

Polyolefin/Polystyrene *In Situ* Compatibilization Using Friedel–Crafts Alkylation

YI-JUN SUN,* WARREN E. BAKER

Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada

Received 17 June 1996; accepted 14 September 1996

ABSTRACT: Polyolefin/polystyrene (PS) blends are difficult to compatibilize using *in situ* reactive compatibilization techniques, because neither of these polymers has any functional groups that one can use in the formation of a copolymer from these polymer components. In this study, the Friedel–Crafts alkylation was realized in a polyethylene/PS (PE/PS) melt blend, which resulted in improved compatibility between PE and PS. A number of Lewis acid compounds were tested as catalysts, among which the AlCl_3 was the most efficient. It was found in this study that the presence of a cocatalyst, such as a cationically polymerizable monomer or a halogenated alkane, significantly enhances the formation of PE-*g*-PS copolymer. The effects of blending parameters, such as temperature and blending time, on the *in situ* copolymer formation were investigated. The mechanical properties of compatibilized PE/PS blends were improved considerably. Such an *in situ* compatibilization technique has potential in the recycling of mixed polymer wastes. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1385–1393, 1997

Key words: *in situ* compatibilization of polyolefin and polystyrene; Friedel–Crafts alkylation of polystyrene; Lewis acid catalyst; recycling of mixed plastic stream

INTRODUCTION

The recycling of postconsumer polymer waste is becoming a more important and interesting area of polymer-processing research. This is true not only from an ecological stand point, but also a commercial one. Postconsumer polymer wastes can be an important resource of polymer materials if they can be properly separated, processed, and/or modified.

In most cases, polymer waste gathered from the consumers is a mixture of different polymers, for example, polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC), polystyrene

(PS), and poly(ethylene terephthalate) (PET). It is common at least to “mine” PET and HDPE bottles in a recycling center and send these streams on for further processing. It is easy to understand that the remaining polymer waste stream will contain a wide diversity of polymers after such a separation process, and poor product quality (for example, mechanical) will be a problem when attempts are made to use this mixed stream. In this case, suitable and economical compatibilization techniques are potentially needed in the recycling of these mixed-polymer wastes.

A key factor for the compatibilization of immiscible polymers which are to be melt blended is to introduce a suitable copolymer, known as a compatibilizer, which will locate preferentially at the interface between blended polymer components and reduce the interfacial tension. This, in turn, aids in ultimate morphology control and interfacial adhesion. Such copolymer(s) can be specifi-

Correspondence to: W. E. Baker.

* Present address: AT Plastics Inc., 134 Kennedy Road South, Brampton, Ontario L6W 3G4, Canada.

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/071385-09

cally synthesized and then used in the polymer blends. However, from an economics point of view, it is sometimes more interesting to form the copolymer during the blending, by adding the constituent components, which subsequently combine chemically in the blend. This method is known as *in situ* compatibilization, which has been developed during the last 15 years. With premade copolymers or reactive polymers, many polymer blends can be effectively compatibilized.¹⁻⁸

The polymer blends of polyolefin/PS are difficult to compatibilize because neither of these polymers contains any functional groups that one can use to form copolymer directly from polyolefin and PS. A number of reactive polymer reagents have been used for the *in situ* compatibilization of polyolefin/PS blends.⁶⁻⁸ This approach, however, usually requires 5-15% of relatively expensive reagents, usually specialty copolymers. A more straightforward method involving less costly additions to compatibilize these polymer blends would be more attractive in polymer recycling.

One possibility to do so is to activate macroradicals of polyolefin and PS in order to form the copolymer. Flaris et al.⁹ found that a suitable organic silane plus peroxide can favor the reciprocal free radical grafting between PE and PS at the interface in PE/PS blends. Further study on the interfacial tension in PE/PS/peroxide/silane-blending systems suggested that the silane tended to spread on the surface of dispersed particles of minor phase in such blends.^{10,11} In this way, the silane plays a role as a "vector fluid" to bring the initiator to the interface between PE and PS.

Another possibility for polyolefin/PS *in situ* compatibilization is to use the benzene ring of PS as the reaction site. An electrophilic substitution of a proton on the aromatic ring by a halogenated alkane or olefin can be realized in the presence of a strong Lewis acid; this is known as a Friedel-Crafts alkylation.^{12,13} Carrick¹⁴ formed a copolymer of PE and PS in solution using AlCl₃ as the catalyst. Using the same method, Heikens et al.^{6,7} prepared a PE-PS copolymer, and then added the copolymer into PE/PS melt blends. The improvements in both the morphology and the mechanical properties of PE/PS/PE-PS blends were reported.

