Free Radical Grafting of Styrene onto Polyethylene in Intensive Mixer

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ABSTRACT: The graft copolymerization of styrene onto low density polyethylene (LDPE) with dicumyl peroxide as an initiator was studied. The existence of the graft copolymer was verified by infrared spectra. The effects of the initiator concentration, the feed composition, the reaction time, and the reaction temperature were discussed. Grafting efficiency reached a maximum value with the increase of reaction time. The effect of increasing the concentration of dicumyl peroxide was to decrease the grafting efficiency up to a minimum value. Grafting efficiency was not affected much by the variation of the reaction temperature. Grafting efficiency decreased largely with the increase of the feed composition of styrene. The compatibilizing effect of the copolymer prepared in this study was demonstrated by the morphology and mechanical properties of high impact polystyrene/LDPE blends. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1307–1317, 1998

Key words: reactive processing; graft copolymerization; polyethylene-*g*-polystyrene copolymer; compatibilizer

INTRODUCTION

The development of useful polymer blends has been the subject of intensive investigation in recent years because of their growing commercial acceptance. While simple blending of polymers can result in a wide variety of blend morphologies, final product properties are often less than satisfactory. Immiscible polymer blends generally suffer from poor interfacial adhesion that results in weak or brittle mechanical behavior. While polystyrene (PS) and polyethylene (PE) have proven to be very important commodity polymers on their own merits, simple melt blends of these two components generally result in poor material properties arising from the inherent incompatibility between the components. Traditional methods for the compatibilization of incompatible blends have involved the addition of block and graft copolymers.[1–9] Heikens and Barensten[7] successfully compatibilized PE/PS blends through an emulsification effect employing suitable block and graft copolymers. Unfortunately these block or graft copolymerizations have been traditionally carried out in solution, and it is relatively expensive to obtain these surface active interfacial modifiers.[10] Recently more attention has been focused on reactive extrusion in which direct grafting of a monomer onto a polymer is achieved in an extruder. This approach has obvious economic advantages, because a modified polymer is produced without an additional new facility, the process time is

shortened, and the costs of solvent recovery are avoided.

Hohfeld[11] compatibilized PS/PE blends using maleic anhydride functionalized PE and oxazoline functionalized PS, but the mechanical property was not improved significantly. Baker et al.[12–14] used carboxylic acid functionalized PE and oxazoline functionalized PS to compatibilize PS/PE blends, but the improvements in mechanical properties were not good. The poor improvement was considered to result from low concentrations of reactive functional groups (oxazoline and carboxylic acid).

Rudin et al.[15,16] carried out direct grafting of PS and PE with dicumyl peroxide and a crosslinking coagent (triallyl isocyanurate) which resulted in limited success because of the difficulty in the generation of a PS radical required in the coupling reaction. They enhanced the reactivity of PS to similar abstraction reactions by incorporation of a comonomer unit *ortho*-vinyl benzaldehyde to obtain a 7.8 wt % of degree of grafting that resulted in poor mechanical properties in reactive extrusion blends of PE and copolymer of styrene and *ortho*-vinyl benzaldehyde. Limited interdiffusion of high molecular weight chains across the polymer–polymer interface was considered to be responsible for the significant inhibition of between-phase grafting reactions. Yamamoto et al.[17] obtained graft copolymers by using a special organic peroxide, *t*-butylperoxy-2-methacryoyloxyethyl carbonate (HEPO). They copolymerized the peroxide monomer (HEPO) that had an O—O bond with styrene at a temperature below the decomposition temperature of the O—O bond and obtained poly(St-stat-HEPO) with a pendant O—O bond. The poly(St-stat-HEPO) was thermally mixed in an extruder with PE and PE-*g*-PS was obtained. The grafting efficiency was about 50–60%, but the gel content was large up to 33%.

