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In situ compatibilization of polyolefin and polystyrene using Friedel–Crafts alkylation through reactive extrusion

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In our preliminary study, it has been revealed that a copolymer of PE-g-PS can be formed during melt blending of polyethylene/polystyrene (PE/PS) blends via a Friedel–Crafts benzene ring alkylation of the PS. This paper reports our further study on the *in situ* compatibilization of polyolefin and polystyrene using a single screw extruder. Polyethylene and polypropylene (PP), respectively, have been blended with polystyrene, in the presence of an $AlCl_3$ catalyst system. The mechanical characterization of the PE/PS and PP/PS blends shows significant improvement in tensile elongation. Further characterization of the PE-g-PS copolymer formed in the blends as well as the ungrafted PE and PS suggests a competition between grafting and PS degradation. This *in situ* compatibilization technique has potential in recycling of mixed polymer wastes. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: reactive extrusion; polymer blend; *in situ* compatibilization)

INTRODUCTION

The key factor for achieving *in situ* compatibilization of immiscible polymers is to form a copolymer by chemically combining the polymer components during the blending process. The copolymer formed plays the role of compatibilizer at the interface and reduces the interfacial tension between polymer phases. This, in turn, aids in creating and setting the ultimate morphology which then leads to an improvement in mechanical properties of the blend.

Polyolefin/polystyrene blends are difficult to compatibilize using *in situ* reactive compatibilization techniques, because neither of these polymers has any functional groups which can be used in the formation of a copolymer from these polymer components. A reactive polymer or copolymer is needed for the compatibilization of polyolefin/polystyrene blends[1–3]. However, from the viewpoint of the recycling of post-consumer polymers, a low cost compatibilization technique would be desirable which bypasses the need for expensive additives.

In our laboratory, two approaches have been taken to develop a low cost *in situ* reactive compatibilization technique which has potential in the recycling of mixed polyolefin/polystyrene wastes. One approach is to use the free radical sensitivity of polyolefins and polystyrene coupled with a 'vector fluid' concept[4,5]. In this approach, an organic functional silane was used to carry the free radical initiator (peroxide) to the polymer interface during melt blending of polyethylene (PE) and polystyrene (PS), in order to favor the reciprocal grafting between the PE and PS. Another approach is to use the reactivity of the benzene ring on PS following Friedel–Crafts benzene ring alkylation mechanism[6]. With each of these different approaches significant amounts of PE-g-PS graft copolymers were formed during PE/PS melt blending.

This paper reports on the development of the polyolefin/polystyrene *in situ* compatibilization using the Friedel–Crafts alkylation mechanism in an extrusion process. Our preliminary study[6] has shown that the PE/PS blends can be well compatibilized during melt blending in the presence of an $AlCl_3$/styrene catalyst system using a Haake batch mixer. A significant amount of PE-g-PS copolymer (up to about 12 wt.% in the blends) was formed in PE/PS blends, and the mechanical properties (including ultimate elongation and impact strength) of the blends were improved. An important advantage of this technique is that the materials used as the catalyst and the co-catalyst are common and inexpensive, so that it has the commercial potential in the recycling of mixed post-consumer polymers containing polyolefin and polystyrene.

The results of PE/PS/$AlCl_3$/styrene reactive compatibilization suggested a mechanism of Friedel–Crafts alkylation in the formation of PE-g-PS copolymer[6,7]. Generally, the Friedel–Crafts benzene ring alkylation is through the substitution of a proton on the benzene ring by a carbocation (R^+), in the presence of a Lewis acid:

$$R^+ + C_6H_6 + AlCl_4^- \rightleftharpoons C_6H_5R + HCl + AlCl_3 \quad (1)$$

In our particular system of PE/PS/$AlCl_3$/styrene, it has been suggested that the styrene monomer can form the initial carbocation in the presence of $AlCl_3$ catalyst. Then the initial carbocation attacks the PE chain, forming a PE macro-carbocation. In the presence of $AlCl_3$ catalyst, the PE macro-carbocation substitutes a proton on the benzene ring of the PS, forming a graft copolymer. The overall, general process is shown below in equation (2). The details of the chemical reactions involved in this process can be found in the literature[6–9].