This article reports our first effort to achieve *in situ* compatibilization of polyolefin/PS blends through the mechanism of Friedel-Crafts benzene ring alkylation during melt blending. A linear low-density PE and a PS homopolymer were used as the model system. The purpose of this

study was to improve considerably the mechanical properties of PE/PS blends by an *in situ* compatibilization process.

CHEMICAL ASPECTS

Friedel-Crafts benzene ring alkylation occurs by the following reaction steps^{12,13}:

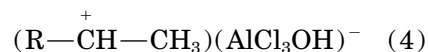
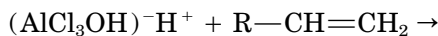


The first step is the formation of an initial carbocation R⁺ by the reaction of a halogenated alkane with aluminum chloride. Then, the initial carbocation substitutes for a proton of the benzene ring, in the presence of a catalyst.

Carrick¹⁴ used aluminum chloride in a hexane solution of PE and PS at 81°C (the boiling temperature of the hexane) and obtained a PE-g-PS graft copolymer. For such a copolymer formation, the following mechanism was suggested.

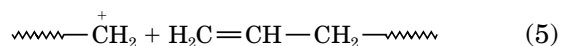
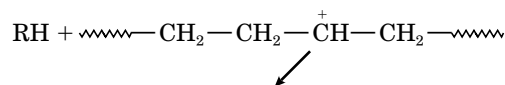
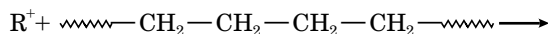
Initiation

Aluminum chloride reacts with impurities (for example, water) to form a complex. This then reacts further with halogenated or unsaturated compounds, which exist in the system as impurities as well, forming the initial carbocation.



Chain Scission of PE

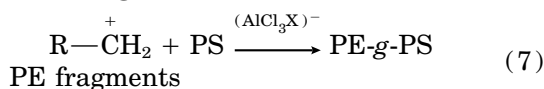
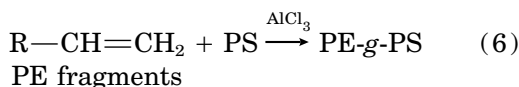
The initial carbocation attacks PE, forming a macrorcarbocation, PE⁺. The PE⁺ ion formed can undergo a chain scission through electron rearrangement near the site of the carbocation.



Grafting

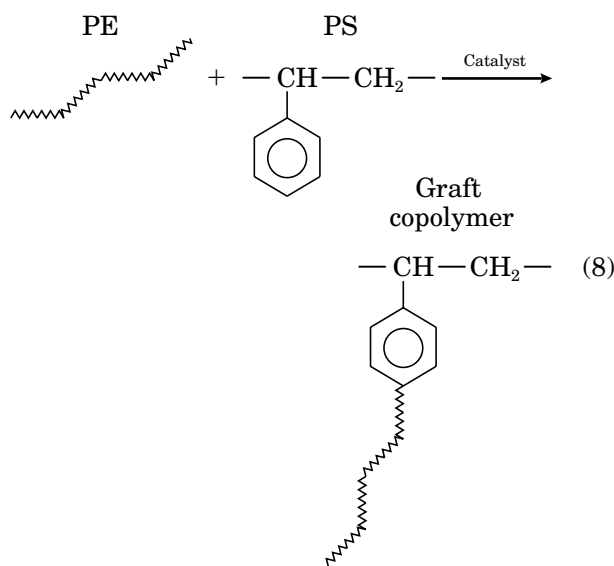
In the presence of a catalyst, fragments of the PE chain, which can possess a carbon-carbon double

bond or carbocation chain end, can substitute for a proton from the benzene ring of PS, forming a PE-*g*-PS copolymer.



The formation of a PE-*g*-PS copolymer in a PE and PS melt using a Lewis acid catalyst is a complicated reaction process. The earlier study¹⁴ suggested a mechanism of Friedel-Crafts alkylation, as mentioned above. However, a detailed study of the mechanism of such a reaction process has not been found in literature. In this case, some points in such a suggested mechanism are not yet clear. For example, how can a PE macrocarbocation (PE⁺) be formed during this process? One possibility is the suggestion made in eq. (5). Another is that a small number of carbon-carbon double bonds exist on the PE chain, which can be the site of carbocation formation, as in eq. (4).

In this study, the central approach is to form a PE-*g*-PS copolymer during the PE/PS melt blending, through the mechanism of Friedel-Crafts benzene ring alkylation, as shown in eq. (8):



EXPERIMENTAL

Materials

The linear low-density PE used in this study was Esso Chemical Canada (Sarnia, ON) Escorene LL-

5103 in powder form (\bar{M}_w , 75 kg/mol; \bar{M}_n , 23 kg/mol). The PS was a homopolymer in pellet form, supplied by Novacor (grade 777; \bar{M}_w , 404 kg/mol; \bar{M}_n , 76 kg/mol).

