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Compatibilisation of polystyrene-polyolefin blends

Impact properties

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Summary

The impact properties of 1:1 polyolefin-polystyrene blends compatibilised with a series of hydrogenated styrene-butadiene block copolymers of various structures have been studied with a view to establishing a structure-property realationship. The most effective compatibiliser in this context appears to be a low molecular weight triblock (Kraton G1652). Addition of only 5% Kraton G1652 affords a ca. three-fold improvement in the impact strength for a 1:1 PP/PS blend over the uncompatibilised blend and leads to near HIPS impact strength for a 1:1 LDPE/PS blend. This compatibiliser is as effective as a high molecular weight tapered diblock and appears to be substantially more effective than either low molecular weight diblocks or a higher molecular weight triblock.

Introduction

The compatibilisation of polyethylene-polystyrene (PE/PS) blends has been extensively investigated.(1-4) The most thorough study of the relationship between compatibiliser structure and effectiveness, can be found in a series of papers by Fayt, Teyssie et al.(2) These authors came to the conclusion that high $\bar{M}_n$ hydrogenated polybutadiene-polystyrene (HPB-PS) diblocks are more effective compatibilisers than the corresponding triblock, star or graft copolymers. On the other hand, a study by Schwartz et al.(3) on HDPE/PS blends found that a low $\bar{M}_n$ triblock (Kraton G1652) was substantially better than either a higher $\bar{M}_n$ triblock (Kraton G1651) or a low $\bar{M}_n$ diblock in improving impact properties.

In contrast, although there is literature on properties and morphology of polypropylene-polystyrene (PP/PS) blends(5,6), relatively little has been published on the compatibilisation of these blends.(7,8) Del Giudice et al.(8) reported that PP/PS blends compatibilised with a high $\bar{M}_n$ PP-PS diblock can give properties approaching those of high impact polystyrene. Their PP-PS diblock was prepared in low yield by living coordination polymerisation. Bartlett et al.(7) have indicated that a commercial HPB-PS triblock (Kraton G1652) is effective in compatibilising PP/PS

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blends (though only a modest improvement in properties was observed). No structure-property relationship for the effectiveness of HPB-PS block copolymers in PP/PS blends has been reported.

This paper describes the synthesis and characterisation of a series of block copolymer compatibilisers and provides preliminary results on the effectiveness of these and a number of commercial materials in improving the impact strength of both LDPE/PS and PP/PS blends. The polymers synthesised as compatibilisers were a series of HPB-PS tapered diblocks with molecular weights in the range 20,000 to 100,000, various HPB:PS ratios, and chemical microstructures for the HPB segment.

Experimental

NMR spectra were recorded on a Brucker AC250 spectrometer. Scanning electron micrographs were obtained with a Jeol JSM 840A instrument on samples coated with gold using a Dynavac Sputter Coater SC150. Differential scanning calorimetry (DSC) was carried out with a Mettler DSC 30.

Poly(Styrene-*block*-Butadiene). The general procedure was as follows:
Butadiene gas was passed through columns of potassium hydroxide and molecular sieves and condensed into a three-necked round bottom flask, containing calcium hydride, which was equipped with a cold finger (dry-ice/acetone). The resultant butadiene-calcium hydride slurry was then allowed to stir under reflux for 5 hours.

A Parr hydrogenation bottle containing a teflon coated stirrer was dried at 120°C for two days and allowed to cool under dry nitrogen. The flask was thoroughly flamed to remove any traces of residual moisture and immediately stoppered with a toluene extracted septum. The flask was then purged with dry nitrogen for approximately 1 hour by use of syringe needles and left slightly pressurised with dry nitrogen.