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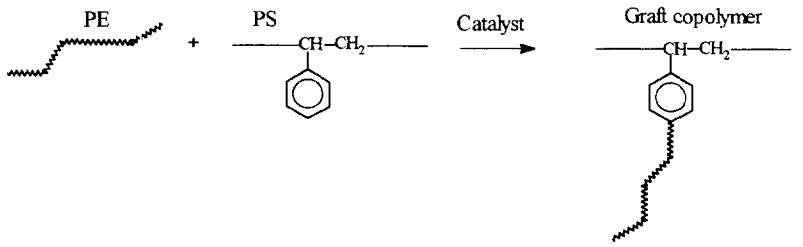
$$R^+ + C_6H_6 + AlCl_4^- \rightleftharpoons C_6H_5R + HCl + AlCl_3 \qquad (1)$$



(2)

This paper presents the development of this polyolefin/polystyrene/$AlCl_3$/styrene *in situ* reactive compatibilization technique using a single screw extrusion process. The PE and polypropylene (PP) were blended respectively with PS, in the presence of the catalyst, using a 25 mm diameter single screw extruder. The mechanical properties of PE/PS and PP/PS blends were measured to evaluate the effectiveness of the compatibilization. A number of chemical and physical characterizations of the resulting PE/PS and PP/PS blends were carried out in order to understand better the dynamics of the reactive extrusion process.

EXPERIMENTAL DETAILS

Materials

The linear low density polyethylene (PE) used in this study was Esso Chemical Canada Escorene LL-5103 in powder form ($\bar{M}_w$ 75 kg mol^{-1}, MFI 7.8 g/10 min). The polypropylene (PP) used in this study was Pro-fax 6801S (Himont) in porous pellet form ($\bar{M}_w$ 750 kg mol^{-1}, MFI 0.5 g/10min). The polystyrene (PS) was a homopolymer in pellet form, supplied by Novacor (grade 777, $\bar{M}_w$ 404 kg mol^{-1}, MFI 0.8 g/10 min).

The aluminum chloride ($AlCl_3$, purity 98%) was used as the catalyst. In order to protect the catalyst from moisture in the air, it was kept in hexane and used in a hexane wetted, sludge-like form. The co-catalyst used was a styrene monomer ($C_6H_5CH{=}CH_2$, purity 99%). These chemicals were purchased from Aldrich and used without further purification.

Extrusion

The PE/PS and PP/PS blends were prepared using a 25 mm diameter single screw extruder (HaakeBuchler System 40).

Two screw configurations were used in this study, shown in *Figure 1*. The longer screw differs from the shorter mainly by the addition of the supplementary mixing section. For a PE/PS (80/20 wt.%) mechanical mixture run at 30 rev min^{-1} and a flat temperature profile of 180°C, the residence time for the short screw was 2–3 min while that for the extended screw was 3–4 min. For the PP/PS (80/20 wt.%) mechanical mixture, at 220°C/30 rev min^{-1}, the residence time for the short screw was 2–3 min.

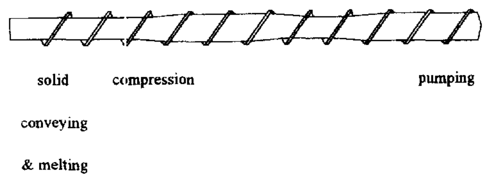
Before extrusion, the $AlCl_3$ was dry-blended with PE powder (or PP pellets), and the styrene was dry-blended with PS pellets. These mixtures were then dry-blended in the hopper of the extruder under nitrogen (N_2) blanket and fed into the extruder in a way of volumetric feeding. The PE/PS (or PP/PS) extrudates passed through a water bath and then were pelletized. This procedure is called the one-step extrusion process.

The pelletized sample of the one-step extrusion process may be used as a master batch product in a second step of extrusion with virgin polymers. This is called a two-step extrusion process. In this two-step procedure, the catalyst was only used in the preparation of master batch (the first step). In the second step, the virgin polymer(s) and master batch product were blended without adding catalyst.

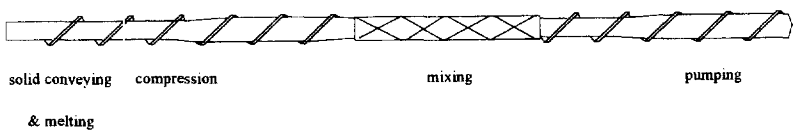
Three different extrusion procedures were used for PE/PS and PP/PS *in situ* compatibilization:

(a) use the short screw and take the sample after pelletizing (one-step extrusion);
(b) use the extended screw and take the sample after pelletizing (one-step extrusion);
(c) take the product of procedure (a) as a master batch and then blend the master batch with virgin polymers to form the final sample (two-step extrusion, see *Figure 2*).