The materials evaluated as catalysts included aluminum chloride (AlCl₃, purity 98%, purchased from Aldrich), aluminum chloride hexahydrate (AlCl₃·6H₂O, purity 99%, purchased from Aldrich), tin(IV) chloride (SnCl₄, purity 99%, purchased from Aldrich), iron(III) chloride (FeCl₃, purity 97%, purchased from Aldrich), and ethylaluminum dichloride (C₂H₅AlCl₂, 25 wt % solution in toluene, purchased from Aldrich). The aluminum chloride, tin(IV) chloride, and iron(III) chloride were in the form of powder. In order to protect them from moisture in the air, they are kept in hexane and used in hexane-wetted, sludgelike form.

The cocatalysts tested were styrene (C₆H₅CH=CH₂, purity 99%, purchased from Aldrich), 1-chloropentane (CH₃(CH₂)₄Cl, purity 99%, purchased from Aldrich), 1,10-decanedicarboxylic acid [HOOC(CH₂)₁₀COOH, purity 99%, purchased from Aldrich], aminoethylaminopropyltrimethoxysilane [silane 6020, (CH₃O)₃Si(CH₂)₃NH-CH₂CH₂NH₂, purity 98%, supplied by Dow Corning]. A PVC polymer and distilled water were also used as cocatalysts.

Polymer Blending

PE and PS were blended using a batch mixer (HaakeBuchler System 40, 50-cm³ capacity). A total charge of 45 g of polymers was blended in the Haake mixer. The catalyst was dry blended with 9 g of PE powder, while the cocatalyst was dry blended with 9 g of PS pellets. These two parts of polymer/catalyst mixture were fed together into preheated Haake mixer and blended for 2 min. Then, the remaining 27 g of polymers was fed and blended together for 5 min at 100 rpm. The resulting blends were cooled in air unless specified otherwise.

Characterization of PE/PS Blends

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 alternatively using THF and *n*-heptane. For the PE/PS blends in which PS was the major phase and matrix, 48 h of THF extraction was the first step, to

remove homopolymer PS. The insoluble part of THF extraction was further extracted with *n*-heptane for 48 h, to remove homopolymer PE. For the PE/PS blends in which PE was the major phase and matrix, the *n*-heptane extraction was the first step, followed by THF extraction.

The reliability of such a THF/*n*-heptane solvent extraction for PE/PS blends was confirmed by extracting PE/PS mechanical mixtures containing no catalyst. The mechanical mixtures of PE/PS in proportions of 20/80 and 80/20 were extracted. The infrared (IR) analysis showed that there was only PE (without PS) in the THF-insoluble part and *n*-heptane-soluble part, and there was only PS (without PE) in the THF-soluble part and *n*-heptane-insoluble part. After the alternating THF and *n*-heptane extraction, the amount of residue of these mechanical PE/PS mixtures was zero. On the basis of these results, for the blends of PE/PS/catalyst, the PS which remained in the THF-insoluble phase (PE phase) can be considered to be in the form of the PE-*g*-PS copolymer, and the PE which remained in the *n*-heptane-insoluble phase (PS phase) was also in the form of PE-*g*-PS copolymer. Furthermore, the residual polymer, which is not soluble in THF or in *n*-heptane, should be the pure copolymer of PE-*g*-PS.

IR Spectrometer for PE-*g*-PS Copolymer Analysis

After extraction, the presence of PS in the PE phase and in the residue copolymer PE-*g*-PS was detected by Fourier transform IR, using film samples. The concentration of PS in the samples starting with 0–50 wt % PS was determined by comparison of the ratio of IR absorption at 700 cm⁻¹ (PS) to that at 719 cm⁻¹ (PE). The ratio of IR absorption at 1,600 cm⁻¹ (PS) to that at 719 cm⁻¹ (PE) was used to determine the concentration of PS in the samples containing 50–100 wt % PS.¹⁴ Calibration curves were prepared using PE/PS mechanical mixtures of known proportions. The IR analysis data given in this article are the average values of at least four measurements.

Mechanical Characterization

The performance of PE/PS blends was evaluated using tensile and impact testing. The specimens used for the tensile and impact tests were injection molded at 210°C and then kept at room temperature for 3 days before testing.

