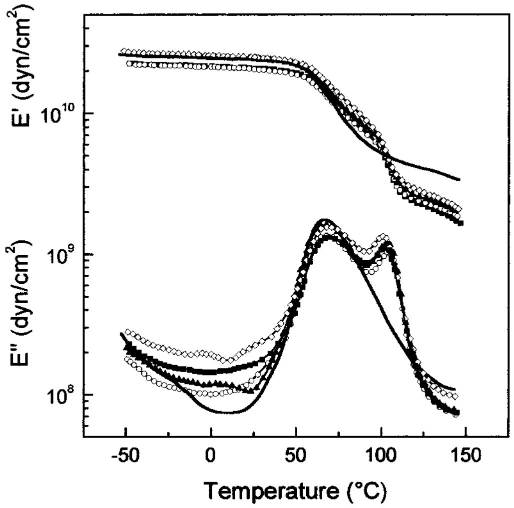
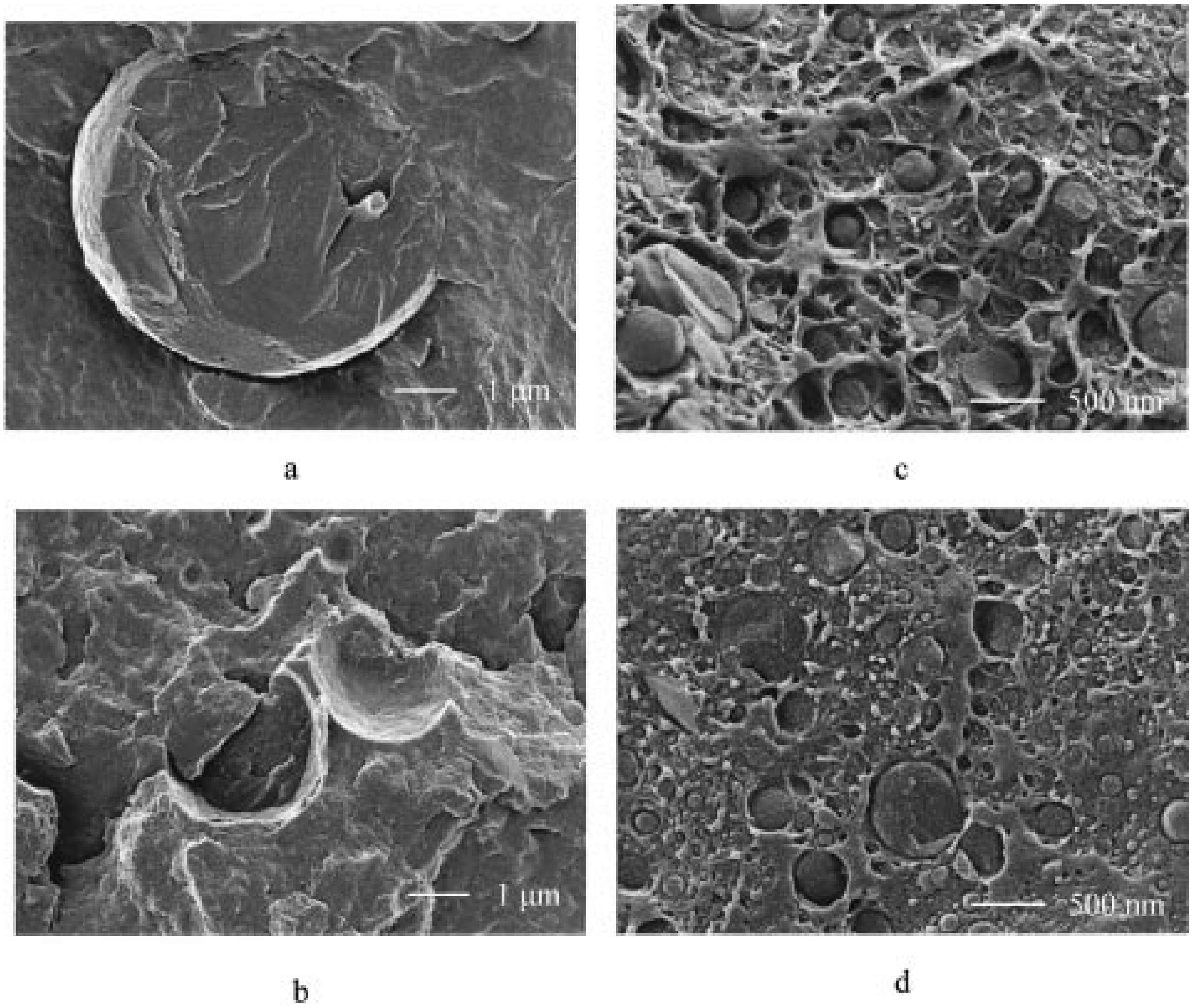


Figure 4. Temperature dependence of the storage (E′) and loss modulii (E″) of pure nylon 6 (—) and of the ternary nylon 6/PS-15/MA–(PS-15)–MA blends: 75/25/0 (-○-); 75/20/5 (-▲-); 75/15/10 (-◇-) and 75/10/15 (-■-).

nated PS. For the preparation of the ternary blends, two different polystyrenes were used in order to elucidate the influence of the molecular weight on the compatibilization process. The first system was based on PS with a molecular weight equal to that of the terminal-modified polystyrene and the other on a commercial PS (PS-130) with a significantly higher molecular weight.