If not specified otherwise, the extrusion conditions were



Short screw (L / D = 25)



Extended screw (L / D = 4)

Figure 1 Screw configurations of Haake 25 mm single screw extruder

180°C/30 rev min^{-1} for the PE/PS blends, and 220°C/30 rev min^{-1} for PP/PS blends, in both extrusion steps.

Characterization of PE/PS and PP/PS blends

Mechanical characterization. The performance of the PE/PS and PP/PS blends was evaluated using a tensile test. The specimens used for the tensile test were injection molded at 220°C and then kept at room temperature for 3 days before testing.

The tensile test was performed using a dog-bone bar sample on an Instron mechanical tester (Instron Universal Test, model 4206) at room temperature, with a cross-head speed of 50 mm min^{-1} (ASTM 638-71A). The dimensions of the gage section of each tensile test specimen were $20 \times 3 \times 4\ \text{mm}^3$.

Solvent extraction of PE/PS blends. In order to determine the quantity of PE-g-PS copolymer formed in the blends, the PE/PS samples were ground into a powder and extracted alternately using *n*-heptane and tetrahydrofuran (THF). After 48 h of *n*-heptane extraction (removing polyethylene homopolymer) and 48 h of THF extraction (removing polystyrene homopolymer), the PE-g-PS copolymer was isolated from the blends. Extraction of blends of PE/PS mechanical mixtures left no copolymer residue. The detail of the procedure and reliability of such an *n*-heptane/THF solvent extraction for PE/PS blends has been reported previously[6].

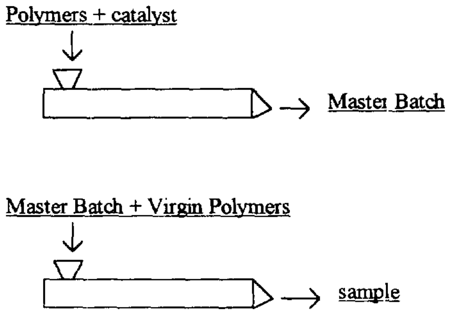


Figure 2 Two-step extrusion procedure

This solvent extraction technique was not applicable to PP/PS blends owing to the low solubility of PP in boiling *n*-heptane. No copolymer isolation was performed for this system.

Fourier transform IR analysis of the PE-g-PS copolymer. After extraction, the degree of grafting of PS in the copolymer PE-g-PS was detected by Fourier transform IR (FTIR) analysis, using film samples. The concentration of PS in the samples containing 0–50 wt.% PS was estimated by comparison of the ratio of IR absorption at 700 cm^{-1} (PS) and 719 cm^{-1} (PE) with a calibration curve. The ratio of IR absorption at 1600 cm^{-1} (PS) and 719 cm^{-1} (PE) was taken for determining the concentration of PS in the samples containing 50–100 wt.% PS[7]. The calibration of the IR spectrometer was carried out using PE/PS mechanical mixtures with known proportions. The IR analysis data given in this paper are the average values of at least four measurements.

Other characterizations. The melting flow indices (MFI) of the resulted blends were measured at 190°C/2.16 kg (for PE/PS blends) and 230°C/2.16 kg (for PP/PS blends).

The molecular weight of homopolymer polystyrene, homopolymer polyethylene and PE-g-PS copolymer, which was separated from PE/PS blends by *n*-heptane/THF extraction, was measured using a high temperature gel permeation chromatography (GPC) equipment (Waters 150-C) at 145°C.

RESULTS AND DISCUSSION

Mechanical properties of virgin polymers and mechanical mixtures

The mechanical properties of virgin PE, PP and PS used in this study were obtained using the tensile test, including

Table 1 Tensile properties of virgin polymers and mechanical mixtures

	M(MPa)	σ_y(MPa)	ϵ_y(%)	ϵ_b(%)
PE	149 ± 6	11 ± 0.5	24 ± 1	856 ± 40
PP	743 ± 16	37 ± 2	18 ± 1	518 ± 41
PS	1520 ± 32	—	—	3.5 ± 0.5
PE/PS(80/20 wt.%)	177 ± 13	12 ± 0.5	14 ± 1	132 ± 34
PE/PS(70/30 wt.%)	262 ± 26	13 ± 1	9 ± 1	14 ± 3
PP/PS(90/10 wt.%)	929 ± 46	42 ± 1	11 ± 0.5	395 ± 104
PP/PS(80/20 wt.%)	875 ± 25	39 ± 1	9 ± 0.3	42 ± 20

