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Stabilization of high-impact polystyrene/polyethylene blends

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Commercial poly(styrene-b-butadiene) copolymers (SBS) can act as effective compatibilizers in blends between high-impact polystyrene (HIPS) and polyethylene (PE), allowing a fine dispersion of PE in the polystyrene matrix, with a good balance of stiffness and impact strength. However, when processed under more severe conditions (e.g. in multiple extrusions, which simulate customer's product scrap recovery), the above blends show rather poor stability and their useful properties are rapidly lost. That undesirable effect is mainly due to cross-linking of SBS, which thus looses its compatibilizing activity. A correlation has been found between the time-to-cross-linking of SBS rubber in a Brabender mixer and the rapid decay of mechanical properties. The analysis of the mixing process and the morphology examinations of the final blend sample by TEM seem to support the above hypothesis. A significant reduction of block copolymer degradation has been achieved by means of a suitable stabilization.

1. Introduction

The blends between polystyrene (PS) and polyethylene (PE) are quite interesting from an industrial point of view: they offer chemical resistance and impact strength; furthermore, they are based on cost-effective and easily processable materials. But, as in many other polyblends, PS and PE are incompatible and the means of alloying them is the use of a suitable compatibilizer.

An outstanding work on that topic has been carried out by P. Teyssie's group [1–7]; so the use of the poly(styrene-b-ethylene) copolymer as a compatibilizer and the influence of its molecular properties on some characteristics of the resulting polyblends are well known. No information has been reported in those works on typical technological properties of these blends, i.e. Izod impact strength, Vicat etc.; a complete characterization requires a rather large quantity of material, possibly from the same batch, and the synthesis of the suitable compatibilizer seems to be the critical point [6].

Other interesting works on PS/PE blends either with [8, 9] or without a compatibilizer [10–12] have been carried out by different researchers. We have recently found [13] that the goal of a good compromise between cost and mechanical properties can be reached in PS–PE blends by using high-impact polystyrene (HIPS) instead of homopolymer PS and employing commercial poly(styrene-b-butadiene) copolymers as the compatibilizers.

A typical end use for these materials is sheet extrusion and thermoforming, but we actually found a rapid decay of mechanical properties (e.g. notched Izod impact strength) after multiple extruder passages, which simulates the scrap recovery in the usual processing cycle of a customer.

In order to understand well the main mechanisms involved in that phenomenon and the role played by the stabilizers, we planned to study the behaviour of the product when processed in a Brabender Plasticorder mixer. No information has been reported so far on antioxidant packages useful to maintain the properties of the blend after a long residence time in a mixing device, either a Brabender type or an extruder.

2. Experimental procedure

The HIPS and the compatibilizer (SBS) were chosen as reported in [13]. The PE used was a commercial type, sold under the tradename of Escorene (melt flow index, MFI = 0.7 g/10 min density = 0.926 g/ml^{-1}). The composition of the reference blend was: 75% HIPS, 15% PE, 10% SBS (all parts by weight).

The antioxidants used were: hydroxyphenylpropionate, (tradename Irganox 1076), and a suitable formulation of phenolic stabilizers.

The polymer blends have been prepared in an internal mixer Brabender Plasticorder, model PLE 651, with a 50 ml cell, recording the torque versus processing time at a given temperature. Blend multiple extrusions have been performed on a Bandera TR45 single screw machine.

Machine features are as follows: screw diameter 45 mm; temperature range 210–240 °C; screw speed 100 r.p.m.; no vent.

For the evaluation of notched Izod impact strength (ASTM D256) and tensile properties (ASTM D638), test specimens were moulded using a Negri and Bossi

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(model V17) injection moulding machine, under the following conditions: injection moulding temperature 180 °C; mould temperature 30 °C; melt flow index (MFI), according to ASTM D1238, was measured at 220 °C/10 kg.

Finally, blend morphology was investigated using a transmission electron microscope (TEM Philips EM 301), using the sample staining technique described by Kato [14].

3. Results and discussion

3.1. Brabender processing

The thermomechanical properties of a freshly prepared HIPS/PE/SBS (75:15:10) polyblend with Irganox 1076, 0.15 p.h.r., as antioxidant are reported in Table I. The above formulation is referred to as the "standard blend".

Typically, after six extrusions, Izod (1/2 in.) (1.27 cm) drops from 310–133 $\mathrm{J\,m^{-1}}$ and MFI, after two passages, from 30/10 min to 12/10 min g. In order to explain the above findings, morphologies in the fresh blend and after the last extrusion were investigated by TEM and are shown in Figs 1. and 2.