The required amount of benzene (freshly distilled from sodium/benzophenone) was then added by syringe. The flask was then tared, cooled to -78°C (dry-ice/acetone), and the butadiene condensed into the Parr flask via a syringe needle. The flask was weighed to determine the exact amount of butadiene added and freshly distilled styrene and 1,2-dipiperidinoethane (for high 1,2-polybutadiene(9)) were then added by syringe. The solution was then allowed to thaw before the sec-butyl lithium was added. After being stirred at room temperature for 24 hours the polymerisation was quenched by addition of an equivalent of methanol and the polymer isolated by precipitation from methanol.

Poly(Styrene-*block*-Ethylene-*co*-Butylene)
(a) Diimide Reduction. A solution of the copolymer (25 g) in dry distilled toluene (400 mL) was heated to reflux under nitrogen and p-toluenesulphonylhydrazide (140g) added. The resulting solution was heated under reflux for a further 2 hours after which the hot solution was filtered. The polymer was then isolated from the filtrate by precipitation from methanol and dried under vacuum at 40° C.

(b) Catalytic Hydrogenation. The catalyst (prepared by addition of $Ni(acac)_2$ (0.5 g) to sec-butyl lithium (5 mL, 0.8M in hexane) under nitrogen) was added to a solution of the polymer (60 g) in dry cyclohexane (500 mL). Hydrogen was then admitted to the vessel via a syringe needle. Hydrogen uptake was followed by gas burette over 6 hours. The polymer was isolated by precipitation from methanol and dried under vacuum at 40° C.

Injection Moulding

A Custom Scientific Instruments mini-injection moulder model CS-183(10) was used to produce test bars 1.6 mm x 13 mm x 38mm. The barrel temperature of the injection moulder was 220°C and the mould temperature was 50°C. The material was pulverised to a fine powder by cryogrinding then placed into the barrel of the mini-injection moulder where it was allowed to mix for approximately 4 minutes prior to injection into the mould. The test bar was removed from the mould and then allowed to cool. There was no significant difference in the impact properties between the samples which were air cooled and those which were cooled rapidly by quenching the mould in cold water.

Table 1. Properties of block copolymers

Sample	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[a]	T_g °C[b] PB-PS	T_g °C[b] HPB-PS	%Butadiene[c] wt%	% 1,2[c]
6	19,100	1.21	-	-	53	13
1	55,000	1.10	-75	-28	54	13
4	76,000	1.09	-73	-26	48	13
7	22,600	1.23	-	-	48	40
5	24,300	1.22	-	-	54	90
2	51,000	1.12	2	-4	46	86
3	79,000	1.09	4	-4	45	89
8	53,200	1.14	-	-	78	10
9	55,000	1.13	-	-	73	90
10	64,000	1.15	-	-	75	40
KG 1652[d]	65,000	1.04	-	-53	75	42
triblock[e]	100,000	-	-	-	67	10
star[e]	300,000	-	-	-	66	10

[a] from GPC in polystyrene equivalents. M_n for hydrogenated polymer (HPB-PS) was found to be same as parent polymer (PB-PS) within experimental error.

[b] T_g of polyolefin segment from DSC, heating rate 20°C/min.

[c] from ^{13}C NMR analysis.

[d] contains ca. 5% hydrogenated butadiene homopolymer.

[e] prepared by hydrogenating samples of PB-PS blocks supplied by Kemcor Australia. The polymers were insoluble in tetrahydrofuran.

Impact Testing

The notched bars were tested in an ICI instrumented impact tester set up in Izod mode with parameter settings as follows: transducer type 2, force full scale 156 or 311 newtons, displacement for trigger 12 or 14 mm, filter cut off frequency 2500 Hz, sweep time 4 ms, regulator pressure 300 psi, height above baseplate 61 mm for reverse notched impact or 70 mm for notched impact. The reverse notched technique was used for PP/PS blends and notched impact method for LDPE/PS blends. The results of these measurements are reported in Table 2.