Table 2 Composition of PE/PS blends prepared by one-step extrusion

Sample	PE/PS (wt.%)	[$AlCl_3$] (wt.%)	[styrene] (wt.%)	Procedure
S1	80/20	0.3	0	(a)
S2	80/20	0.3	0.3	(a)
S3	80/20	0.2	0.2	(a)
L1	80/20	0.3	0.3	(b)
L2	80/20	0.2	0.2	(b)
S4	70/30	0.2	0.2	(a)
S5	70/30	0.1	0.2	(a)

Table 3 Tensile properties of PE/PS blends prepared using one-step extrusion

	M(MPa)	σ_y(MPa)	ϵ_y(%)	ϵ_b(%)
PE/PS (80/20 wt.%)mechanical mixture	177 ± 13	12 ± 0.5	14 ± 1	132 ± 34
S1	246 ± 30	12.6 ± 0.8	13.8 ± 1.1	64 ± 15
S2	229 ± 21	11.7 ± 0.6	15.3 ± 0.8	272 ± 57
S3	155 ± 12	11.2 ± 0.3	17.1 ± 0.6	126 ± 35
L1	177 ± 8	13.1 ± 0.3	18.2 ± 0.6	111 ± 23
L2	164 ± 16	12.4 ± 0.3	17.8 ± 1.0	150 ± 32
S4	208 ± 37	11.6 ± 0.7	11.1 ± 1.2	25 ± 8
S5	330 ± 33	13.6 ± 0.7	8.7 ± 0.7	20 ± 3
PE/PS (70/30 wt.%)mechanical mixture	262 ± 26	13 ± 1	9 ± 1	14 ± 3

Table 4 Composition of PE/PS master batches

Sample	PE/PS(wt.%)	[AlCl$_3$](wt.%)	[styrene](wt.%)	Procedure
M1	64/36	0.2	0.4	(a)
M2	64/36	0.4	0.6	(a)
M3	46/54	0.2	0.2	(a)
M4	46/54	0.4	0.4	(a)
M5	70/30	0.2	0.2	(a)

Table 5 Composition of PE/PS blends prepared by two-step extrusion

Sample	Master batch	Master batch/PE/PS (wt.%)	Overall PE/PS (wt.%)
C1	M1	56/44/0	80/20
C2	M2	56/44/0	80/20
C3	S3	50/40/10	80/20
C4	L2	50/40/10	80/20
C5	M3	62/38/0	70/30
C6[a]	M3	62/38/0	70/30
C7	M4	62/38/0	70/30
C8	M5	50/35/15	70/30

[a] Extended screw was used in the second step of extrusion

Young's modulus (M), yield strength (σ_y), yield elongation (ϵ_y) and elongation at break (ϵ_b), as shown in *Table 1*. The PE and PP are ductile materials, having low moduli and high elongations at break, while the PS is a brittle material, having a high modulus and a very low elongation at break. Owing to the immiscibility between PE (PP) and PS, the mechanical mixtures of PE/PS and PP/PS presented poor tensile behavior, notably lower elongations at break compared to the virgin PE and PP (*Table 1*). It can also be seen from these data that the elongation at break of PE/PS and PP/PS mechanical mixtures decreases significantly with an increase of PS concentration in the blends. This is consistent with earlier studies[3].

Compatibilization of PE/PS blends by one-step extrusion process

Different PE/PS blends were prepared using one-step extrusion processes which have been mentioned above as procedures (a) and (b). The compositions of these blends are shown in *Table 2*. The effectiveness of the compatibilization of these PE/PS (80/20 and 70/30) blends is shown in *Table 3*, in terms of the tensile properties. The elongation at break is the most sensitive parameter reflecting this effectiveness.

Without using the styrene as a co-catalyst, the performance of PE/PS blend was not improved (sample S1) compared with the PE/PS mechanical mixture. This is probably due to an insufficient formation of PE-g-PS copolymer which will be discussed later. In the presence of styrene as a co-catalyst, the mechanical properties (particularly the elongation at break) of the blend (sample S2) were improved. These results confirmed again the importance of using co-catalyst in such a system[6].

The compositions of samples S2 and S3 are comparable with those of samples L1 and L2, but the samples L1 and L2 were prepared using the extended screw which provides more intense mixing to the polymer melt. Comparing with the short screw, the use of the extended screw did not result in improved compatibilization. This is believed to be due to a chain scission of PS branches of the PE-g-PS copolymer during the blending process. This point will be discussed later in this paper.

