# Stress–Strain Behavior and Impact Strength of Polystyrene/ Polyamide-6 Blends Compatibilized with Poly(styrene-g-ethylene oxide)

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ABSTRACT: The mechanical properties of polystyrene/polyamide-6 (50/50 wt/wt) blends were improved by additions of small amounts of poly(styrene-g-ethylene oxide) (SEO) during compounding by extrusion. Tensile testing of injection-molded samples revealed that the blends developed a yield point after addition of 1 wt % SEO. The elongation at break increased by almost a factor of 6, and the impact strength increased by a factor of 1.5 after adding 3 wt % SEO. Morphological analysis by electron microscopy showed that additions of SEO resulted in decreased domain sizes, and seemed to promote interfacial adhesion. The morphologies of the compatibilized blends also had a higher degree of anisotropy, as compared with the uncompatibilized blend. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1887–1891, 1998

**Key words:** polymer blends; compatibilization; graft copolymer; ultimate mechanical properties

# INTRODUCTION

Graft copolymers of appropriate architectures can be utilized for modifying the interfacial properties of immiscible blends, thereby alleviating the poor mechanical properties and poor morphological stability normally associated with these blends. Although some experimental findings indicate that block copolymers are more effective in this respect,<sup>1</sup> it is more convenient to use graft copolymers in some blend systems. Generally, graft copolymers are more readily prepared, for example through *in situ* formation during compounding.<sup>2</sup>

We have previously shown that low concentrations of poly(styrene-g-ethylene oxide) (SEO) can successfully compatibilize polystyrene/polyamide-6 (PS/PA6) blends.<sup>3</sup> Hydrogen bonding between ether oxygens and amide hydrogens was found to pro-

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mote the miscibility of PA6 and poly(ethylene oxide) (PEO). The domain size decreased with increasing amounts of SEO in the PS/PA6 blends up to a concentration of 2–3%. At concentrations above 2–3% the PS/PA6 interface seemed to be saturated with SEO, and SEO phase separated into dispersed domains, 20–200 nm in size.<sup>4</sup> Furthermore, an interphase of SEO between the PS and PA6 phases was observed by electron microscopy. Different SEO copolymers have also been found to compatibilize poly(2,6-dimethyl-*p*-phenylene oxide)/poly(methyl methacrylate) blends,<sup>5,6</sup> as well as PS blends with polyamide-12,<sup>3</sup> poly(butyl acrylate-*co*-acrylic acid),<sup>7</sup> and poly(octyl thiophene).<sup>8</sup>

The blends mentioned above were all prepared in small amounts ( $\sim 20$  g) using batch mixers. In the present article we report on the ultimate mechanical properties of compatibilized PS/PA6 (50/50 wt/wt) blends produced in an upscaled and more commercially relevant process. The number of different blends studied was limited because of the relatively large quantities of SEO needed to

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compound by continuous extrusion and to prepare test specimens by injection molding.

### EXPERIMENTAL

The graft copolymer, designated SEO, was prepared by ethoxylating an amide-containing styrene copolymer. The styrene copolymer was first synthesized by free radical copolymerization of styrene and acrylamide, and grafting of this copolymer was subsequently achieved by using the amide anions as initiator sites for anionic polymerization of ethylene oxide. Details of the preparation and characterization of SEO have been described previously.<sup>9</sup> The molecular data of SEO is shown in Table I. All SEO concentrations are given in weight percent.

The homopolymers used were standard polystyrene, Vestyron<sup>®</sup> 1202 from Svenska Polystyrenfabriken AB (Hüls AG), Trelleborg, Sweden, with a melt flow rate (MFR) of 16 (230°C, 5 kg), and Ultramid<sup>®</sup> B4 polyamide-6 from BASF AG, Ludwigshafen, Germany, with MFR of 13 (230°C, 5 kg). The MFR values were measured according to ISO 1133 using a Davenport MFR apparatus. All homopolymers were vacuum-dried for 48 h at 80°C, and SEO was dried for 1 wk at ambient temperature under vacuum prior to extrusion.

Blends of PS/PA6 (50/50 wt/wt) containing 0, 1, and 3% of SEO were prepared with a Berstorff ZE25 co-rotating twin-screw extruder having a diameter of 25 mm and a length-to-diameter ratio of 43. The extruder was operated at 230°C with a rotation rate of 100 rpm and a feed rate of approximately 100 g/min.

