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Compatibilization of low-density polyethylene/polystyrene blends by segmented EB(PS-*block*-EB)$_n$ block copolymers

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Summary

Hydrogenated segmented poly[butadiene-*block*-(styrene-*block*-butadiene)$_n$] block copolymers, which were developed by use of a polymeric iniferter technique, were tested on their compatibilizing effectiveness for (10/90) LDPE/PS blends. They were found to be effective compatibilizers for this mixture, already giving a pronounced improvement in both tensile strength and strain of the blend at block copolymer concentrations of one percent. A concentration of five weight percent of segmented block copolymer provided a tenfold improvement in blend toughness. The effectiveness of the segmented block copolymers was found be dependent on the block copolymer composition. Block copolymer compositions of close to 50:50 EB:PS gave the best results.

Introduction

Polymer blends could provide materials having a wide variety of mechanical properties by adjusting the type and quantity of polymers in the mixture. However, because most polymers are immiscible, the blend components usually phase separate into macroscopic domains and consequently show poor mechanical properties, particularly regarding ductility. It is well known that block or graft copolymers, containing blocks of the same chemical structure as the hetero phases in an incompatible binary polymer blends, are capable of compatibilizing these polymer mixtures (1-4). When localized at the interface between the immiscible polymers, the block copolymers lower the interfacial tension, thereby dispersing the polymer blend into smaller domains due to reduced coalescence of the stabilized particles. Consequently, the blends may show improved ductility, because of enhanced force transfer between the different phases.

Although the compatibilization of blends has been investigated extensively, the effect of compatibilizer architecture is still rather questionable. The number of blocks appear to play a significant role here. In various experimental studies quite different effects of the number of blocks in a block copolymer on its compatibilizing effectiveness have been reported. For example, in a paper by Teyssié et al. diblock copolymers have been found to be more efficient compatibilizers than triblock copolymers (5), while in some other works quite the opposite effect is presented (6-8), and another one states that there is no difference in compatibilizing effectiveness between di- and triblock copolymers (9).

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A number of recent theoretical papers seem to lead to the conclusion that multiblock copolymers would be the most efficient compatibilizers. For example, in a theoretical analysis by Noolandi (10), it is argued that, because of its structure, less $(AB)_n$ multiblock copolymer than AB diblock copolymer is lost in bulk phases as micelles and mesophases. Also, he argues that a diblock copolymer is oriented perpendicularly to the interface plane while a multiblock copolymer will lie in the plane of the interface. Therefore, a multiblock copolymer molecule would cover a larger part of the interfacial surface than a diblock copolymer. This prediction is in line with results of recent computer simulations by Anna Balazs (11,12), who compared the compatibilizing effectiveness of various copolymers with different architectures. According to these simulations the determining factor for the improvement in interfacial adhesion is the number of effective crossings or 'stitches' which a block copolymer chain is able to form across the interface. So, an increasing number of alternating A and B blocks in the block copolymer at a polymer/polymer interface will give an increase in interfacial adhesion, provided that the blocks are long enough to be able to form entanglements with the bulk polymers, thereby reducing the risk of chain pull-out.

To look at the effectiveness of multiblock copolymers, we prepared several types of multiblock copolymers by use of a polymeric iniferter technique. The term 'iniferter' is used for free radical initiators with simultaneous chain transfer and terminating properties, thereby providing a pseudo-living polymerization (13-16). This technique enabled us to synthesize a novel type of multiblock copolymer, consisting of alternating polybutadiene (PB) and (styrene-*co*-acrylonitrile) (SAN) blocks (17,18), or alternating polybutadiene and (styrene-*co*-maleic anhydride) (SMA) blocks (19). The former multiblock copolymers proved to be very efficient compatibilizers for blends of polyethylene and poly(vinyl chloride) (20). Also, segmented block copolymers of polybutadiene and polystyrene (PS) were prepared by the polymerization of styrene, using a polybutadiene-based iniferter as the initiating species. In the present study, the compatibilizing effectiveness of the hydrogenated PB(PS-*block*-PB)$_n$ multiblock copolymers, which we will designate as EB(PS-*block*-EB)$_n$ block copolymers (EB meaning ethylene-*co*-butylene) from here on, for (10/90) low-density polyethylene/ polystyrene (LDPE/PS) blends, which are inherently brittle, was investigated.