The blend of PE/PS (70/30) is more difficult to compatibilize. With this one-step extrusion, the performance of these blends was improved little over that of the mechanical mixtures.

The results obtained using the one-step extrusion process offer potential for reactive compatibilization of PE/PS blends, but the effectiveness was inconsistent. The main reason was the polymer degradation during the reactive blending. This point will be discussed in Section Section 4 of this paper. In order to improve further the mechanical properties, a master batch preparation approach was taken. A master batch was first prepared in a one-step process and then this master batch was mixed with virgin polymer(s) in a

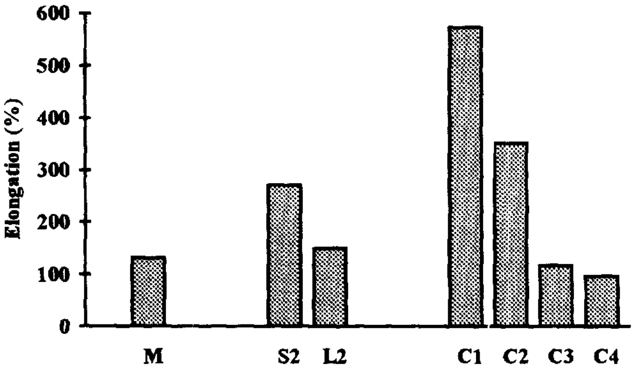


Figure 3 Elongation at break of different PE/PS (80/20) blends (M represents the mechanical mixture)

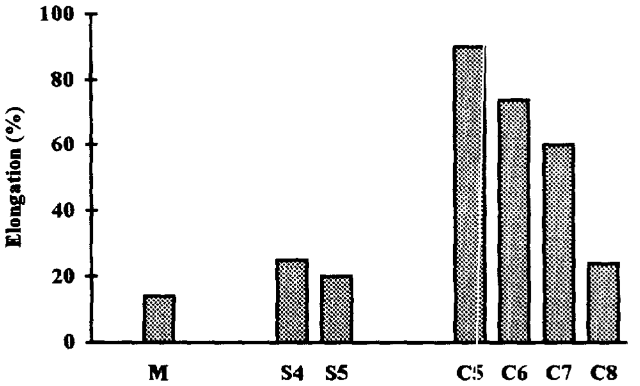


Figure 4 Elongation at break of different PE/PS (70/30) blends (M represents the mechanical mixture)

second extrusion process (two-step extrusion). In this way, the virgin polymers used in the second extrusion operation avoid the catalyst attack, so that the degradation of polymers can be reduced. This is an essential consideration in the use of the two-step extrusion process.

Compatibilization of PE/PS blends by two-step extrusion

The compositions of the master batches of PE/PS blends are shown in *Table 4*, and the proportions of master batch and virgin polymers are shown in *Table 5*. Note that some samples which were prepared by one-step extrusion were used as a master batch in the two-step extrusion process.

Comparing with the one-step extrusion processes, the two-step extrusion process (procedure (c)) was more effective in compatibilizing the PE/PS blends. *Figures 3* and *4* show a comparison of the values of elongation at break of the PE/PS blends prepared using the various extrusion procedures. It can be seen that PE/PS (80/20) blends compatibilized using the two-step extrusion process achieved high elongation values, and the performance of PE/PS (70/30) blends was also much improved. However, in order to obtain the high elongation values, specially prepared master batch products (*Table 3*) were needed in which the proportions of PS were higher (36 and 54 wt.%) than in the final blends (20 and 30 wt.%). In order to prepare C1 and C2, only PE was added to the master batch. When the master batch was prepared using a 'normal' PE/PS proportion, i.e. 80/20 or 70/30, the performance of the final blends was not improved, as the cases of samples C3 and C4 and C8. For the PE/PS blends, it seems that when the virgin PS was added to the blends in the second step of extrusion, the effectiveness of compatibilization became worse.