Specimens used for impact and tensile testing were prepared using an Engel ES 200/50HL injection-molding machine operated at 230°C. The mold temperature was kept at 50°C. The specimens were vacuum-dried for 48 h at 80°C before mechanical testing. Unnotched Charpy impact strengths were determined according to ISO/ R179 with a CEAST impact tester. The tensile

Table I Molecular Data of SEO

| $ar{M}_n$ of PS<br>Backbone<br>(g/mol) | $ar{M}_n$ of PEO Grafts (g/mol) | PEO<br>Content<br>(%) | $ar{M}_n$<br>Between<br>Grafts<br>(g/mol) | $T_{ m melt}$ (°C) |
|----------------------------------------|---------------------------------|-----------------------|-------------------------------------------|--------------------|
| 80,000                                 | 5,400                           | 34                    | 10,400                                    | 50                 |



**Figure 1** The influence of added amounts of SEO on the stress-strain behavior of PS/PA6 (50/50) blends.

properties were evaluated according to ISO/R527 using a Schenk tensile tester at a crosshead speed of 10 mm/min. All mechanical testing was performed at 20°C, and at least 25 specimens were tested for each value given.

Freeze-fracture surfaces of both injection- and compression-molded samples were examined using an ISI 100A scanning electron microscope (SEM) operating at 15 kV. Compression-molded bars were molded at 230°C for 5 min from already injection-molded material.

### **RESULTS AND DISCUSSION**

The mechanical properties of polyamides, and blends containing polyamides, are known to be very sensitive to moisture. The PS/PA6 (50/50 wt/wt) blends were therefore compounded by extrusion, molded by injection molding, and tested directly after drying. Further drying of the test specimens was not found to influence the test results. Figure 1 shows the stress-strain behavior of the blends containing 0, 1, and 3% of SEO, and Table II contains the data from the evaluation of the tensile properties of the blends and PS. The uncompatibilized blend showed a typical brittle behavior, similar to that of pure PS. With 1% SEO added, the blend showed a clear yield point and the elongation at break increased. Necking of the sample bars was observed at the yield point shortly before break. When the concentration of SEO was further increased to 3%, the samples showed necking and thereafter a period of cold

| Sample                             | Tensile<br>Modulus<br>(MPa) | Yield<br>Stress<br>(MPa) | Tensile<br>Strength<br>(MPa) | Elongation<br>at Break<br>(%) |
|------------------------------------|-----------------------------|--------------------------|------------------------------|-------------------------------|
| PS                                 | 3,200 (50)                  | _                        | 48 (2)                       | 3.0 (0.2)                     |
| PS/PA6                             | 1,570 (50)                  | _                        | 47(3)                        | 3.3(0.2)                      |
| PS/PA6 + 1% SEO<br>PS/PA6 + 3% SEO | 1,150(30)<br>1,000(40)      | 47(2)<br>45(2)           | 46 (2)<br>41 (3)             | 5.2(0.3)<br>23.0(0.6)         |
| 10/1R0 + 5% DEO                    | 1,000 (40)                  | HO (2)                   | 41 (0)                       | 20.0 (0.0)                    |

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|--------------------------|----------|--------------|
|--------------------------|----------|--------------|

Figures in parentheses are standard deviations.

flow. As a consequence, the elongation at break increased by a factor of 6 as compared with the uncompatibilized blend. The yield stress was at the same level for the two compatibilized blends, while the tensile strength was somewhat lower for the blend containing 3% SEO. Additions of SEO also made the blends less stiff, as indicated by a decrease in the tensile modulus with increasing concentrations of the graft copolymer.

The development of yielding after compatibilization normally indicates an increased toughness of the polymer blend. A measure of the fracture energies, and thus the toughness, of the blends can be obtained by integrating stress-strain curves. The integrals of the curves in Figure 1 were 70, 130, and 895 MPa for the blends containing 0, 1, and 3% SEO, respectively. The fracture energy of the blend increased gradually with the concentration of SEO, as the blend was transformed from a brittle material to a more ductile material.

