

# Morphology and Properties of SEBS Block Copolymer Compatibilized PS/HDPE Blends

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**ABSTRACT:** The objective of this study is to examine the influence of poly [styrene-*b*-(ethylene-co-butylene)-*b*-styrene] (SEBS) compatibilizer on the morphology and properties of atactic polystyrene/high density polyethylene (aPS/HDPE) blends. The rheological behavior of the blends melt during processing is followed. The concentration of SEBS does not significantly influence the processing parameters. The morphology is determined by SEM and TEM. aPS/HDPE/SEBS blends exhibit fine dispersion of HDPE or aPS particles in the matrix and better adhesion at the interface. Higher concentration of SEBS results in better compatibility. Transmission electron micrographs confirm existence of the SEBS interfacial layer between the aPS and the HDPE phase. This effect is stronger in the blends with higher SEBS concentration and HDPE as matrix. The mechanical properties are determined. The tensile strength decreases while the elongation at break and the impact strength increase with the SEBS content. The results prove that SEBS acts as a compatibilizer in aPS/HDPE blends and its effect is more expressed in blends with a higher SEBS content and HDPE as matrix.

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**KEY WORDS:** aPS/HDPE/SEBS blends, morphology, processing, rheological properties, mechanical properties.

## INTRODUCTION

THE BLENDING OF polymers provides an efficient way of developing new materials with tailored properties, which is often a faster and more cost-effective means of achieving a desired set of properties than synthesizing a new polymer [1]. It is of special interest for the modification of commodity low-cost polymers. Polystyrene (PS) and polyethylene (PE) are two of the most widely used plastics in the world. A decrease in stiffness and an increase in impact strength of PS can be achieved by adding PE with substantially higher impact strength [2,3]. For this reason the PS/PE blends exhibit more balanced properties, which is advantageous for a number of applications, e.g., in packaging where different barrier properties of PE and PS can be beneficially combined. The PS/PE blends are very important for mixed plastic waste recycling [4]. The recycling of mixed plastic waste has attracted much interest because of economical and ecological advantages over compounding each component separately [2,5–10]. PS is incompatible with PE. Therefore, PS/PE blends exhibit weak interfacial adhesion and poor dispersion of the component, which results in heterogeneous morphology with macrophase separation and poor mechanical properties. Compatibility of these blends can be improved with compatibilizers [10–19]. Block copolymers with sequences chemically identical or similar to the blend component [20] are usually added into incompatible polymer blends as compatibilizers. It was shown that the compatibilization efficiency of block copolymer depends on the molecular parameters, such as the length and the number of blocks in the copolymers and interaction parameters,  $\chi$ , between the blocks and the related blend components [13,18,19,21]. In most cases, compatibilizers act as emulsifiers reducing the interfacial tension between immiscible polymers in the blend during blending, which results in a fine dispersion of one phase in the other. For the PS and high density polyethylene (HDPE) blends, poly [styrene-*b*-(ethylene-co-butylene)-*b*-styrene] (SEBS) is usually used as a compatibilizer [12–17]. The influence of SEBS addition on the tensile and impact properties of the PS/HDPE blends has been studied by Xu and Tjong [14] and Tjong and Xu [15]. They found that SEBS content in PS/HDPE blends improved the elongation at break and ductility. Abis et al. [12] investigated syndiotactic

PS (sPS) and HDPE blends with SEBS compatibilizer. On the basis of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) better adhesion in blends was found. However, the improvements of mechanical properties were not achieved. Chen et al. [13] compared the compatibilization effects of three triblock copolymer of SEBS of different molecular weights and one diblock copolymer of poly [styrene-*b*-(ethylene-co-butylene)] (SEB) in sPS/HDPE blends. In all blends, interfacial adhesion and elongation at break were improved, especially with higher SEBS content. They concluded that medium molecular weight triblock copolymer SEBS was the most effective. Kallel et al. [16] investigated the influence of processing conditions on morphology, complex viscosity of melt, and Charpy impact test of PS/HDPE/SEBS blends. The better dispersion was found in the PS/HDPE/SEBS blends prepared by single or twin screw extruder in comparison with internal mixer. The better impact strength was obtained in the PS/HDPE/SEBS blends prepared by single screw extruder. Karrad et al. [17] investigated the compatibilizing ability of SEBS in PS/HDPE blends and influence of the copolymer concentration on mechanical properties. The ductility, toughness, and impact properties were improved, while the strength and modulus were reduced by SEBS addition.