Table 6 Composition of PP/PS (80/20) blends prepared by one-step extrusion

Sample	[$AlCl_3$] (wt.%)	[styrene] (wt.%)	Procedure
S7	0.1	0.5	(a)
L5	0.1	0.5	(b)
L6	0.3	0.5	(b)

Table 7 Composition of PP/PS (80/20 wt.%) blends prepared by two-step extrusion

Sample	Master batch	Master batch/PP/PS (wt.%)
C9	L5	50/40/10
C10	L6	50/40/10
C11	S7	50/40/10
C12	S7	33/53/14

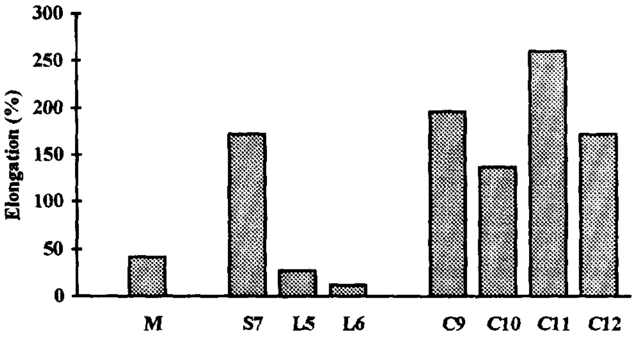


Figure 5 Elongation at break of different PP/PS (80/20) blends (M represents the mechanical mixture)

Without further study on such a reactive process, we cannot give a clear explanation for this point. It looks like a more efficient mixing and a better control of the PS degradation are needed in such a process. Furthermore, these results suggest that the influence of the PE/PS proportions are important in the formation of PE-g-PS copolymer.

Comparing the samples C1 and C2, it can be seen that a higher concentration of $AlCl_3$ led to a lower performance of the compatibilized blends. This is believed to be due to the degradation of polymers in the presence of the catalyst. This point of view was supported by MFI data for the samples, which are shown later in Section Section 4 of this paper.

Generally, the PE/PS blends can be well compatibilized using $AlCl_3$/styrene catalyst system through a single screw extrusion. The PE/PS (80/20) can be compatibilized using one-step extrusion, but the performance of the blends was better when a specially prepared master batch product was used in a two-step process. The PE/PS (70/30) blends were more sensitive to the extrusion procedure: the improvement can be achieved only using a specially prepared master batch product and a two-step extrusion process. Furthermore, the improvement in elongation at break of these PE/PS (70/30) blends was very considerable when compared with the mechanical mixture, but showed fairly large variations. These difficulties in the compatibilization of PE/PS (70/30) are probably due to the higher PS proportion in the blends, which requires more PE-g-PS copolymer. Another reason could be the degradation of PS during melt blending in the presence of catalyst.

Mechanical properties of PP/PS blends

Polypropylene is also common in mixed plastic waste streams and, furthermore, is prone to degrade by β-scission during processing in contrast to PE. Thus parallel compatibilization trials were made with the PP/PS system.

Various PP/PS (80/20) blends were prepared using different extrusion procedures. The compositions and procedures used for PP/PS blending are shown in *Tables 6* and *7*. The performance of these blends is demonstrated in *Figure 5* in terms of elongation at break. Similar improvements to those obtained for PE/PS blends were obtained for PP/PS (80/20) blends. Using the one-step extrusion process with the same composition, the short screw gave higher elongation (samples S7 compared to L5). The two-step extrusion process gave even higher elongations however (samples C9 to C12). A more important observation for the PP/PS blends is that effective master batch products were prepared in the proportion of PP/PS 80/20 wt.%, the same as that of the final samples (*Table 7*). This indicates that a master batch of the mixed plastic can first be made and then added to the same proportions of uncompatibilized PP/PS mixture in the second stage. This was not achieved with the PE/PS system (sample C4).

A single screw extruder was selected for this work, not because it is the preferred melt mixing device, but rather because the cost and availability of this equipment is more suitable for recycling activities than a twin screw extruder, for example. It is encouraging that significant amounts of copolymer have been produced under these conditions and that significant mechanical property improvements have been obtained.