Results and Discussion

In instigating a systematic study involving HPB-PS block copolymers it is necessary to consider a number of factors relating to the polymer microstructure. These include: diblock vs. triblock, tapered vs. non tapered, ethylene-butylene ratio, HPB:PS ratio, molecular weight, etc.

conventional **AAAAAAAAAAAAAAAABBBBBBBBBBBBBBBBBB**

tapered **AAAAAAAABABBABABBABBBABBBBBBBBBBBB**

Fig. 1. Schematic representation of conventional and tapered diblock copolymers.

All the block copolymers prepared for this study are tapered block copolymers. Fayt, Teyssie et al.(2) have found that tapered HPB-PS diblock copolymers are more effective than similar conventional diblocks in compatibilising LDPE/PS blends. PB-PS block copolymers are conventionally prepared by sequential addition of the monomers to the anionic initiator. If, however, a mixture of the two monomers is polymerised, the disparate reactivity ratios ensure that a tapered diblock is formed. The synthetic procedure for formation of tapered diblocks was found to be generally more reliable. When only one monomer addition step is involved, opportunities for adding contaminants which terminate chains are minimised. Polymers prepared using this procedure possessed a monomodal distribution with polydispersities typically in the range 1.05-1.15 (see Table 1).

The literature(11) alludes to polybutylene being variously miscible or compatible with polypropylene (tacticity of polymers unstated, though both, almost certainly, isotactic - see later discussion). Since atactic polybutylene can readily be formed by hydrogenation of 1,2-polybutadiene, it was decided to also examine the effectiveness of (atactic polybutylene)-PS diblocks as compatibilisers for PP/PS blends.

The HPB-PS block copolymers are prepared by hydrogenation of PB-PS block copolymers. Hydrogenation of polybutadiene gives rise to an ethylene-butylene copolymer. The ethylene:butylene ratio is determined by the ratio of 1,2:1,4 butadiene units in the parent polymer and is a function of the reaction conditions used in the synthesis of the butadiene block. Conditions which give rise to high 1,4 addition or high 1,2 addition in butadiene polymerisation are established.(9) NMR analysis shows that commercial HPB-PS block copolymers (*eg*. Kraton G1652) contain ca. 40% butylene units.

The PB-PS block copolymers were prepared under reaction conditions similar to those reported by Falk et al.(12) Polymerisations were conducted in septum sealed pressure bottles under inert atmosphere. This procedure allows for easy scale up of the polymerisation. Careful purification of monomers, solvents and any additives were crucial to the success of the polymerisations. It was found that molecular weights in excess of 100,000 were difficult to achieve without resorting to vacuum line techniques.

The polymers were hydrogenated either by diimide reduction(13) or by catalytic hydrogenation. Residual double bonds were <1% (NMR).

Compatibiliser Effectiveness. Preliminary assessment of the relative effectiveness of the various compatibilisers was measured by determining the impact strength of samples prepared from 1:1 blends of PS (Huntsman, Austrex 103) with either PP (Shell, VM6100K) (Table 2 and Fig. 2) or LDPE (ICI, XDS34) (Table 2 and Fig. 3) and a 5% (w/w) compatibiliser level. The impact strength of the PP/PS blends was too low to be examined by notched impact method. Reversed notched impact results are reported in Table 2 and Fig. 2.