In the mentioned papers [12–17], the rheological properties in the extruder during processing of atactic polystyrene (aPS) and HDPE blends with SEBS as compatibilizer as well as the localization of SEBS by means of TEM were not studied. This article studies the effect of the SEBS addition on the rheological properties of the molten blends during processing, on the morphology obtained by means of SEM and TEM, and on tensile and impact properties of aPS/HDPE blends. The influence of the amount of SEBS in blends was also investigated. The principal objective was to find the correlation between morphology, processing parameters, and mechanical properties of the aPS/HDPE/SEBS blends.

## EXPERIMENTAL DETAILS

### Materials

The following materials were used:

Atactic polystyrene (aPS), Dow Styrene 678E GPPS, Dow Plastics;  $M_w = 259,207$  g/mol,  $M_n = 115,364$  g/mol, MFR 10.5 g/10 min. (200°C/5 kg);

High density polyethylene (HDPE), Lupolen 5031 L, Basel;  $M_w = 80,000$  g/mol,  $M_n = 14,000$  g/mol, MFR 6.5 g/10 min (190°C/2.16 kg), density 0.952 g/cm<sup>3</sup>;

Triblock copolymer, poly [styrene-*b*-(ethylene-co-butylene)-*b*-styrene] (SEBS), Kraton G 1650, Shell Chemical,  $M_w = 112,368$  g/mol,  $M_n = 100,943$  g/mol,  $M_n$  (PS-block) = 10,300 g/mol,  $M_n$  (EB-block) = 53,300 g/mol (with the content of 29 wt% of PS and ethylene/butylene, EB, as rubbery middle block). SEBS was used as a compatibilizer.

### Preparation of the Blends

Samples of neat polymers and blends of aPS/HDPE with and without a compatibilizer were prepared by Haake Record 90 twin screw extruder with intensive mixing profile, Haake TW 100, with the zone temperatures of 180/195/210/210°C and at 60 rpm. After the extrusion, dumbbell test specimens were prepared by injection molding with Zwick injectometer at 230°C, the injection rate of 200 mm/s, and the mold temperature of 40°C, according to ISO 527. The compositions of the prepared aPS/HDPE blends were 100/0, 80/20, 40/60, and 0/100 wt%. Five percent and 7% of SEBS block copolymer were added to aPS/HDPE blends. For example, a blend containing 80 g of aPS, 20 g of HDPE, and 5 g of SEBS, has the following notation: aPS/HDPE/SEBS 80/20/5.

### Processing Parameters

Torque ( $TQ$ ) versus time was recorded during the processing of the blends in the extruder at 6 s intervals. Output ( $Q$ ) and melt back pressure ( $p$ ) were followed by computer during the processing of the blends.

### Scanning Electron Microscopy (SEM)

The samples of aPS/HDPE blends were fractured in liquid nitrogen and sputtered with a thin gold layer to prevent charging. The fracture surfaces were observed by a scanning electron microscope (JSM 5800, Jeol), using secondary electrons detector. The samples of aPS/HDPE/SEBS blends were prepared in the same way, but sputtered with a platinum layer (instead of gold) and observed by a different scanning electron microscope (JSM 6400 Jeol), also with secondary electrons detector.

## Transmission Electron Microscopy (TEM)

The specimens for TEM were prepared as follows: small pyramids were cut from the middle of the prepared samples, fixed in ultramicrotome Ultracut UCT (Leica, Austria) and cut at cryo conditions (knife – 110°C, sample – 50°C). The ultrathin sections were stained in ruthenium tetroxide ( $\text{RuO}_4$ ) vapors for 50 min. Stained ultrathin sections were transferred to support grids and observed by a transmission electron microscope (JEM 200CX, Jeol) at 100 kV. Under these conditions, the resulting transmission electron micrographs show gray aPS phase, white HDPE, and black SEBS.