Experimental

Synthesis of segmented EB(PS-block-EB)$_n$ block copolymers

The synthesis of the polybutadiene iniferter and corresponding block copolymers was performed as described previously (17).

Hydrogenation reactions of the segmented block copolymers were carried out in a three-necked flask, equipped with a reflux condenser, under nitrogen atmosphere. The segmented PB(PS-*block*-PB)$_n$ block copolymer was placed in the vessel and dissolved in dry toluene (approximately one gram per fifty ml. of toluene). Upon complete dissolution of the polymer, *p*-toluenesulfonyl hydrazide (TSH; as the diimide producing species) and tri-*n*-propyl amine (to avoid protonation of the unsaturated polymer and consequent addition of the *p*-toluene-sulfinate anion) were added to the solution (both in a molar ratio of two per site of unsaturation in the block copolymer). TSH is only slightly soluble in toluene at room temperature but dissolves completely upon heating. The system was heated to reflux (110 °C) for 2 hours. The polymer was isolated by washing the toluene solution twice with 100 ml. deionized water, and precipitating the polymer into methanol. The recovered polymer was dried *in vacuo*. Hydrogenation

Blend preparation by melt mixing in a twin-screw micro-extruder

Ninety parts of a general-purpose polystyrene (Dow Styron 686E) together with ten parts of a low-density polyethylene (Stamylan LD 2100 TN00; DSM Geleen, The Netherlands) were premixed in a Brabender. A small amount of this mixture (approximately 4 grams) was then melt mixed together with the required amount of block copolymer in a co-rotating twin-screw micro-extruder for five minutes at 160 °C and a rotation speed of 75 rpm. After processing, the blend was immediately cooled into cold water and subsequently dried *in vacuo* at 40 °C for at least two days. For each blend composition, two separate mixing experiments were conducted.

Blend characterization

Tensile specimens (ASTM D1708) of the obtained blends were prepared by compression molding at 150 °C. After a preheating time of four minutes, and subsequential thorough degassing of the mixture, the specimens were compression molded for three minutes and finally quenched into cold water. The tensile properties were measured in an Instron tensile tester at room temperature, using a crosshead speed of 10 mm/min. The results were averaged over 4 tests per sample.

The morphology of the blends was studied by carrying out scanning electron microscopy (SEM) on cryo-fractured specimens, using a Jeol 6320 F Field Emission Scanning Electron Microscope.

Results and discussion

Block copolymers used in this study

In this work we studied the compatibilizing behavior of EB(PS-*block*-EB)$_n$ block copolymers having different compositions and molecular weights. These multiblock copolymers were prepared by synthesis of a polybutadiene-iniferter, followed by thermal polymerization of the required amount of styrene, using the polymeric iniferter as the initiating species (see Scheme 1). Because of primary radical termination and chain transfer reactions during polymerization, there is a distribution of the number of blocks in the obtained block copolymers. This number was calculated from the block copolymer composition and molecular weight. The characteristics of the synthesis of this type of block copolymer were described previously (17). The hydrogenation of their polybutadiene blocks was performed by a diimide reduction technique (21,22), using toluene sulfonyl hydrazide as the diimide generating species. Hydrogenation efficiency was checked by NMR and found to be practically quantitative (≥ 99 %).

Scheme 1. Synthesis of segmented PB(PS-*block*-PB)$_n$ block copolymers.

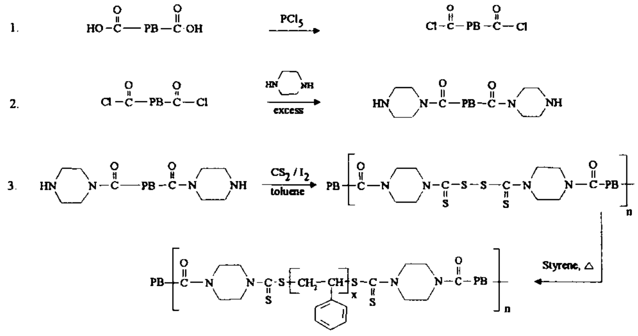

Table 1. Characteristics of block copolymers used in this study.