The tensile test was performed using the dog-bone test specimen with an Instron mechanical tester (Instron Universal Test, Model 4206) at

Table I Comparison of the Efficiency of Different Lewis Acid Compounds

Catalyst	[PS] _g (wt %)
AlCl ₃	15.7
AlCl ₃ · 6H ₂ O	0
C ₂ H ₅ AlCl ₂	4.2
SnCl ₄	0
FeCl ₃	0

room temperature, with a crosshead speed of 50 mm/min. (ASTM 638-71A). The dimension of the gauge section of the tensile test specimen was 20 × 3 × 4 mm.

The impact test was carried out with a Rheometrics 5000 instrumented drop-weight impact tester at room temperature, with a head speed of 7.62 m/sec (300 in/s). The diameter and thickness of the specimens were 40 and 3 mm, respectively. The impact strength was taken to be the area under the force-displacement graph in Joules.

Other Characterizations

The molecular weight of homopolymer PS, which is the soluble part in the THF extraction of PE/PS blends, was determined with gel permeation chromatography (GPC) equipment (Waters Associates) at room temperature. The molecular weight of homopolymer PE, which is the soluble part in the *n*-heptane extraction of PE/PS blends, was measured using high-temperature GPC (Waters 150-C) at 145°C. The morphology of PE/PS blends was examined by scanning electronic microscopy (SEM; JEOL JSM-840) on the fresh fractured and gold-sputtered surface of PE/PS samples, which were obtained from the Haake mixer.

RESULTS AND DISCUSSION

Evaluation of Catalyst

Five Lewis acid compounds were used as catalysts in PE/PS (20/80 wt %) blends, in order to compare them in terms of their catalytic effect in the polymer melt. The reaction was carried out in the Haake batch mixer at 180°C. The catalyst concentration was 0.3 g in 100 g of polymers. No cocatalyst was used. The blends obtained were extracted in THF to remove homopolymer PS. The concentrations of PS which remained in PE phases after THF extraction (referred to as [PS]_g) are listed in Table I. Among these different Lewis acids, the

Table II Efficiency of Different Compounds as Cocatalyst

Cocatalyst (g) (in 100 g of Polymer)		[PS] _g (wt %)
Without cocatalyst	0	13–16
Styrene	0.6	43.9
1-Chloropentane	0.3	42.6
PVC	1.5	3.5
C ₁₀ H ₂₀ (COOH) ₂	0.6	0
Silane 6020	1.1	0
H ₂ O	0.1	0

aluminum chloride is the most efficient catalyst for PE-*g*-PS copolymer formation.

Use of Cocatalyst

The purpose of using a cocatalyst is to provide the source of initial carbocation, R⁺, which can attack the PE. The compounds which can be the potential cocatalyst include halogenated alkanes and cationic polymerizable monomers. An organic acid and water were also used to check if such polar molecules can play the role of a cocatalyst. The organic silane was also tried, because calculations show it able to spread onto the surface of dispersed particles in a PE/PS blend system.^{9–11} The cocatalysts were added into the blends of PE/PS (20/80 wt %) with 0.3 g of AlCl₃ per 100 g of polymers, blended in Haake batch mixer at 180°C. The efficiency of different cocatalysts is compared in Table II, in terms of the concentration of PS which remained in the PE phase after THF extraction.

The styrene and 1-chloropentane were used as the representatives of cationically polymerizable monomers and halogenated alkanes, respectively. They resulted in a high level of PE-*g*-PS copolymer formation: compared with the no-cocatalyst case, the grafted PS concentration in the PE phase increased about threefold when one of these cocatalysts was used. This should be due to the strong ability of these compounds to produce the carbocation when they react with AlCl₃. It should be noted that, according to the reaction mechanism in eq. (2), a strong acid (HCl, which is corrosive) is produced in such a polymer reaction when a chloroalkane is used as the cocatalyst. However, using styrene as the cocatalyst does not produce acid. For this reason, the styrene was used as the cocatalyst in the remainder of this study.

It is still not clear why PVC was not an efficient

cocatalyst, while the 1-chloropentane was so efficient. It is possible that the low miscibility and high molecular weight of the PVC result in poor distribution of this cocatalyst in the melt and thus reduced effectiveness.

Adding the other polar compounds, such as the organic acid, silane, and water, did not favor the PE-*g*-PS copolymer formation, presumably because they are not able to provide the initial carbocation, which can attack PE chains. Furthermore, these compounds can react quickly with AlCl₃, destroying the catalyst.