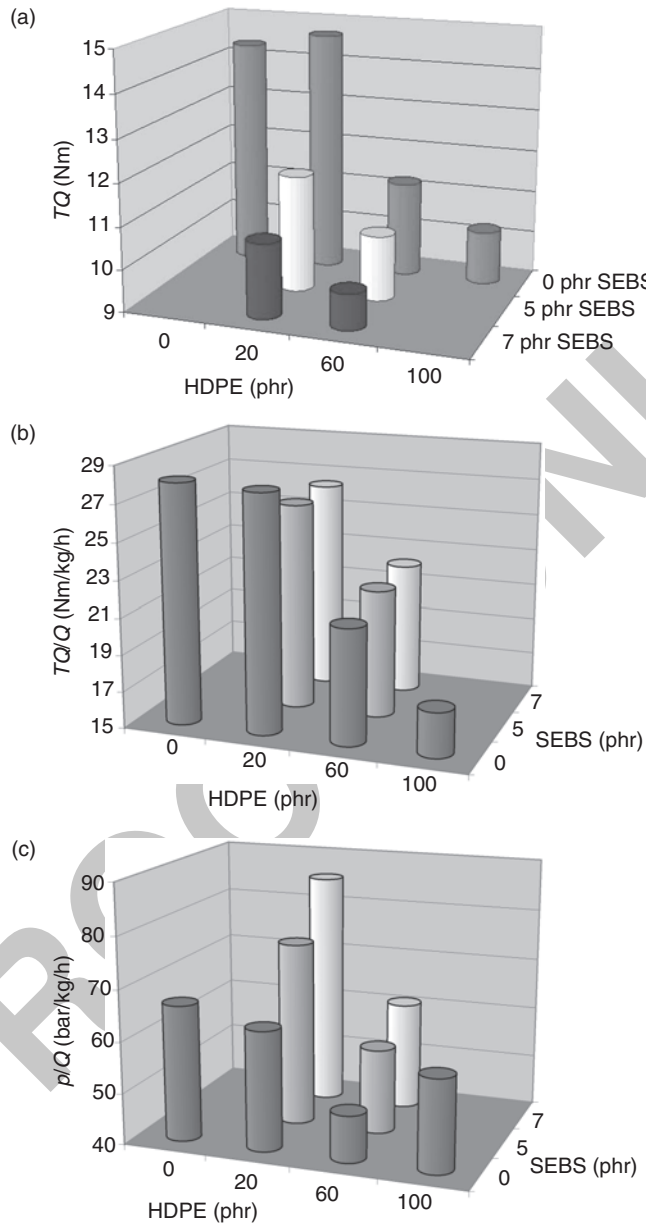
## Mechanical Properties

The measurements of tensile properties, tensile strength, and elongation at break of dumbbell shaped samples were carried out by an Instron 1185 tester according to standards ISO 527-1: 1993 and ISO 527-2: 1993, at a crosshead speed of 50 mm/min. The Izod impact strength was measured according to ISO 180: 1993. For each analysis, five specimens were tested and the average values were reported.