Table 2. Impact Strengths of Blends

Components^a	Composition (wt %)	Impact strength (J/m)^b
(a) homopolymers (reverse notched impact)		
PP	100	119±12 (10)
PS	100	97±5 (8)
HIPS^c	100	445±23 (8)^d
(b) polypropylene blends (reverse notched impact)		
PP/PS	50 : 50	48±3 (10)
PP/PS/Kraton G1652	47.5: 47.5 : 5	138±10 (10)
PP/PS/Sample 1	47.5: 47.5 : 5	45±5 (10)
PP/PS/Sample 2	47.5: 47.5 : 5	43±3 (10)
PP/PS/Sample 3	47.5: 47.5 : 5	67±6 (10)
PP/PS/Sample 4	47.5: 47.5 : 5	111±12 (10)
PP/PS/Sample 5	47.5: 47.5 : 5	45±3 (10)
PP/PS/Sample 6	47.5: 47.5 : 5	48±3 (10)
PP/PS/Sample 7	47.5: 47.5 : 5	55±3 (10)
PP/PS/Sample 8	47.5: 47.5 : 5	46 (10)
PP/PS/Sample 9	47.5: 47.5 : 5	35 (10)
PP/PS/Sample 10	47.5: 47.5 : 5	43 (10)
PP/PS/star	47.5: 47.5 : 5	41±4 (8)
(c) homopolymers (notched impact)		
PS	100	22±1 (8)
HIPS^c	100	76±1 (8)
(d) polyethylene blends (notched impact)		
PE/PS	50:50	16±1 (10)
PE/PS/Kraton G1652	47.5: 47.5 : 5	67±3 (7)
PE/PS/Sample 1	47.5: 47.5 : 5	32±3 (8)
PE/PS/Sample 4	47.5: 47.5 : 5	55±2 (8)
PE/PS/triblock	47.5: 47.5 : 5	50±1 (8)
PE/PS/star	47.5: 47.5 : 5	45±2 (8)

[a] refer to Table 1 for description of compatibilisers.

[b] energy to break. The uncertainty is expressed as standard deviation from mean. The number of determinations is indicated in parentheses.

[c] Austrex 5300 (Huntsman)

[d] partial break.

When measured against the results reported by Del Giudice et al.(8) for their very high $\bar{M}_n$ isotactic PP-PS diblock compatibiliser, the HPB-PS compatibilisers examined in this study do not appear especially effective in compatibilising 1:1 PP/PS blends. The best results were obtained with a low $\bar{M}_n$ triblock (Shell, Kraton G1652)(7) and a high (76,000) $\bar{M}_n$, high 1,4 HPB-PS tapered diblock both of which gave a ca. three-fold improvement in impact strength over that of the uncompatibilised blend though only a marginal improvement over that of either homopolymer was detected (see Fig. 2). Low miscibility of the atactic, high 1,2 HPB segment with the largely isotactic PP phase may account for the relatively poor performance of the high $\bar{M}_n$, high 1,2 HPB-PS diblock (Sample 3). However, the 'tacky' nature of the atactic polybutylene block, which led to difficulties in achieving effective mixing, may also be a contributing factor.

Although, the use of Kraton G1652 as a compatibiliser in PE/PS blends has been reported previously(1,3), the effectiveness of this triblock copolymer has not been compared with that of high $\bar{M}_n$ diblocks. Contrary to the hypothesis of Fayt, Teyssie et al.,(2) it was found that the low $\bar{M}_n$ HPB-PS triblock is as, or more, effective than diblock compatibilisers for LDPE/PS blends. The impact strength of the blend with only 5% Kraton G1652 approaches that of high impact polystyrene (HIPS) (see Fig. 3). This triblock is also more effective than a higher $\bar{M}_n$ triblock, of similar $\bar{M}_n$ to one included in the studies of Fayt, Teyssie et al.(2), (a low $\bar{M}_n$ triblock was not examined in their studies nor was a 1:1 blend).

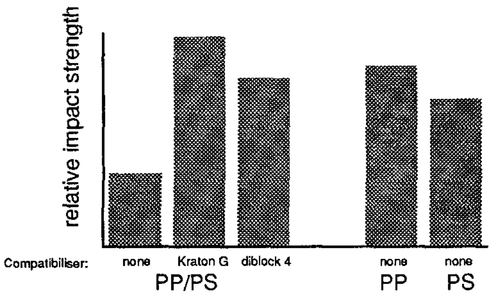

Fig. 2. Effect of 5% (w/w) compatibiliser [Kraton G1652 or 1:1 HPB-PS tapered diblock $\bar{M}_n$ 76,000 (sample 4)] on reverse notched impact strength of 1:1 PP/PS blends.