Formation of PE-*g*-PS Copolymer During Blending

In order to study the copolymer formation during blending, samples were taken after 2, 5, 7, and 10 min of blending in a Haake batch mixer at 180°C and immediately being quenched in liquid nitrogen to stop the reaction. Note that for this blending equipment, 2 min is the shortest time to get meaningful blending results. The polymer blends were PE/PS (20/80), with two compositions of catalyst: with 0.3 g of AlCl₃ and 0.6 g of styrene per 100 g of polymers, and 0.3 g of AlCl₃ per 100 g of polymers, without styrene. The rise in the concentration of PS which remained in PE phase after THF extraction is shown in Figure 1. It can be seen that, when AlCl₃ was used alone without cocatalyst, the increase of copolymer quantity leveled off after about the first 2 min of blending. When styrene was used as the cocatalyst, it seems that the presence of styrene prolonged the copolymer formation reaction: [PS]_g leveled off at about 4–5 min, instead of at 2 min without styrene. A similar tendency can be seen

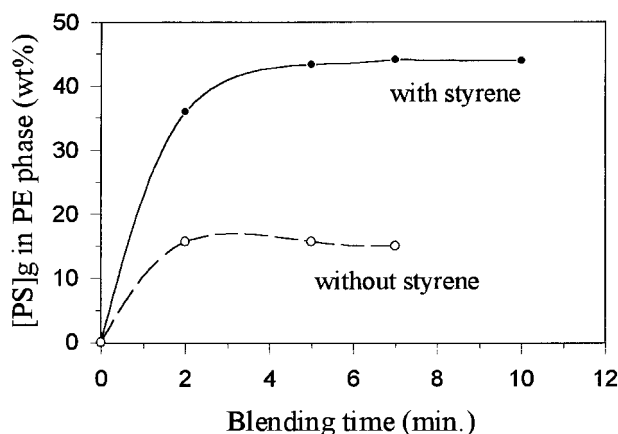


Figure 1 Grafting degree of PS in PE phase, increasing with time.

Table III Amount of Unextractable PE-*g*-PS Copolymer Remaining with Time as Weight Percent

	2 min	5 min	7 min	10 min
With styrene	11.0	12.1	11.9	11.7
Without styrene	5.5	5.3	5.7	

in Table III, which shows the increase in the amount of PE-*g*-PS copolymer remaining in the blends after both THF and *n*-heptane extractions. The composition of these PE-*g*-PS copolymers was determined using IR analysis, shown below in Table IV. These results show again that the copolymer formation has been much more favored by using a suitable cocatalyst.

The molecular weight of PE and PS phases of these samples, which were separated, respectively, by *n*-heptane and THF extraction, were measured using GPC (Figs. 2 and 3). When styrene was used as the cocatalyst, the molecular weight of PE remained a little higher than that of PE obtained from the blends which were prepared without using styrene (Fig. 2). Furthermore, a generally higher molecular weight was also observed for the PS [Fig. 3(a,b)] when styrene was used as the cocatalyst. The general drop in molecular weight of the PE in Figure 2 seems to be consistent with the mechanism suggested in eq. (5). It is interesting to note that the PS concentration in the PE-*g*-PS copolymer had a peak value at 5 min of blending when styrene was used as the cocatalyst (Table IV). Carrick¹⁴ also reported a peak value in the degree of graft of PS on PE with reaction time in a PE/PS/AlCl₃ reaction system in boiling cyclohexane. It appears that a competition occurs between the polymer chain scission and copolymer formation during the blending process.

Without an in-depth study on such a complicated reaction system, we cannot give a further explanation for these phenomena. What is encouraging is that this method of forming graft copolymer "*in situ*" does not result in undesirable cross-linking, which can occur when peroxides are used.

Effect of Temperature

Blends of PE/PS (20/80), with 0.3 g of AlCl₃ per 100 g of polymer, without cocatalyst, were prepared in the Haake batch mixer at different temperatures, to investigate the influence of temperature on the PE-*g*-PS copolymer formation. Again, the concentration of PS which remained in the PE phase after THF extraction was compared for different samples.

It was found that the copolymer formation was favored by lower temperature, as shown in Figure 4. Without further study on this point, one possible hypothesis can be given here to explain the phenomenon. The minor impurities which exist in the system (and which are potentially involved in the mechanism) are mainly low-molecular-weight molecules. They can be more quickly devolatilized at a higher temperature. The AlCl₃ could be in contact with less impurity (cocatalyst) at higher temperature to form less activated complex and R⁺ [eqs. (3) and (4)]. Such a hypothesis is consistent with the data shown above in Figure 1 and Table III; the existence of a cocatalyst prolonged the effective reaction time of the AlCl₃ in the high-temperature polymer melt.