## RESULTS AND DISCUSSION

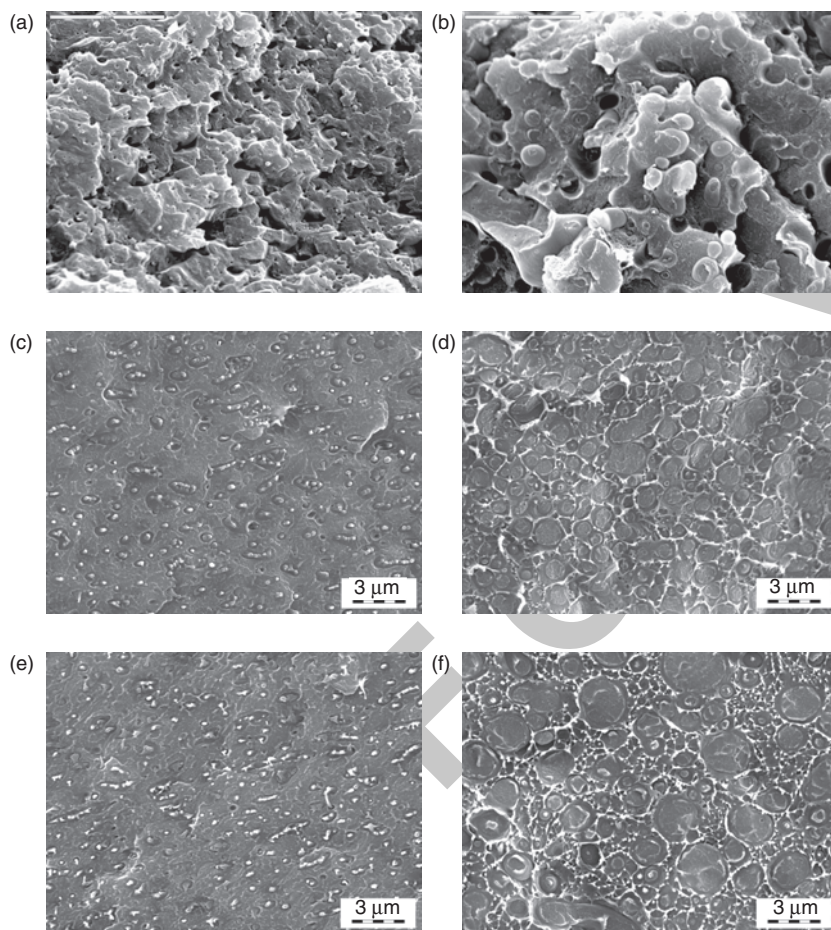
### Processing Parameters

The processing parameters are presented in Figure 1. The torque value ( $TQ$ ) obtained from the extruder was used as a measure of viscosity. The  $TQ$  of pure aPS homopolymer was higher than that of pure HDPE homopolymer (Figure 1(a)). The  $TQ$  values of the aPS/HDPE and aPS/HDPE/SEBS blends were decreased with the increasing HDPE content except for the blend aPS/HDPE 80/20 (Figure 1(a)). Besides by viscosity of the components, the dependence of  $TQ$  on the blend composition is affected also by the blend morphology and interactions (number of entanglements) between phases [2,22]. Somewhat surprising decrease of  $TQ$  at the addition of SEBS compatibilizer is apparently caused by the changes in morphology (Figure 2(a) with (c) and (e), and (b) with (d) and (f)). The torque/output ( $TQ/Q$ ) and melt back pressure/output ( $p/Q$ ) ratios are reported in Figure 1(b) and (c). The  $TQ/Q$  and  $p/Q$  ratios were decreased with the HDPE content in all examined blends. The amount of SEBS did not significantly influence on the  $TQ/Q$  and  $p/Q$  ratios.



**Figure 1.** Processing parameters of aPS/HDPE/SEBS blends: (a)  $TQ$ , (b)  $TQ/Q$ , and (c)  $p/Q$ .





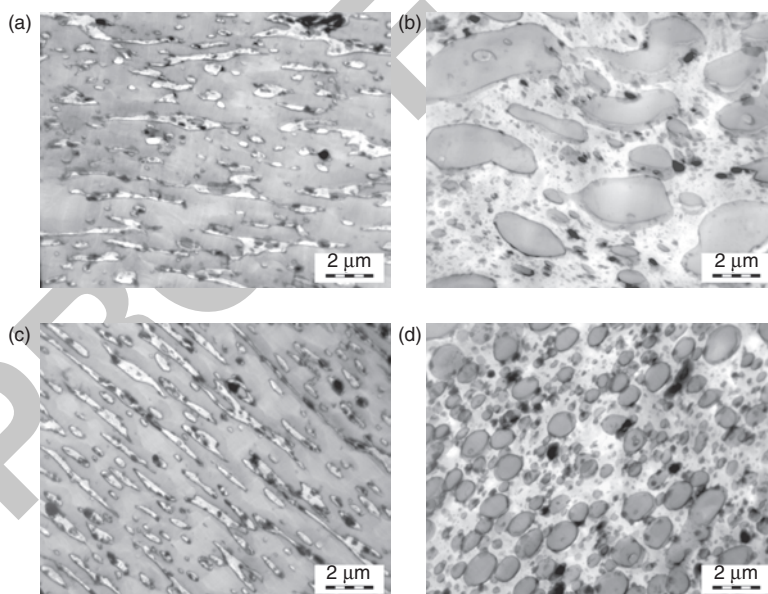
**Figure 2.** Scanning electron micrographs of the fracture surface: (a) aPS/HDPE 80/20, (b) aPS/HDPE 40/60, (c) aPS/HDPE/SEBS 80/20/5, (d) aPS/HDPE/SEBS 40/60/5, (e) aPS/HDPE/SEBS 80/20/7, and (f) aPS/HDPE/SEBS 40/60/7.