Flaris and Baker[18] proposed a new technique for the compatibilization of PS/PE blends. In their system linear low density PE (LLDPE) and PS were blended in the presence of a peroxide and a vector fluid that carries the reactive ingredient to the interface between the two components. Levels of 3% grafting were attained using the silane compound as a vector fluid.

The above approaches had limited success due to a low level of degree of grafting or a large amount of gel. Early in the 1960s Jones and Nowak[19] grafted styrene to PE in a reactive extrusion process. Styrene monomer in an admixture

with dicumyl peroxide was fed to a molten stream of PE in an extruder. They obtained PE-*g*-PS copolymer containing 4–15% graft PS. But they did not show whether this graft copolymer could be used as a compatibilizer in PS/PE blends, and very little is known about the chemistry and kinetics of this reaction.

To simulate the graft copolymerization in an extruder, we designed a novel experiment for PE-*g*-PS copolymer reactive extrusion with a modified Haake Rheometer and conducted a corresponding experimental study. For that purpose the effects of reaction parameters such as reaction time, dicumyl peroxide concentration, reaction temperature, and feed composition on the degree of grafting and conversion were investigated. Investigation of the capability of the particular graft copolymer prepared in this study to behave as a compatibilizer for high impact PS (HIPS)/LDPE blends was also conducted.

EXPERIMENTAL

Materials

The starting material was an LDPE in pellet form with a density of 0.923 g/mL and a melt index of 6.3 g/10 min. Its weight average molecular weight (M_w) was 161,300 and its M_w/number average molecular weight (M_n) was 4.6. Styrene (Aldrich, 99%, inhibited with 20 ppm 4-*tert*-butylcatechol) was used as received. Dicumyl peroxide (Aldrich) was used as a free radical initiator whose half-life in benzene was 1 min at 171°C and 10 h at 117°C. To evaluate the compatibilizing effect of the copolymer prepared in this study, commercial LDPE and HIPS were used. The HIPS resin HR-1360H was obtained from Cheil Industries and the LDPE resin 210H was from Samsung General Chemicals. The viscosity of HIPS at 180°C and 100 s^{-1} was 650 Pa s and that of LDPE was 867 Pa s.

Grafting Procedure

The graft copolymerization was conducted in a Haake Rheomix 600 mixer, a batch type internal intensive mixer with a capacity of about 50 mL. Because the boiling point of styrene is 145–146°C, it is liable to be lost through evaporation. Therefore, we made a special well-sealed mixer with two refluxing condensers. PE was dried at 80°C

for 4 h before use. The amount of material fed into the mixer had a constant weight of 45 g. The required amount of PE was fed to the preheated mixer. The rotor rotation speed of 30 rpm was selected.

Premixed monomer and initiator were added to the PE melt and allowed to react for the specified time. Initiator concentrations of 0.01–0.09 mol/L, based on the volume of styrene, and styrene concentrations of 20–80 wt %, based on the PE charge size, were used. The reaction temperature varied between set temperatures of 140 and 170°C. The reaction product was removed from the mixer and quenched into liquid nitrogen.

Purification

Two grams of the reaction product was dissolved at 120°C in 80 mL of xylene and the solution was cooled at room temperature. Five hundred milliliters of equal volume methyl ethyl ketone (MEK) and acetone was added to the solution. The precipitate was filtered and dried to yield PE and PE-g-PS copolymer (W_1). The filtrate was evaporated at 50°C, and the remaining xylene solution was added to the excess methanol to obtain PS homopolymer (W_2). Experiments with model blends of LDPE and PS showed that PS is soluble in a xylene/MEK/acetone mixture. Although the graft copolymer in this study would have a relatively broad styrene compositional distribution, the graft copolymer was completely precipitated in the xylene/MEK/acetone mixture. This was verified by analyzing the soluble fraction. It contained only homo PS and the absorption bands due to PE in the FTIR spectrum were not observed.