Fig. 1 (the fresh blend) shows both HIPS typical rubber particles and the PE dispersion among them, in tiny clear droplets surrounded by SBS rubber darker areas. In Fig. 2 (the blend after six extrusions) a completely different situation appears: HIPS particles are still present, but tend to agglomerate, while the fine PE dispersion has collapsed to rather large domains without darker boundaries. Thus, an extensive blend demixing has taken place which we attributed to the degradation of SBS component, which could no longer act as a PE emulsifier.

A Brabender Plasticorder machine was chosen for small-scale, quick preliminary testing of the degradation mechanism.

The second step was to correlate the Brabender test results to multiple extrusion scrap recovery: notched Izod impact strength, elongation at break and MFI have been measured after each extrusion.

TABLE I HIPS/SBS/PE blend properties

	ASTM method	Value
Tensile properties	D 638	
yield stress		19 $\mathrm{N\,mm^{-2}}$
stress at break		18 $\mathrm{N\,mm^{-2}}$
elongation at break		65%
elastic modulus		1400 $\mathrm{N\,mm^{-2}}$
Flexural properties	D 790	
flexural stress		29 $\mathrm{N\,mm^{-2}}$
elastic modulus		1400 $\mathrm{N\,mm^{-2}}$
Notched Izod impact strength	D 256	
3.2 mm, 23 °C		400 $\mathrm{J\,m^{-1}}$
12.7 mm, 23 °C		310 $\mathrm{J\,m^{-1}}$
VICAT	ISO 306	
1 kg, 50 °C $\mathrm{h^{-1}}$		100 °C
5 kg, 50 °C $\mathrm{h^{-1}}$		78 °C
MFI	D 1238	
220 °C/10 kg		30 g/10 min

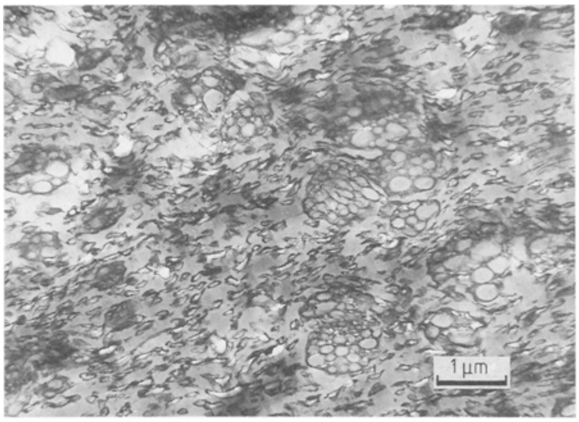

Figure 1 Standard blend (TEM).

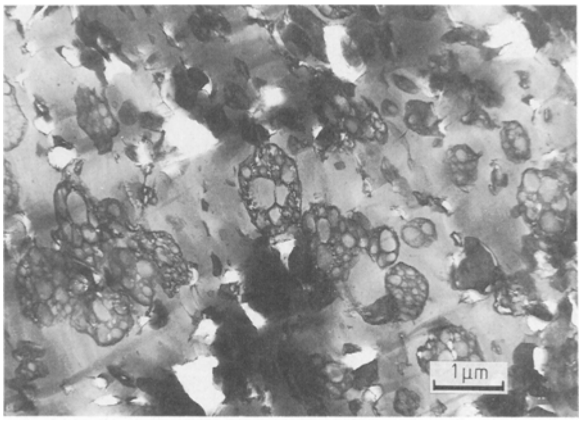

Figure 2 Standard blend after six extrusions at 210 °C (TEM).

The observation of the torque value in the Brabender machine is a simple and reliable tool for evaluating cross-linking and/or degradation phenomena in blend preparation, especially if based on rubbers or rubber-like materials [15–18]. For example, in processing HIPS at 220 °C and 100 r.p.m. (Fig. 3), the viscosity, and therefore the torque value, is very high in the feeding stage at the beginning of mastication. When plastification is over, a plateau is reached; for longer processing times, the torque values tend to decrease smoothly owing to a slow polymer degradation.

This behaviour has been taken as a reference and the profile of the HIPS plot as a "baseline" for the following experiments on HIPS/PE/SBS blends.

When processing the standard blend, a shoulder in the torque–time plot has been observed after about 135 s mastication (Fig. 4). We have interpreted that as the onset of SBS cross-linking, which causes an increase, even small, in viscosity of the system. For a longer processing time, as before, the torque value begins to decrease, because degradation phenomena prevail. In fact, the toluene insoluble fraction of the blend (HIPS gel + PE) increases from 34% to 39%, indicating that some new "gel" phase has been created after Brabender treatment. Transmission electron micrographs are consistent with what was previously shown (Figs 1 and 2).