Code	Mn block copolymer $\times 10^{-4}$	average number of altern. blocks	weight % PS in block copolymer	Mn EB-blocks (10^4g/mol)	Mn PS-block length (10^4g/mol)
EBS-1	15.0	3.2	85.6	1.0	11.7
EBS-2	12.4	4.2	79.0	1.0	6.1
EBS-3	6.6	4.3	59.3	1.0	2.4
EBS-4	5.5	5.2	41.9	1.0	1.1

In Table 1, the characteristics and code names of the segmented block copolymers are listed. The molecular weight of the hydrogenated polybutadiene blocks is the same for all block copolymers, since this is predetermined in their synthesis. The EB block length is well above the entanglement molecular weight (M_e (PE) ≈ 2000 g/mol). Only EBS-4 contains PS blocks which are shorter than the PS entanglement molecular weight (M_e (PS) ≈ 17.000 g/mol). Further, the difference between the four block copolymers is mainly the composition, number of blocks and molecular weight.

(10/90) LDPE/PS blends processed in a micro-extruder

For the blends, which were processed in a co-rotating twin-screw micro-extruder, we used a commercial polystyrene (Dow Styron 686 E; Mn $=1.13\times10^5$ g/mol, Mw = 2.83×10^5 g/mol), while the low density polyethylene used was Stamylan LD 2100 TN00 (DSM Geleen, The Netherlands, meltflow index 0.3 dg/min). The processing temperature was 160 °C for every blend, while the compression molding temperature was 150 °C. Table 2 shows the mechanical properties of the (10/90) LDPE/PS blends, compatibilized with various segmented EB(PS-*block*-EB)$_n$ block copolymers, added in amounts varying from 1 to 10 weight percent. The (10/90) polyethylene/polystyrene blend exhibits very poor mechanical properties compared to those of the pure polymers, especially regarding both elongation at break of the material (ε_b = 1.2 %) and tensile strength (σ_b = 8.9 MPa). However, there is a distinct improvement in mechanical properties of the LDPE/PS blend when a small amount of segmented block copolymer is added. Both the tensile strength and the elongation at break of the blend increase significantly by the addition of the segmented block copolymer, leading to an

Table 2. Mechanical properties of compatibilized (10/90) LDPE/PS blends.

compatibilizer	compatibilizer content (wt.%)	E_{young} (GPa)	σ_{break} (MPa)	ε_{break} (%)	toughness (MPa)
-	0	1.4	8.9 ± 0.4	1.2 ± 0.2	0.07 ± 0.04
EBS-1	1	1.1	21.7 ± 1.8	2.5 ± 0.6	0.34 ± 0.10
	5	1.2	22.4 ± 1.0	3.7 ± 0.7	0.53 ± 0.08
	10	1.2	25.2 ± 1.4	3.3 ± 0.4	0.57 ± 0.11
EBS-2	1	1.4	21.4 ± 2.9	3.0 ± 0.4	0.46 ± 0.12
	5	1.1	22.5 ± 1.0	2.8 ± 0.5	0.40 ± 0.07
	10	1.2	23.7 ± 0.9	2.7 ± 0.2	0.39 ± 0.04
EBS-3	5	1.2	25.7 ± 2.3	3.7 ± 0.8	0.61 ± 0.11
	10	1.1	30.1 ± 1.6	4.4 ± 0.4	0.76 ± 0.08
EBS-4	1	1.3	12.9 ± 1.2	2.1 ± 0.3	0.15 ± 0.05
	5	1.2	27.4 ± 2.4	4.0 ± 0.7	0.72 ± 0.14
	10	1.1	26.3 ± 0.9	4.0 ± 0.2	0.67 ± 0.04