Determination of Degree of Grafting and Grafting Efficiency

The degree of grafting of separate LDPE and PE-g-PS mixtures was determined by FTIR analysis. Films for FTIR analysis were compression molded at 170°C and 2000 psi. FTIR spectra were obtained on a Perkin–Elmer 1769X spectrometer at a resolution of about 1 cm^{-1}. The peak areas at 1527–1404 cm^{-1} (A_1) and at 1632–1567 cm^{-1} were analyzed (A_2). The 1527–1404 cm^{-1} peak region was due to the overlapping absorption of the —CH$_2$ group on the PE and the benzene group on the PS. The 1632–1567 cm^{-1} peak region was due to the benzene group on the PS. Therefore,
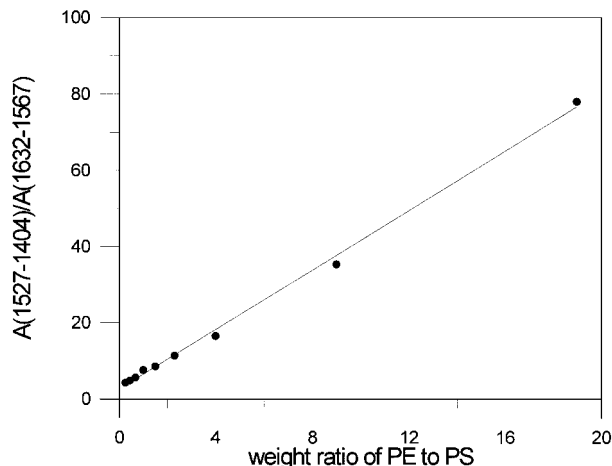

Figure 1 Calibration curve for determining PS content from the FTIR spectrum.

the ratio of the two absorption peaks is given by relation (1):

$$A_1/A_2 = k_1 \quad C_{\mathrm{PE}}/C_{\mathrm{PS}} + k_2 \tag{1}$$

where C_{PE} and C_{PS} are the weight concentration of PE and PS, respectively.[20] Figure 1 shows the calibration curve. The degree of grafting was calculated from the integrated absorbances as follows:

degree of grafting (DG, %) = $C_{\mathrm{PS}}/C_{\mathrm{PE}} \times 100$

$$= \frac{4.10593 \times 100}{A_1/A_2 - 2.24121} \tag{2}$$

The weight fraction of PS in W_1 is

$$\varphi_{\mathrm{PS}} = \frac{\mathrm{DG}}{100 + \mathrm{DG}}$$

Then grafting efficiency was calculated as follows:

grafting efficiency (%)

$$= \frac{W_1 \times \varphi_{\mathrm{PS}}}{W_1 \times \varphi_{\mathrm{PS}} + W_2} \times 100 \tag{3}$$

Molecular Weight Measurement

Molecular weight distributions were examined by Waters gel-permeation chromatography (GPC). The molecular weight of PS homopolymer was de-

termined at 25°C with tetrahydrofuran as the solvent and that of purified PE-*g*-PS copolymer was determined at 130°C using trichlorobenzene as the solvent.

Transmission Electron Microscopy (TEM)

The microdomain structure of graft copolymer was examined by TEM. For this purpose a small piece of compression-molded film was stained with ruthenium tetraoxide (RuO_4) and embedded in epoxy resin. Ultrathin sections of about 50-nm thickness were obtained by microtoming at $-100°C$ with a Reichert–Jumg Knifemaker low temperature sectioning system. Electron microscopic observation was made with a JEOL transmission electron microscope at 100 kV.

Impact Test and Morphology Observation of HIPS/LDPE Blends

In order to assess the compatibilizing effect of graft copolymer, 70/30 HIPS/LDPE blends were prepared in a Haake Rheomix 600 at 180°C and 30 rpm for 10 min either with or without graft copolymer.