### Morphology of the Blends

Scanning electron micrographs of the non-compatible aPS/HDPE blends revealed a particular two-phase morphology (Figure 2(a) and (b)). The sharp edges of particles and holes on the fracture surface indicate poor interfacial adhesion [16]. The coarse morphology of the blends and the detachment of dispersed particles confirmed bad adhesion at the interface between the homopolymers [12] and pointed to incompatibility, which is likely to stem from the high interfacial

tension occurring between components during the melt mixing process. The compatibilization was achieved for aPS/HDPE blends in the presence of SEBS (Figure 2(c)–(f)).

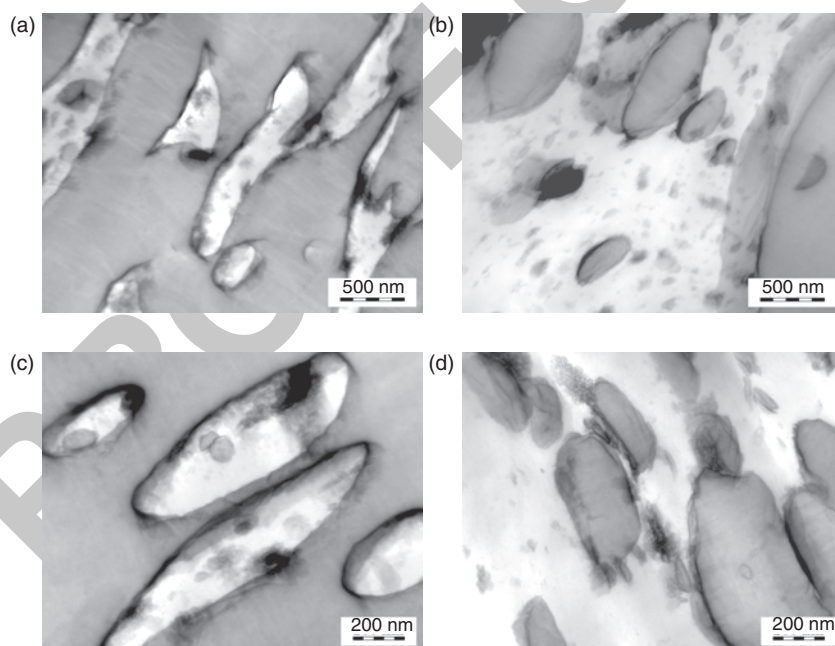
The improvement of the interfacial adhesion in the compatibilized aPS/HDPE/SEBS blends was a result of localization of the SEBS at the interface, which was confirmed by transmission electron micrographs (Figures 3 and 4). Scanning electron micrographs of aPS/HDPE/SEBS 80/20/5 exhibited a more homogeneous morphology compared with aPS/HDPE 80/20. The size of the HDPE dispersed particles was reduced and no holes coming from detached particles were observed, which indicated lower interfacial tension. In the aPS/HDPE/SEBS 80/20/7 blend the HDPE dispersion was very fine and the distinction between phases was scarcely detectable [12]. In the blend with HDPE matrix, the aPS/HDPE/SEBS 40/60/5 coalescence of HDPE particles into a continuous phase was found [12]. Scanning electron micrographs of the blends with lower and higher SEBS content are quite similar (Figure 2(c), (d) with Figure 2(e), (f)), but the improved mechanical properties (Figure 5(b),(c)) suggest that interfacial adhesion between the dispersed and the continuous phase further increased as the concentration of the added compatibilizer increased [1].