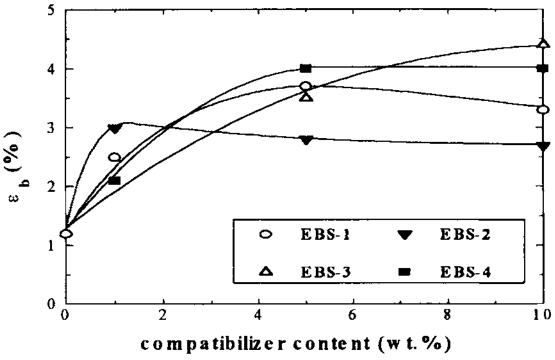

Figure 1. **Elongation at break of a (10/90) LDPE/PS blend versus compatibilizer content for various segmented block copolymers.**

improvement in the blend toughness (which corresponds to the area under the stress-strain curve) of up to ten times the value of the uncompatibilized blend. Table 2 indicates that the relatively low molecular weight block copolymers EBS-3 and EBS-4 are the most effective compatibilizers, although all of the tested multiblock copolymers gave the desired improved blend properties. In Figure 1, the elongation at break of the blend is plotted as a function of compatibilizer content for the four different segmented block copolymers. The elongation at break seems to be levelling off at a concentration of approximately five weight percent block copolymer. Possibly, at this compatibilizer content the interface is saturated with block copolymer. Addition of more block copolymer will lead to the formation of bulk phases of block copolymer (or possibly multi-layers at the interface) and the effect on the blend properties of this excess amount of block copolymer will therefore depend upon the mechanical properties of the block copolymer itself. Formation of micelles or other aggregates of block copolymer could lead to a rubber toughening effect by the additional block copolymer.

Of course, it is difficult and rather risky to explain the difference in compatibilizing effectiveness of the segmented block copolymers because both number of blocks and composition of the block copolymers are different. Because EBS-2 and EBS-3 have practically the same average number of blocks, it is relatively 'safe' to compare these two block copolymers in terms of their molecular weight. From Table 2, it is obvious that the lower molecular weight EBS-3 is more effective in improving both the elongation at break and the tensile stress than EBS-2. Both block copolymers have blocks long enough to form entanglements and therefore they can be considered as effective interfacial adhesion promoters (23). So, probably the lower molecular weight block copolymer EBS-3 is more effective, because migration to the blend interface is easier for a low molecular weight polymer. Moreover, micellization might occur less frequently with EBS-3 compared to EBS-2 because of its more symmetric composition, although these segmented block copolymers are not expected to form micelles easily anyway (10). Furthermore, EBS-3 is the only block copolymer which still gives an increase in elongation at break of the material with ten weight percent added EBS-3. This might be due to an additional toughening effect of formed bulk

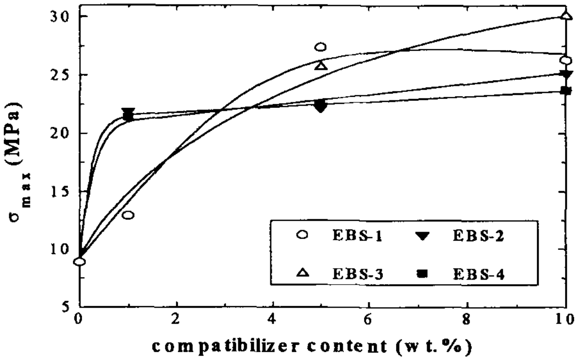

Figure 2. **Blend tensile strength versus compatibilizer content for different segmented EB(PS-*block*-EB)$_n$ block copolymers.**

phases of excess block copolymer material (at the interface or in the bulk material), but more research has to be done on this subject to conclude anything from this observation.

Finally, it is actually surprising that the lowest molecular weight segmented block copolymer EBS-4 gives such good results in this study, since its polystyrene blocks have a molecular weight well below the entanglement molecular weight. Therefore, this block copolymer should be considered as an emulsifier for this blend, because it can only lower the interfacial tension and cannot promote interfacial adhesion (23). However, because these block copolymers have fairly large polydispersities (2 to 3), it is possible that a part of the polystyrene blocks is long enough to form entanglements and the block copolymer is linked to both blend phases at the interface.

The same trend can be seen in Figure 2 for the tensile strength of the blend after addition of segmented block copolymer. The addition of one percent of block copolymer already gives rise to an increase in tensile strength, while addition of more block copolymer further highers the blend's tensile strength. There is no obvious trend to be seen for the effect of block copolymer on the blend tensile strength as a function of block copolymer structure. It is remarkable, however, that again EBS-3 gives the best result of the four block copolymers.