Izod impact tests were carried out on a Toseiki impact tester using notched specimens. The specimens were cut according to ASTM D256 from the compression molded sheet at 200°C and 200 kgf/ cm^2 with dimensions of $150 \times 200 \times 2$ mm. Each impact value reported was the average of five tests.

Fracture surfaces prepared at room temperature from impact tests were examined by scanning electron microscopy (SEM, JEOL 840A).

RESULTS AND DISCUSSION

Graft Copolymerization in Intensive Mixer

The route to a graft copolymer proposed here involves grafting a vinyl monomer to PE at reactive sites generated by abstraction of a hydrogen atom from the PE. Dicumyl peroxide is a peroxy initiator with a 10-h half-life in benzene at 117°C and has been used for crosslinking PE in the melt. It is capable of abstracting hydrogen from the PE under conditions similar to those used in our experiments.[21] Styrene is one of the vinyl monomers that undergo rapid thermal polymerization.[22,23] The thermal initiation mechanism for styrene
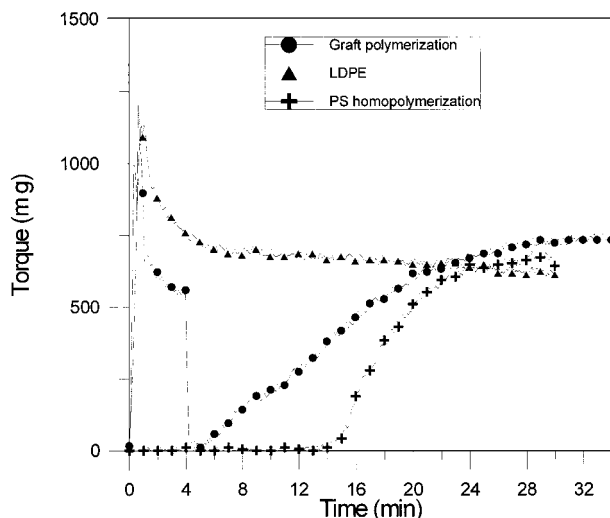

Figure 2 The relationship of torque and time for graft copolymerization, PS homopolymerization, and pure LDPE.

polymerization involves the formation of a Diels–Alder dimer of styrene followed by transfer of a hydrogen atom from the dimer to a styrene molecule. But it is not known whether the Diels–Alder dimer or styryl radical can abstract the hydrogen atom from PE under conditions similar to those used in our experiments. To elucidate this, thermal polymerization of styrene without dicumyl peroxide in the presence of PE was conducted. The analyses described below showed that no grafting occurred. Because the thermal styrene polymerization did not contribute to the grafting reaction, other monomers (e.g., methyl methacrylate, acrylonitrile, vinyl acetate) homopolymerized much more rapidly than styrene under peroxide initiation because the reactivities of the radicals formed during the thermal polymerization were too stable to abstract the hydrogen atom from PE.