About the influence of the processing conditions, higher temperatures speed up SBS cross-linking (90 s

TABLE II HIPS/SBS/PE blends

	P1	P2	P3	P4	P5	P6	P7	P8
HIPS (%)	75	75	75	85	75	75	80	60
PE (%)	15	15	15	15	15	15	10	30
SBS (%)	10	10	10			10	10	10
SEBS (%)					10			
Irganox 1076 (p.h.r.)	0.15	0.15	0.15	0.15	0.15	[a]	0.15	0.15
Temperature (°C)	220	235	250	220	220	220	220	220
Cross-linking time (s)	135	120	90	> 400	> 400	330	135	135

[a] Improved stabilization package

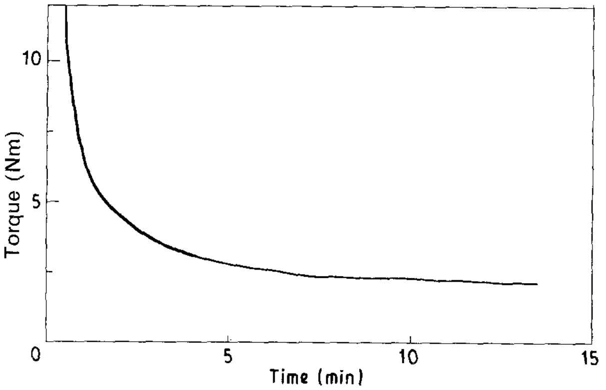

Figure 3 Torque–time evaluation of HIPS, in a Brabender PLE 651 at 220 °C and 100 r.p.m.

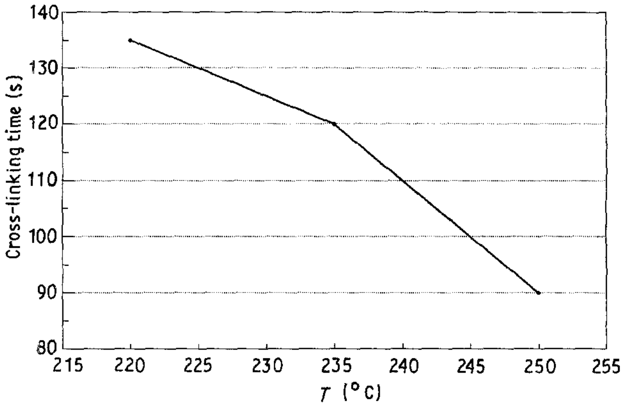

Figure 5 Cross-linking-time evaluation of HIPS/SBS/PE blend (P1) in a Brabender PLE 651 at different temperatures.

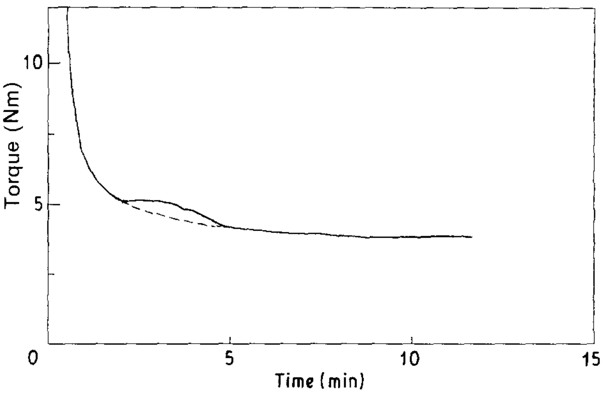

Figure 4 Torque–time evaluation of HIPS/SBS/PE (P1) in a Brabender at 220 °C and 100 r.p.m. Time-to-cross-linking = 135 s.

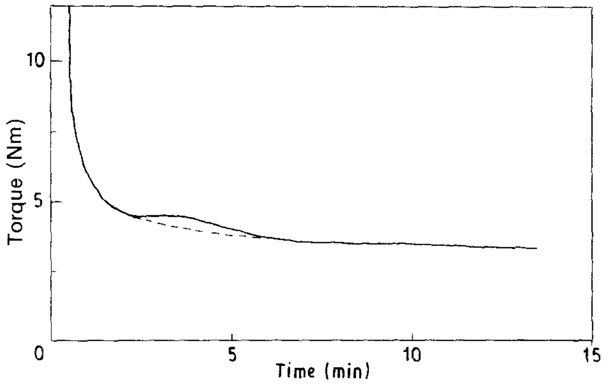

Figure 6 Torque–time evaluation of HIPS/SBS/PE (P7) in a Brabender at 220 °C and 100 r.p.m. Time-to-cross-linking = 135 s.

mastication at 250 °C, with respect to 135 s. 220 °C, Fig. 5). The cross-linking time depends on the chemical structure of the compatibilizer, as shown by the behaviour of P1 and P5 (Table II), under the same processing conditions (temperature, blend composition and antioxidant level); the higher the double bond or insaturation content, the shorter is the time of cross-linking onset. Saturated rubbers such as SEBS triblock show higher times to cross-link (> 400 s, P5 blend).