Mechanical Performance of PE/PS Blends Prepared in the Batch Mixer

The PE/PS blends were prepared at 160°C in the Haake batch mixer with different PE/PS proportions. The concentrations of AlCl₃ was 0.2 g per 100 g of polymers, while that of styrene was 0.4 g per 100 g of polymers. The elongation at break values in the tensile test of these blends, compared with that of mechanical mixtures and pure

Table IV Concentration of Grafted PS in PE-*g*-PS Copolymers (wt %)

	2 min	5 min	7 min	10 min
With styrene	63	71	67	65
Without styrene	42	47	38	

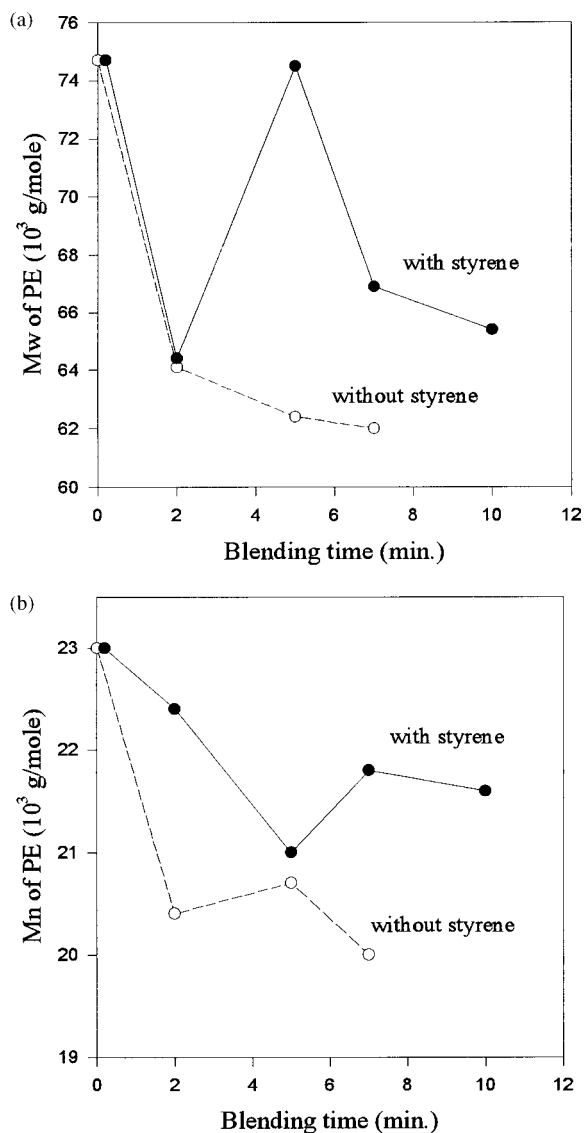


Figure 2 Change of the molecular weight of PE during blending. (a) Change of the weight-average molecular weight (\bar{M}_w) of PE during blending, with (●) and without (○) styrene as cocatalyst. (b) Change of the number-average molecular weight (\bar{M}_n) of PE during blending, with (●) and without (○) styrene as cocatalyst.

polymers, are shown below in Table V. The most improved blend was PE/PS (80/20). The extraction and IR analysis shown that a relatively large amount of PE-g-PS copolymer had been formed during the blending (Table VI). It is believed that the poor elongation value for the blends of PE/PS (50/50) and (20/80) is due to the brittle PS becoming the continuous phase. The observation on the morphology of PE/PS (80/20) blends using SEM (Fig. 5) shows that the size of dispersed PS

particle in the PE matrix was much reduced when the AlCl_3 /styrene catalyst system was used in the blending.

The performance of the PE/PS (80/20) blend was confirmed further by impact testing (Table VII). The PE/PS (80/20) blend was so well compatibilized that its impact strength reached the same level as that of pure PE. The results in Tables V–VII indicate that the application of this Friedel–Crafts reactive system in PE/PS melt