Table 5 depicts the influence of the increase of the modified polystyrene amount on the mechanical properties of the nylon 6/PS/MA–PS–MA system. An improvement on the ultimate properties is obtained as the amount of MA–PS–MA is increased. More specifically, σ_b values show a steep increase with the addition of 5% of the modified polystyrene and a further increase as its amount increases. In analogy, ϵ_b values show a continuous increase as the amount of the modified polystyrene increases, an effect which is here more pronounced since ϵ_b is more sensitive to the compatibilization process and nylon 6 is more ductile than PS.

The dynamic viscoelastic spectra of blends quenched at 0 °C from the melt are shown in Figure 4 in terms of the temperature dependence of the loss E'' and storage E' moduli for the nylon 6/PS/MA–PS–MA system. The main relaxation of nylon 6 associated with T_g in the uncompatibilized blend is located at ca. 66 °C (α), while the main relaxation for the PS phase in the same blend is detected at 104 °C (α). As shown in Table 5, there is a systematic shift of the nylon 6 (α) and PS (α)



a

c

b

d

Figure 5. Scanning electron micrographs of cryofractured nylon 6/PS-15/MA–(PS-15)–MA blends: (a) 75/25/0; (b) 75/20/5; (c) 75/15/10; (d) 75/10/15.

relaxations toward each other with increasing MA−PS−MA content. More specifically, a maximum shift of 3−4 °C for both phases is seen for the blends with a compatibilizer content higher than 10%. The presence of two distinct transitions in all cases indicates a polymeric alloy with a mixed interface as the converging T_g's indicate. The existence of such interface was attributed to an in situ formation of a copolymer as a result of chemical reactions occurring at the phase boundaries during melt mixing. Thermal examination of this ternary system showed that the presence of the PS phase had no significant influence on the crystalline properties of nylon 6.

SEM was used to study the particle sizes of the dispersed phase in the blends (Figure 5). The fracture surface of the noncompatibilized nylon 6/PS 75/25 blend (Figure 5a) was characterized by a relatively smooth type of fracture with no deformation at all with rather large lumps of the minor PS phase. These features are typical of poor interfacial adhesion. On the other hand, the micrographs of the compatibilized blends (Figure 5b−d) demonstrated that increasing the amount of MA−PS−MA produced smaller dispersed domain sizes of PS phase into the nylon 6 matrix. The strong deformation of the matrix was also enhanced with the incorporation of higher amounts of modified polystyrene. These results are consistent with the considerable improvement in their mechanical properties with increasing amount of the modified polystyrene as discussed previously.

It is known that, for blends of a homopolymer with a block copolymer, the homopolymer molecular weight must be less than or equal to that of the corresponding block of the copolymer for solubilization to occur, but certain amount of solubilization occurs even at higher molecular weights.[32−37] So it was interesting to examine the compatibilization effect of the in situ formed copolymer when a commercial PS (PS-130) with higher molecular weight was used ($\bar{M}_n \approx 130\,000$). Table 5 shows the effect of the addition of the MA−PS−MA as well as the effect of its concentration on the mechanical properties of the ternary blends by means of mechanical properties under large deformation. The good mechanical properties of the binary blend can be attributed to a pseudoadhesion behavior originating from a contraction of the crystalline matrix onto a rigid dispersed phase.[38] The improvement of the mechanical properties of this ternary blend with an increase in the concentration of the MA−PS−MA blend can be characterized as moderate when compared with the results of the respective ternary with the PS of the lower molecular weight (Table 5). This behavior can be attributed to the higher molecular weight of the PS used as discussed above.

Dynamic mechanical measurements for the nylon 6/PS-130/MA−PS−MA blends were also performed. A two-phase system is obtained also for this ternary system, and the results in terms of glass transition temperatures are depicted in Table 5. These blends show a also a T_g shift of nylon 6, while there is no noticeable T_g shift for the case of the PS phase contrary to the respective ternary blends with the PS of equal molecular weight to that of the modified PS. This is expected because the higher molecular weight of the PS homopolymer limits its miscibility with the PS domain of the in situ formed compatibilizer. This evidence further supports the view that two different interphases are formed and that the observed T_g displacement is probably due to the presence of such interphases.

Conclusions

A simple method for the synthesis of maleic anhydride terminated polystyrenes has been presented. This method uses a "living"-controlled radical polymerization technique and is based on the fact that maleic anhydride cannot be homopolymerized. The functionality of these modified polystyrenes was determined by derivatization with poly(ethylene glycol methyl ether) followed by gel permeation chromatography and ^{1}H NMR analysis. These maleic terminated polystyrenes were used for the compatibilization of the nylon 6/PS binary in the melt. Thus, ternary blends with PS of the same and much higher molecular weight of the modified PS were examined, and the results showed effectiveness of the in situ formed nylon 6-PS copolymer. Even when the polystyrene used was of higher molecular weight than the respective block of the copolymer, the mechanical properties of the ternary blends were significantly enhanced compared to the respective binaries. The effectiveness of the in situ formed copolymer as compatibilizer was also revealed by SEM examination of the cryofractured samples. The strong deformation of the matrix and the diminishing of the domain size of the dispersed phase with an increase in the maleic terminated polystyrene confirmed the success of the in situ formed nylon 6-PS copolymer.

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