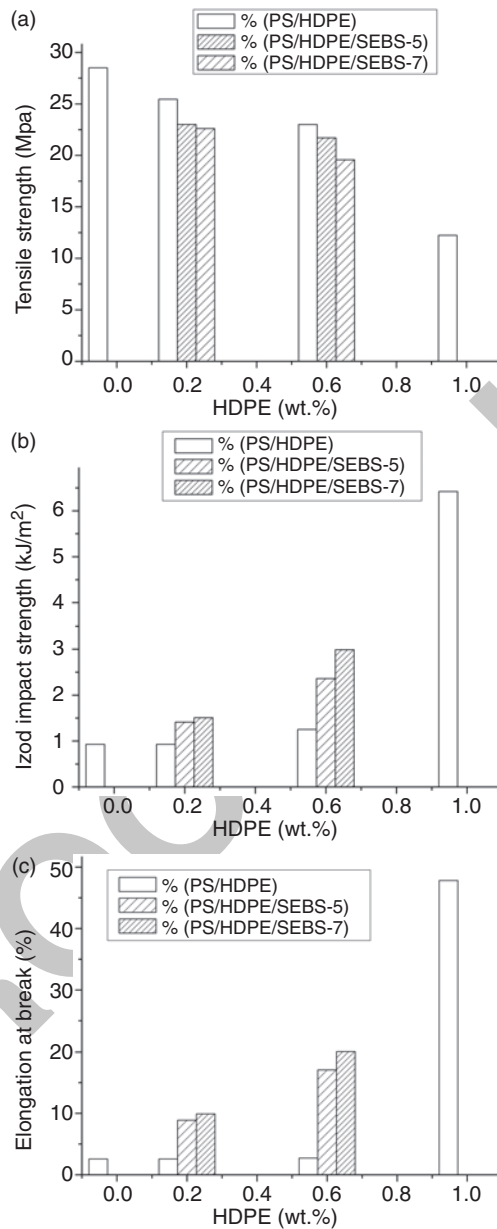
**Figure 3.** Transmission electron micrographs of RuO<sub>4</sub>-stained ultrathin sections: (a) aPS/HDPE/SEBS 80/20/5, (b) aPS/HDPE 40/60/5, (c) aPS/HDPE/SEBS 80/20/7, and (d) aPS/HDPE/SEBS 40/60/7; magnification  $\times 10,000$ .



Transmission electron micrographs are presented in Figures 3 and 4. In the aPS/HDPE/SEBS 80/20/5 blend (Figures 3(a) and 4(a)), the dispersed HDPE particles were mainly elongated as a consequence of lower HDPE viscosity in comparison with the aPS viscosity, which was confirmed by rheological measurements of homopolymers, which were carried out during the processing. Apparently, deformation of low-viscous HDPE particles in high-viscous aPS matrix should be higher than for systems with the opposite viscosity ratio. The SEBS interface layer between the aPS and the HDPE phase was visible, which indicated lower interfacial tension and better adhesion. Inclusions of SEBS were observed inside the HDPE domain (Figures 3(a) and 4(a)). Such an effect is probably due to a major dissolution of aliphatic blocks of SEBS into the HDPE phase rather than that of polystyrene blocks into the PS phase [12]. It can be tentatively explained using Table 1 with molecular weight of components of aPS/HDPE/SEBS blends. Owing to molecular weight of EB block being higher than that of S blocks and HDPE and  $M_n$  of S blocks being substantially lower than



**Figure 4.** Transmission electron micrographs of RuO<sub>4</sub>-stained ultrathin sections: (a) aPS/HDPE/SEBS 80/20/5, (b) aPS/HDPE 40/60/5, (c) aPS/HDPE/SEBS 80/20/7, and (d) aPS/HDPE/SEBS 40/60/7; magnification  $\times 50,000$ .



**Figure 5.** Mechanical properties of examined systems: (a) tensile strength, (b) Izod impact strength, and (c) elongation at break; notations 5 and 7 are for the amount of added SEBS.

Table 1. Summary of average molecular weights of components of all aPS/HDPE/SEBS blends.

Components of aPS/HDPE/SEBS blends $M_n$ (kg/mol)				
aPS	PS-block	SEBS	EB-block	HDPE
115	10		53	14

$M_n$  of PS, formation of SEBS supermolecular structures in HDPE phase is more advantageous than those in aPS phase [23].

In aPS/HDPE/SEBS 80/20/7 (Figures 3(c) and 4(c)) the SEBS interface layer was more pronounced and the inclusion of SEBS in the HDPE domain was observed as in the 80/20/5 blend. The size of dispersed HDPE phase was reduced compared to aPS/HDPE/SEBS 80/20/5. Better homogeneity of blend was found. In the aPS/HDPE/SEBS 40/60/5 blend (Figures 3(b) and 4(b)), the dispersed aPS particles were mainly spherical, which can be attributed to higher viscosity of PS [2,3]. The SEBS interface layer was visible. In the HDPE matrix, some of the SEBS particles were observed due to the higher affinity of aliphatic blocks of SEBS in the HDPE phase. It can be explained also with comparison of molecular weight of EB-block and molecular weight of HDPE homopolymer (Table 1). Localization of copolymers on interfacial layer in polystyrene/polyolefin blends is affected mostly by the length and the number of blocks [18,19,23].