To evaluate the results obtained with these segmented block copolymers, they were compared with the results from a study by Fayt *et al.* (5), who compared the compatibilizing activity of various copolymer architectures for LDPE/PS blends of different compositions. It can be seen in Table 3, that the segmented block copolymers, used in this study are the most effective compatibilizers together with the pure diblock copolymer. Comparing the diblock and the multiblock, the segmented block copolymers is more efficient in improving the tensile strength (probably due to the multiple stitches through the interface), while the diblock is more effective for the improvement of the elongation at break (because of less conformational constraints at the interface for the diblock). The diblocks and the segmented block copolymers both effectuate a 1100% improvement of the energy to break (which corresponds to the total amount of energy dissipated during the tensile test).

Table 3. **Maximum improvement in tensile strength ($\Delta\sigma_b$), elongation at break ($\Delta\varepsilon_b$) and energy to break (ΔE_B) for 10/90 LDPE/PS blends added with 10 wt.% of various copolymers**

Copolymer structure	$\Delta\sigma_b$ (%)	$\Delta\varepsilon_b$ (%)	ΔE_B (%)
Pure Diblock[a]	43	800	1100
Tapered Diblock[a]	66	125	275
Triblock (Kraton G1651)[a,b]	20	0	-[c]
Graft[a,b]	55	0	-[c]
Star-shaped[a,b]	20	0	-[c]
Multiblock (EBS-3)	238	267	1100

a *data taken from reference (5)*
b *for 20/80 LDPE/PS blends*
c *data were not available*

However, to make a detailed and complete comparison between the different architectures, compatibilization of LDPE/PS blends of several compositions by the segmented block copolymers should be studied.

To look at the emulsifying properties of these block copolymers more closely, we studied some blends with Scanning Electron Microscopy. In Figure 3, a Scanning Electron Micrograph of a cryo-fractured (10/90) LDPE/PS blend is shown, which reveals rather big lumps of polyethylene particles (indicated by arrows in Figure 3), while the surface of the material is very rough. Figure 4 shows a SEM of a 10/90 LDPE/PS blend, compatibilized with 10 weight percent of EBS-3. At the same magnification no separate polyethylene phase can be detected anymore, while the surface of the material is considerably smoother.

This is a clear indication that the blend has indeed been compatibilized by the segmented block copolymer and the improvement in mechanical properties of the blend is not just a rubber toughening effect. Therefore, the conclusion seems to be justified that the segmented EB(PS-*block*-EB)$_n$ block copolymers are effective compatibilizers for blends of polystyrene and low-density polyethylene.

Conclusions

The synthesized hydrogenated segmented block copolymers of polybutadiene and polystyrene are effective agents for the compatibilization of (10/90) blends of low-

Figure 3. SEM of a cryo-fractured (10/90) LDPE/PS blend, (arrows indicate PE-particles).

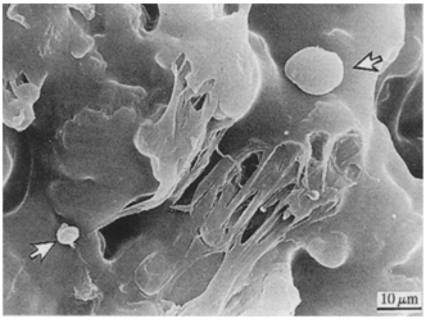

Figure 4. SEM of a cryo-fractured (10/90) LDPE/PS blend, compatibilized by 10 wt.% EBS-3.

density polyethylene and polystyrene, resulting in significantly improved mechanical properties of the blend by addition of only a small amount of block copolymer (one weight percent). Both the tensile strength and the elongation at break are improved by the addition of a segmented EB(PS-*block*-EB)$_n$ block copolymer, indicating a reduced interfacial tension and an enhanced force transfer between the separate phases in the blend. Addition of ten weight percent segmented block copolymer gave a more than tenfold improvement of the blend toughness, while SEM indicated a considerable reduction in LDPE particle size in the blend due to compatibilization. Comparison of the obtained results with results obtained for other architectures leads to the conclusion that these segmented block copolymers are the most efficient architectures for the improvement of the blend's tensile strength, and only diblock copolymers are more effective in improving the elongation at break (because of less conformational constraints at the interface for the diblock). However, a study of the compatibilization of LDPE/PS blends of other compositions by the segmented EB(PS-*block*-EB)$_n$ block copolymers will have to be performed in the future to make a complete comparison with other architectures.

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