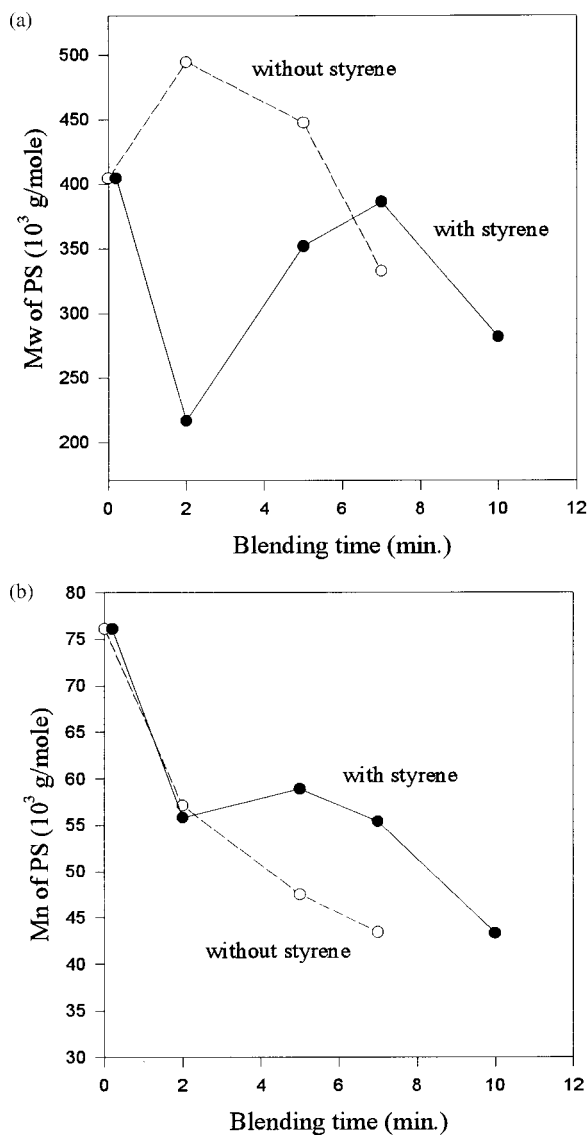


Figure 3 Change of the molecular weight of PS during blending. (a) Change of the weight-average molecular weight (\bar{M}_w) of PS during blending, with (●) and without (○) styrene as cocatalyst. (b) Change of the number-average molecular weight (\bar{M}_n) of PS during blending, with (●) and without (○) styrene as cocatalyst.

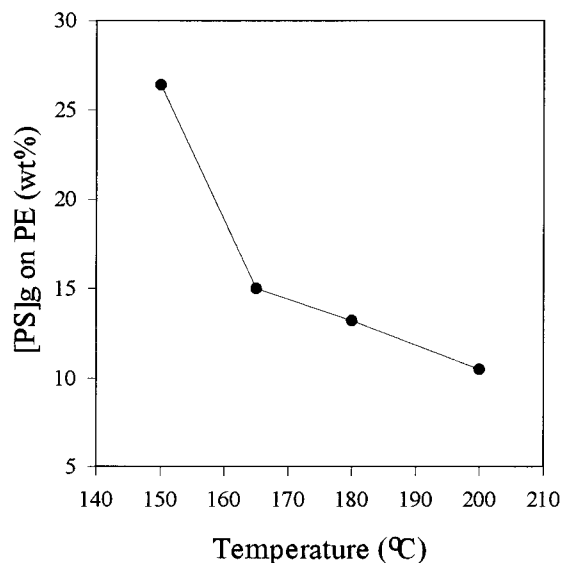


Figure 4 Influence of temperature on PE-*g*-PS copolymer formation.

blending can be very efficient for *in situ* compatibilization using only a small quantity of inexpensive compounds as catalysts. While these results are preliminary, they show promise as a low-cost compatibilizer for the PE/PS ratio commonly found in mixed-waste plastics.

CONCLUSIONS

The use of a Friedel–Crafts alkylation reaction in a melt-blending process signals a potentially economical method for compatibilizing the mixed streams of polyolefin/PS, which can be applicable in mixed-plastics recycling. Both the AlCl_3 and the styrene, used as the catalyst system, are common and inexpensive compounds. This catalyst system has been confirmed to be efficient in the PE/PS melt-blending process in a batch processor. The main achievements include a high PE-*g*-PS copolymer concentration formed during a

Table V Elongation at Break (%) (with Cross-Head Speed of 50 mm/min)

Sample	Mechanical Mixture	Blends with Catalyst
PE/PS 80/20	170 ± 19	720 ± 15
50/50	7.0 ± 0.6	8.8 ± 1.2
20/80	5.4 ± 1.4	6.8 ± 1.0
PE raw		About 830
PS raw		3.5 ± 0.5

Table VI Copolymer Concentration in PE/PS Blends

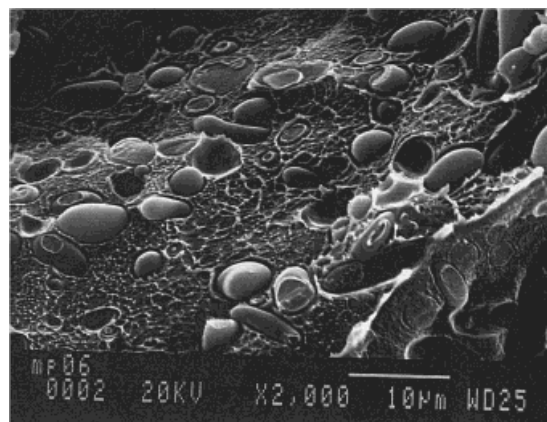
Sample	[PE- <i>g</i> -PS] ^a (wt %)	[PS] _g ^b (wt %)
PE/PS = 80/20 wt %	18	22
PE/PS = 50/50 wt %	8	6
PE/PS = 20/80 wt %	20	78

^a PE-*g*-PS copolymer concentration in PE/PS blends.