We have also found, surprisingly, that on increasing the PE content at constant 10% SBS level in the mixture (Figs 6 and 7) the dashed area increases too; it should be pointed out that the time-to-cross-linking is the same (135 s), because the amount of PE has no effect on this.

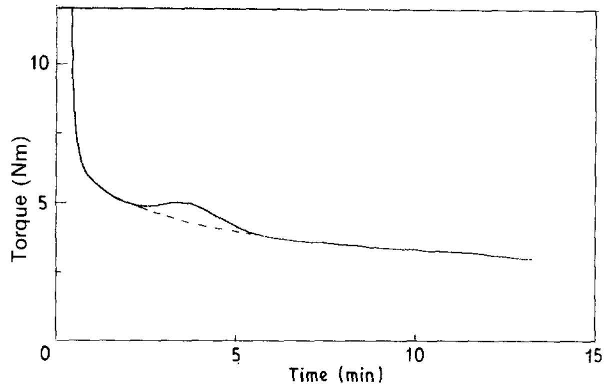

Figure 7 Torque–Time evaluation of HIPS/SBS/PE (P8) in a Brabender at 220 °C and 100 r.p.m. Time-to-cross-linking = 135 s.

With SBS+PE contents of 20% (P7 sample) the change in the torque is hardly detectable; this composition appears to be the limit of the method used.

The P6 blend shows a cross-linking time much higher than that of the standard blend (Table II, 330 s versus 135 s), proving that a useful stabilization package delays the degradation of SBS rubber.

3.2. The single screw extrusion

The hypothesis concerning the behaviour of the blend HIPS/SBS/PE 75/10/15, based on the test carried out in Brabender machine, was confirmed by multiple extrusion in a single screw extruder, which simulates the customer's scrap recovery. Izod impact strength (1/2 in.), tensile properties and MFI (220 °C/10 kg), were tested after two, four and six steps.

The blends were extruded at two different temperatures, 210 and 240 °C, with a residence time of nearly 50 s each passage. The sample containing only Irganox 1076 shows a considerable loss of both toughness and elongation at break even at 210 °C (Table III).

Izod impact strength drops from 310 J m^{-1} to 273 J m^{-1} after four passages and to 195 J m^{-1} after six passages. The elongation at break shows a similar pattern with a sharp drop from 65% to 31% after six passages.

The rheological behaviour is quite different because the SBS cross-linking lowers the viscosity of the system, as seen previously in the Brabender mixer with the increase of the torque. MFI drops from 30 g/10 min to 11.4 g/10 min (minimum value) after four passages, then increases to 18 g/10 min after six passages.

At higher temperature (240 °C) the loss of impact strength is dramatic, with only 133 J m^{-1} after six passages; the increase in temperature speeds up the degradation phenomena and MFI reaches a minimum value (12 g/10 min) after two passages (Fig. 8). An increase in the temperature from 220 °C to 250 °C in Brabender mixer lowered the time-to-cross-linking from 135 s to 90 s, speeding up SBS degradation. The change in morphology after six passages at 210 °C seems to be dramatic: HIPS particles are still present but tend to agglomerate while the fine PE dispersion collapsed to rather large domains without any darker boundary.

TABLE III Multiple extrusion at 210 °C. Blend stabilized with Irganox 1076

	0	II	IV	VI
Tensile properties				
yield stress (N mm^{-2})	19	18	19	18
stress at break (N mm^{-2})	18	18	19	18
elongation at break (%)	65	54	34	31
elastic modulus (N mm^{-2})	1400	1400	1450	1400
Izod impact strength (J m^{-1})	310	295	273	195
Izod impact strength^{a} (J m^{-1})	310	260	180	133
MFI (220 °C/10 kg) (g/10 min)	30	21	11.4	18
MFI (220 °C/10 kg)^{a} (g/10 min)	30	12	23.4	26.4

[a] Extruded at 240 °C.