Transmission electron micrographs of aPS/HDPE/SEBS 40/60/7 (Figures 3(d) and 4(d)) exhibited a reduction of the dispersed aPS particles and a more pronounced interface layer. This suggests that despite the existence of SEBS particles in HDPE matrix, HDPE-PS interface is not fully saturated by the addition of 5% of SEBS. Therefore, aPS/HDPE blends containing 7% of SEBS show better interfacial adhesion and lower interfacial tension than the blends with 5% of SEBS. The SEBS particles were also visible in the HDPE matrix.

## Mechanical Properties

The mechanical properties of the investigated systems are reported in Figure 5.

The results of the Izod impact strength and the elongation at break indicated that a modification of a typical brittle aPS polymer with HDPE did not result in ductile material unless the compatibilizer was used (Figure 5(b),(c)). It can be explained by weak interfacial adhesion and

poor dispersion of the components, which is characteristic for incompatible polymer blends [1] and documented by scanning electron micrographs of aPS/HDPE blends (Figure 2(a),(b)). In the presence of SEBS block copolymer, the addition of HDPE as a ductile component in a brittle aPS polymer increased significantly the Izod impact strength and the elongation at break. It is worth noting that the SEBS triblock copolymer plays an important role in improving the tensile ductility of HDPE-rich blends [15]. The presence of SEBS leads to an increase in the adhesion between the rigid aPS particles and the HDPE matrix and a decrease in the dispersed phase size. In the latter case, it is known that the size of dispersed particles has a dramatic effect on the deformation behavior in ductile matrix/brittle dispersed phase systems [24,25]. The ductility of such systems generally increases with finer phase dispersions due to the lower resultant stress concentration when a small particle cracks [15,24]. Finer phase dispersions were also evident from scanning electron micrographs (Figure 2(c)–(f)). The tensile strength is presented in Figure 5(a). The effect of the HDPE addition as a component with a lower tensile strength value was visible in aPS/HDPE blends. The addition of SEBS slightly reduced the tensile strength. This suggests that the tensile strength of compatibilized blends is determined not only by the interfacial adhesion but also by the strength of the matrix that is highly affected by the amount of the compatibilizer [13].

## CONCLUSIONS

The measured processing parameters, i.e.,  $TQ$  values,  $TQ/Q$  and  $p/Q$  ratios were decreased in the aPS/HDPE and aPS/HDPE/SEBS blends with the increasing HDPE content, except for the aPS/HDPE 80/20 blend.  $TQ$  values of aPS/HDPE/SEBS blends were lower than the aPS/HDPE values.  $TQ/Q$  and  $p/Q$  ratios were not modified significantly with the SEBS addition. Scanning electron micrographs of aPS/HDPE blends exhibited a clear macrophase separation and indicated poor interfacial adhesion. The aPS/HDPE/SEBS blends indicated more homogeneous morphology, size reduction of the dispersed particles, and no voids. The localization of SEBS block copolymer at the interphase and in the HDPE phase was confirmed by TEM. The formation of SEBS interface layer and the size reduction of the dispersed particles were more pronounced at a higher content of SEBS block copolymer. In all compatibilized blends, the improvement of interfacial adhesion was confirmed by electron microscopy: the compatibilized blends exhibited

less coarse structure and better interfacial adhesion according to scanning electron micrographs. Incompatibility of aPS/HDPE blends resulted in a poor modification of the aPS Izod impact strength and the elongation at break with the addition of HDPE. The Izod impact strength and the elongation at break were increased by the SEBS addition into the aPS/HDPE blends and were more pronounced in the blends with higher SEBS and HDPE contents. The tensile strength decreased in all blends but not significantly. The decrease was more pronounced in the blend with higher SEBS and HDPE contents. In the investigated aPS/HDPE blends, the SEBS block copolymer improved interfacial adhesion and acted as an impact modifier. The effects are enhanced by an increase in SEBS concentration. Therefore, SEBS can be considered as an efficient compatibilizer for aPS/HDPE blends.

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