Cheng and White<sup>10</sup> have studied PS/PA6 (40/60 wt/wt) blends compatibilized by 5% of poly(styrene-co-maleic anhydride) (SMA), poly-(styrene-co-acrylonitrile) (SAN), and poly(styrene-block-(ethylene-co-butylene)-block-styrene) (SEBS), the latter functionalized with maleic anhydride.<sup>10</sup> They found that the elongation at break increased from 6% for the uncompatibilized blend to 27% for the blend containing SEBS. Blends containing SMA and SAN showed no increase in the elongation at break.

Figure 2 shows the unnotched Sharpy impact strengths of the blends as a function of the concentration of SEO. As compared with the uncompatibilized blend, the impact strength increased by 28 and 43% after adding 1 and 3% of SEO, respectively. The results from the impact test were in agreement with the stress–strain behavior of the blends, and showed that the blends were toughened by SEO. In the study by Cheng and White,<sup>10</sup> the Izod impact strengths of the blend containing 5% SAN and the blend containing 5% SEBS were found to be approximately 130% higher than for the uncompatibilized blend. The blend containing SMA showed a 30% lower impact strength.<sup>10</sup>

The mechanical properties of a polymer blend are typically closely related to its morphology; for example, the mechanical properties of an anisotropic blend are strongly dependent on the orientation of the sample. Injection-molded impact test specimens were freeze-fractured and examined by SEM in order to study the morphology and the interfacial adhesion of the PS/PA6 blends. SEM micrographs of fracture surfaces of the blends are shown in Figure 3. The uncompatibilized blend, seen in Figure 3(a), seemed to have a cocontinuous morphology containing PS and PA6 domains with sizes in excess of 10  $\mu$ m. However, the large



**Figure 2** Unnotched impact strengths of PS/PA6 (50/ 50) blends as a function of added amount of SEO. Standard deviations are indicated by error bars.



**Figure 3** SEM micrographs of freeze-fracture surfaces of injection-molded samples containing (a) 0%, (b) 1%, and (c) 3% of SEO. The surfaces were oriented perpendicular to the flow direction during molding.

domains had inclusions of smaller domains in the sub-micron region. Furthermore, the fracture surface had a rough appearance, with a high degree of mechanical failure along the PS/PA6 interface. As seen in Figure 3(b), the morphology after adding 1% SEO consisted of elongated domains oriented in the flow direction, perpendicular to the



**Figure 4** SEM micrographs of freeze-fracture surfaces of compression-molded samples containing (a) 0%, (b) 1%, and (c) 3% of SEO. The samples were compression-molded using injection-molded material.

plane of the surface. In addition, the average domain size was smaller, and the fracture surface of the blend appeared smoother, with a lower degree of interfacial failure. With 3% SEO added, the fracture surface was even smoother, and it was more difficult to identify individual domains from the micrographs [Fig. 3(c)].

One of the factors determining the morphology in immiscible polymer blends is the minimization of the interfacial tension. This is particularly true to uncompatibilized blends where the interfacial tension between the components is high. The minimization of interfacial tension usually leads to isotropic morphologies with spherical particles in a matrix. Because injection molding of polymer blends involves high shear and high cooling rates, the morphologies of these materials can, however, be expected to be anisotropic and far from equilibrium. Injection-molded material was compression molded into bars at 230°C in order to evaluate the morphological stability of the injectionmolded blends. As seen in Figure 4(a), the morphology of the uncompatibilized blend was transformed into a morphology containing particles, with a decreased interfacial area per volume unit. In contrast, the morphologies of the compatibilized blends, shown in Figure 4(b,c), were much less affected by the compression-molding operation, and the blends retained their anisotropic morphology to a high degree. Thus, the morphologies of the compatibilized blends seem to be stabilized largely by the graft copolymer.

In conclusion, additions of SEO made the PS/ PA6 blends tougher, as shown by both tensile and impact testing. However, the observed improvement in the mechanical properties of the compatibilized blends, as compared with the uncompatibilized blend, may also be linked to a higher degree of anisotropy of the injection-molded sample bars. The SEM study suggested a higher degree of dispersion and interfacial adhesion in compatibilized blends. These morphological observations agree well with the information obtained in the previous investigations on batch-mixed blends.<sup>3,4</sup>

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