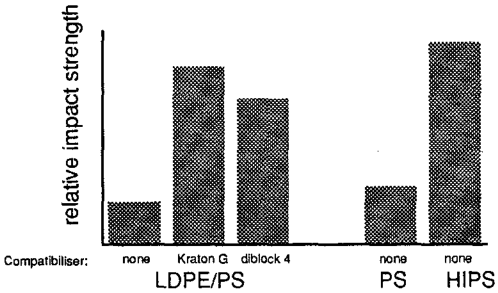

Fig. 3. Effect of 5% (w/w) compatibiliser [Kraton G1652 or 1:1 HPB-PS tapered diblock $\bar{M}_n$ 76,000 (sample 4)] on notched impact strength of 1:1 LDPE/PS blends.

The scanning electron micrographs in Figs. 4a-d show the cryofracture surfaces of samples impacted in the ICI impact tester (samples cooled to dry ice temperature then impacted). Discrete particles are not evident in the micrographs of the blends prepared with added compatibilisers (Fig. 4b-d) indicating the effectiveness of these materials as dispersing agents. The blends show evidence of a lamellar morphology. The fracture surface for the Kraton G blend (Fig. 4b) appears rough compared to those with Sample 1 (Fig. 4c) and Sample 4 (Fig. 4d) and is characteristic of a cooperative fracture mechanism.

It is planned to examine other properties (tensile properties, melt rheology) of these blends, to extend the range of compositions, and to move to testing the blends on a larger scale. The effect of processing conditions on the mechanical properties of these blends also warrants more attention. The information generated in this study has already been applied in selecting compatibilisers for a multicomponent polyolefin/PS blend designed as a more chemically resistant high impact polystyrene replacement. This work will be the subject of forthcoming publications.

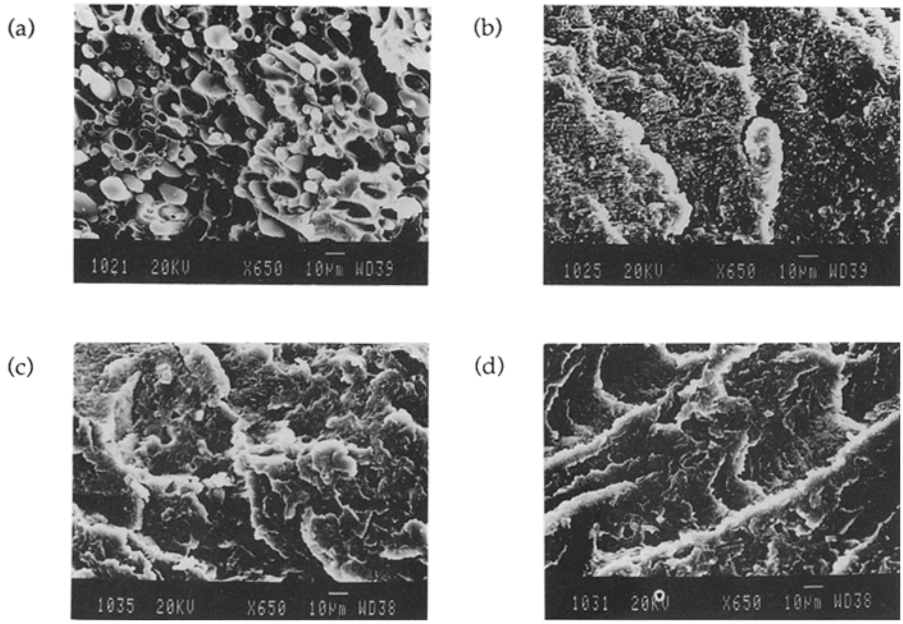

Fig. 4. Scanning electron micrographs showing cryofracture surfaces of 1:1 PP/PS blends with (a) no compatibiliser (b) 5% Kraton G, (c) 5% Sample 1 (d) 5% Sample 4.

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