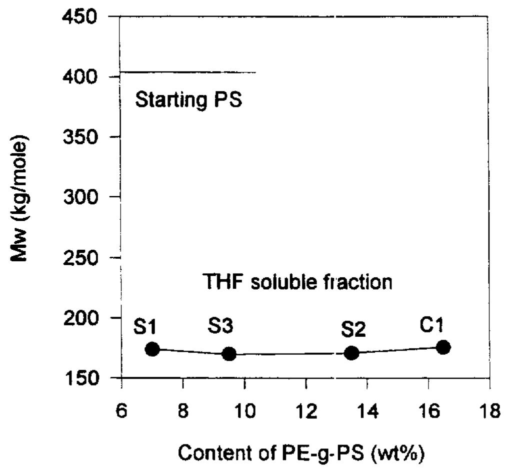


Figure 6 Change of molecular weight of PS of S1, S2, S3 and C1

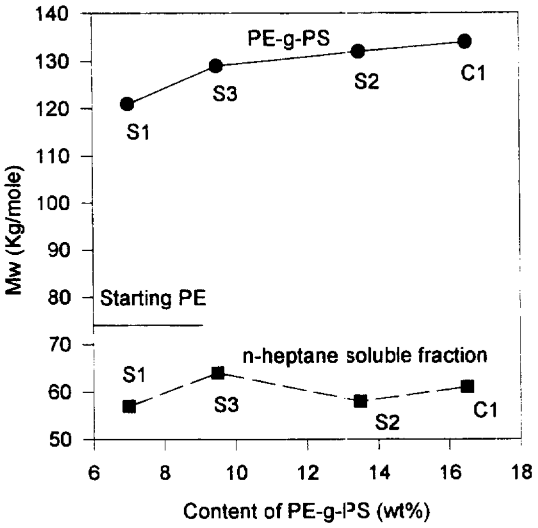


Figure 7 Change of molecular weight of PE and PE-g-PS of S1, S2, S3 and C1

DISCUSSION

Further characterization of polyolefin/polystyrene blends is needed to understand better what is occurring to the component polymers during this reactive compatibilization process. Selected samples of PE/PS blends were analyzed in order to obtain such data as the molecular weight of the PE, PS and PE-g-PS copolymer, the amount and composition of the copolymer formed, and the MFI of the blends.

Molecular weight of PE, PS and PE-g-PS obtained in blending

Molecular weight is an important factor in reactive blending because the mechanical properties of resulting blends depend largely on the molecular weight of the polymer components after blending. In the PE/PS/$AlCl_3$/styrene system, the molecular weights of the PE, PS and PE-g-PS copolymer were determined. The changes in the molecular weights of PS (THF soluble fraction) and PE (*n*-heptane soluble fraction), PE-g-PS of S1, S2, S3 and C1 samples are shown in *Figure 6* and *Figure 7* respectively. During blending, the PS degraded producing a drop in molecular weight of about 55% from that of virgin PS. The PE degraded with a decrease in molecular weight of about 18% from that of virgin PE. The degradation of the PS was more evident than that of the PE. The PE-g-PS copolymer formed in the blends had a relatively high molecular weight, about 1.7 fold higher than that of virgin PE. These data indicate that both PS degradation and copolymer formation are contributing to the mechanical properties and blend viscosity. The data in *Tables 8* and *9* show that the viscosity of the compatibilized blends was higher than that of the mechanical mixtures. These higher viscosities indicate an important contribution of copolymer formation on the

Table 8 MFI and elongation data of PE/PS (80/20) blends

Sample	[$AlCl_3$] (wt.%)	MFI (g/10 min)	ϵ_b (%)
PE/PS (80/20) mechanical mixture	0	12.3	132 ± 34
M1	0.2	6.3	—
M2	0.4	7.1	—
C1 (final sample of M1)	—	9.0	575 ± 64
C2 (final sample of M2)	—	9.3	352 ± 81

Table 9 MFI and elongation data of PP/PS (80/20) blends

Sample	MFI (g/10 min)	ϵ_b (%)
PP/PS (80/20) mechanical mixture	2.5	42 ± 20
S7	1.5	172 ± 62
L5	1.4	27 ± 11
L6	1.9	12 ± 2
C11	2.1	260 ± 90

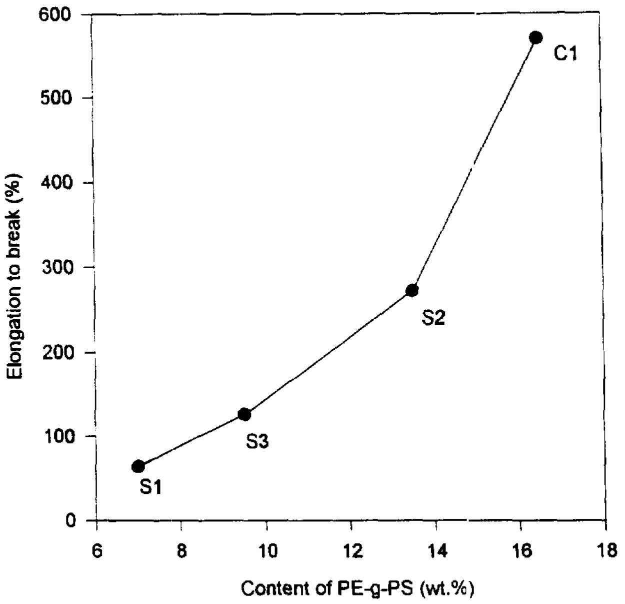


Figure 8 Effect of content of PE-g-PS on elongation to break of S1, S2, S3 and C1