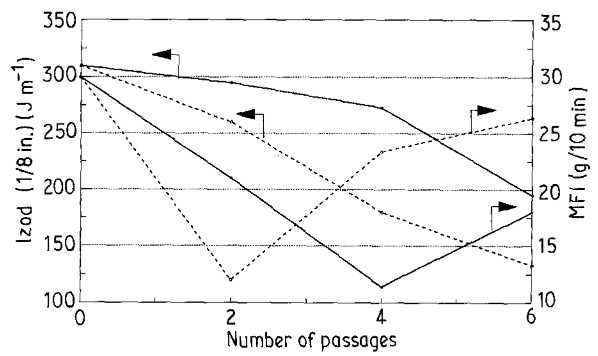

Figure 8 Izod impact strength and MFI (220 °C, 10 kg) evaluation of HIPS/SBS/PE blend (P 1) after two, four and six passages in a single screw extruder, at (——) 210 °C and (- - -) 240 °C.

TABLE IV Multiple extrusion at 210 °C. Improved stabilization package

	0	II	IV	VI
Tensile properties				
yield stress (N mm^{-2})	19	18	19	18
stress at break (N mm^{-2})	18	18	18	19
elongation at break (%)	65	65	60	54
elastic modulus (N mm^{-2})	1400	1350	1400	1400
Izod impact strength (J m^{-1})	310	304	300	294
Izod impact strength^{a} (J m^{-1})	310	280	210	177
MFI (220 °C/10 kg) (g/10 min)	30	29.4	27	22
MFI (220 °C/10 kg)^{a} (g/10 min)	30	16.8	19.5	25.5

[a] Extruded at 240 °C.

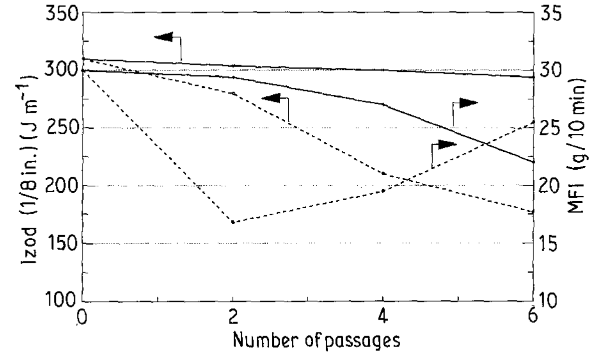

Figure 9 Izod impact strength and MFI (220 °C, 10 kg) evaluation of HIPS/SBS/PE blend (P6) after two, four and six passages in a single screw extruder, at (——) 210 °C and (- - -) 240 °C.

SBS rubber, acting as a compatibilizer, is no longer present at the interface between PE and PS but seems to be collapsed into rather large and dark domains. A suitable stabilization package delays the degradation phenomena with a less evident decay of the mechanical–rheological properties with respect to the decay shown by the standard blend (Table IV). The stabilized blend shows a better impact strength after multiple passages, from 310 J m^{-1} (fresh blend) to 294 J m^{-1} (blend after six passages at 210 °C). Elongation at break drops from 65% to 54% while the MFI steadily lowers from 30 g/10 min to 22 g/10 min at 210 °C without reaching any minimum value. At

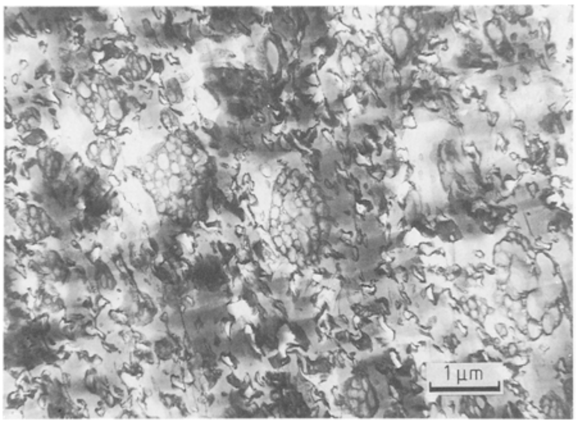

Figure 10 Blend with improved stabilization after six extrusions at 210 °C (TEM)

240 °C the MFI decay is less evident than that shown by the standard blend (Fig. 9).

The morphology after six extrusions at 210 °C is consistent with the good mechanical–rheological properties of the blend. The change in morphology is less dramatic, compared to the change shown by the standard blend: a fine PE dispersion is still detectable while HIPS rubber particles are not agglomerated (Fig. 10).

4. Conclusion

A useful method to investigate the thermostability of a HIPS/SBS/PE blend has been found. A blend with a suitable stabilization shows a delayed time-to-cross-linking of the SBS rubber. This quick and reliable method is consistent with a multiple extrusion test, which simulates the customer's scrap recovery.

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