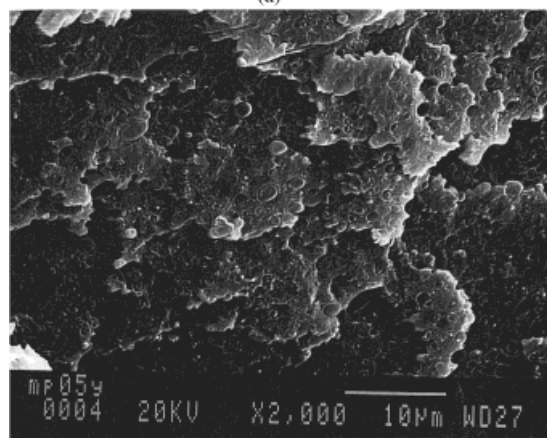
^b Degree of grafting of PS on PE in PE-*g*-PS copolymer.

short melt-blending period and very much improved elongation at break and impact strength for these blends.

The blending results suggest a mechanism in which the PE chain is grafted onto the benzene ring of PS in the melt state, along with PE chain scission. It is believed that the fragments of the PE chain be the important reactants in the elec-



(a)



(b)

Figure 5 Morphology of PE/PS blends. (a) Mechanical mixture of PE/PS (80/20). (b) *In situ* compatibilized blend of PE/PS (80/20).

Table VII Impact Strength of PE/PS (80/20) Blends

	Mechanical Mixture	Blend with Catalyst	Virgin PE
Impact strength (J)	3.6 ± 0.9	10.1 ± 1.0	9.0 ± 0.9

trophilic substitution of proton on the benzene ring. In this case, a careful balance must be found during the blending to favor the formation of PE-g-PS copolymer, while reducing as much as possible the PE chain scission.

The cocatalyst plays an indispensable role in the reaction, providing the initial carbocation to attack the PE chain. From the viewpoint of practical application, the styrene, or more generally a monomer which is cationically polymerizable, is more interesting, because it does not produce corrosive acid during the reaction.

The authors are grateful to the Ontario Center of Materials Research for its financial support of this work. The authors thank Dr. K. Russell and Dr. R. A. Whitney for their helpful discussions.

REFERENCES

1. D. R. Paul, J. W. Barlow, and H. Keskkula, *Encyclopedia of Polymer Science Engineering*, J. I. Kroschwitz, Ed., Wiley, New York, 1988.
2. S. Y. Hobbs, R. C. Bopp, and V. H. Watkins, *Polym. Eng. Sci.*, **23**, 380 (1983).
3. D. F. Aycock and S-P. Ting, U.S. Pat. 4,600,741 (1986) (to General Electric).
4. E. J. Olivier, U.S. Pat. 4,594,386 (1986) (to Copolymer Rubber & Chemical).
5. M. Lambla and M. Seadan, *Polym. Eng. Sci.*, **32**, 1677 (1992).
6. D. Heikens and W. M. Barentsen, *Polymer*, **14**, 579 (1973).
7. D. Heikens, N. Noen, W. M. Barentsen, P. Piet, and H. Laden, *J. Polym. Sci. Polym. Symp.*, **62**, 309 (1978).
8. W. E. Baker and M. Saleem, *Polym. Eng. Sci.*, **27**, 1634 (1987).
9. V. Flaris, W. E. Baker, and M. Lambla, *Polym. Networks Blends*, **6**, 29 (1996).
10. S. Y. Hobbs, M. E. J. Dekkers, and V. H. Watkins, *Polymer*, **29**, 1598 (1988).
11. Y-J. Sun, V. Flaris and W. E. Baker, *Can. J. Chem. Eng.*, to appear.
12. R. T. Morrison and R. N. Boyd, *Organic Chemistry*, 3rd ed., Allyn and Bacon, New York, 1973, Chap. 11.
13. J. March, *Advanced Organic Chemistry*, 3rd Ed., Wiley, New York, 1985, Chap. 11.
14. W. L. Carrick, *J. Polym. Sci., Part A-1*, **8**, 215 (1970).