Table 10 Characterization of PE-g-PS copolymers

Master batch	[PE-g-PS][a] (wt.%)	[PS]g[b] (wt%)	$\bar{M}_w$ (kg mol^{-1})	$\bar{M}_n$ (kg mol^{-1})
M3	9.8	14.0	107	42
M5	12.9	0.5	115	49

[a] PE-g-PS copolymer concentration in the master batch
[b] Degree of PS grafting in the PE-g-PS copolymer

blends. They also show that despite the extensive inter-polymer chemistry which has occurred, the blends remain readily processable.

These results suggest that there is a competition between the PS degradation and copolymer formation during the blending. This could be the reason that the extended screw tended not to improve the compatibilization performance: the relatively long residence time caused more polymer degradation. The two-step extrusion process yielded a better blend performance: this is due to the fact that virgin polymers fed in the second extrusion step did not bear the catalyst attack and the average polymer degradation was reduced. The influence of catalyst concentration is to enhance catalytic degradation of polymers at least at higher $AlCl_3$ concentrations. The master batch M2 which used a higher catalyst concentration had a higher MFI value than that of M1 (*Table 8*), and M1 led to a higher elongation value in the final sample (C1).

The results of GPC analysis suggested that the PS degradation was more significant than that for PE. This could be the reason that the PE/PS (70/30) blends were more difficult to compatibilize. With a higher concentration of PS, the contribution of PS degradation should be more important during the blending.

Graft copolymerization of PE and PS

The amount of PE-g-PS copolymer formed is important because it is believed that this is the necessary compatibilizer involved. The effect of the content of PE-g-PS copolymer on the elongation to break of S1, S2, S3 and C1 is shown in *Figure 8*. As the content of PE-g-PS copolymer increases from 7% to 16%, the elongation to break of the PE/PS blends increases from 65% to 570%.

The composition of PE-g-PS copolymer is also significant. The *n*-heptane/THF extraction and IR analysis of two PE/PS master batch products, the samples M3 and M5, showed that the M3 had a high copolymer concentration and high degree of PS grafted to the PE, while the M5 had a high copolymer concentration but the degree of PS grafting in the copolymer was low (*Table 10*). The master batch M3 resulted in better final blend properties (comparing samples C5 and C8 in *Figure 4*). The master batch M3 had a PE/PS proportion of 46/54 wt.%, while that of M5 was 70/30 wt.% (*Table 4*). The concentration of catalyst and the extrusion conditions were the same for these two master batches. This indicates that the formation of PE-g-PS in such a system was affected by the PE/PS proportion.

The degree of grafting of PS was lower than 1 wt.% in the copolymer formed in the sample M5. The GPC analysis of the copolymers obtained from M3 and M5 showed that these two copolymers had similar molecular weight. These copolymers can be dissolved readily in hot toluene or trichlorobenzene so there is no crosslinking evident in them. As these copolymers were insoluble neither in *n*-heptane nor in THF, they should have a grafted PE-g-PS structure. In this case, the low degree of PS grafting in the copolymer suggests short PS branches and that the PS branches which grafted on the PE suffered some chain scission. It seems reasonable to propose that the grafting and chain scission of PS occurred simultaneously during this reactive blending, and that there was a competition between scission and grafting.

CONCLUSIONS

The *in situ* compatibilization of polyolefin/polystyrene blends was achieved using Friedel–Crafts alkylation in an extrusion process. The low cost $AlCl_3$/styrene catalyst system was confirmed to be efficient for both PE/PS and PP/PS compatibilization. The compatibilized blends had significantly improved mechanical properties, notably the elongation at break. Reasonably low catalyst concentrations and short residence times for extrusion led to a better compatibilized blend. The two-step extrusion procedure gave better results than one-step extrusion. This is a result of a limitation of degradation of polymers when the master batch product and virgin polymers were extruded in the second extrusion step. No significant crosslinking is observed as might be observed with peroxide compatibilization of PE rich blend. Good processability can be retained.

Further characterization of these compatibilized polymer blends strongly suggests a competition between the formation of PE-g-PS copolymer and PS degradation during the reactive blending. The PS branches of PE-g-PS copolymer also experience chain scission, resulting in a copolymer with a lower degree of PS grafting. The degradation of these polymers needs to be managed for effective polyolefin/polystyrene reactive compatibilization.

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