Figure 2 shows the change of torque for the rotation of the mixer for LDPE, PS homopolymerization, and the graft copolymerization under the polymerization temperature of 140°C. Because the torque of the system is related to its viscosity, the measured magnitude of torque can be used to characterize the variation of the viscosity indirectly. For pure LDPE, the torque curve rises quickly and shows a peak as the PE pellets are fed into the mixer. The polymer is reduced to a molten state within a few seconds after polymer feeding is completed. After completion of feeding, the torque curve gradually falls to a steady-state value as the material temperature rises and levels
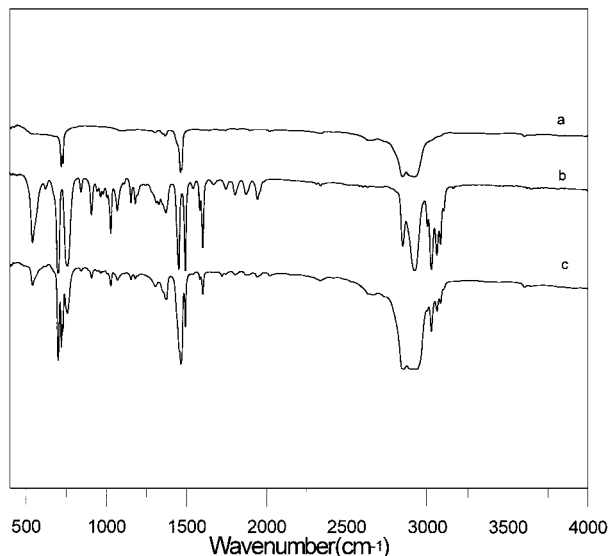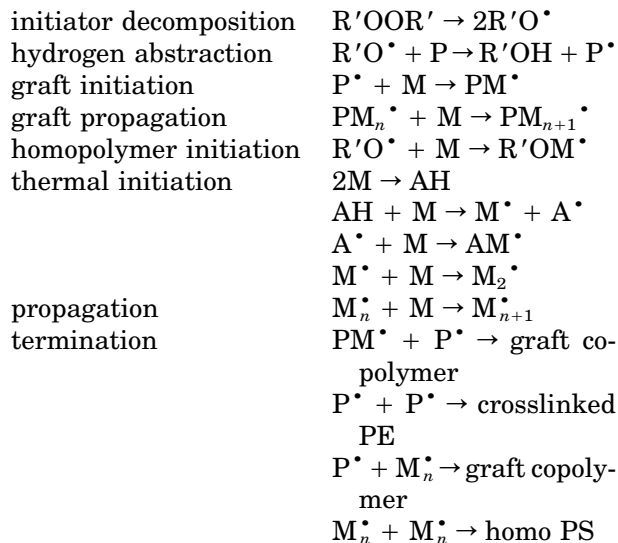
Figure 3 FTIR spectra of (a) LDPE, (b) PS, and the (c) purified reaction product.

off. For the homopolymerization of styrene at a dicumyl peroxide concentration of 0.05 mol/L in the first 14 min, the system viscosity is very low and almost constant. After the viscosity rises very rapidly and as the polymerization approaches completion, the viscosity reaches the steady-state value. For the graft copolymerization of styrene at a dicumyl peroxide concentration of 0.05 mol/L and a feed composition of 70% styrene, within 2 min after the styrene solution was fed, the torque began to increase; as the polymerization approached completion, the viscosity became almost constant. Note that the torque value at the steady state for the graft copolymerization was almost the same as the pure LDPE or homo PS. In this case, styrene monomer could be initiated with the dicumyl peroxide and homo PS could be formed. The styrene monomer could also react with the radical sites generated on the PE to form a graft copolymer with grafted PS chains.

Figure 3 shows the FTIR spectra of a purified reaction product obtained under the feed composition of 30% styrene and a dicumyl peroxide concentration of 0.05 mol/L and those of pure LDPE and homo PS. The IR spectrum of PE reveals the CH_2 rocking vibration at 1463 cm^{-1} and the CH_3 symmetric vibration at 1376.2 cm^{-1}. The spectrum of PS shows a $C=C$ plane vibration peak at 1450–1600 cm^{-1}. The IR spectrum of purified reaction product reveals a $C=C$ plane vibration peak at 1450–1600 cm^{-1}. This reveals the existence of PS in the purified reaction product.

Figure 4 shows the TEM of the purified reaction product. Note that the light area represents the LDPE phase, while the dark area represents the PS phase stained with ruthenium tetraoxide. Figure 4 shows the spherical PS domains of approximately 50 nm dispersed in the LDPE matrix, which means that the immiscible units of LDPE and PS are connected.[24] It can be inferred that segregation of PS into microdomains proves the existence of the PE-*g*-PS copolymer. Therefore, the overall mechanism of graft polymerization is as follows:

initiator decomposition	$R'OOR' \rightarrow 2R'O^{\bullet}$
hydrogen abstraction	$R'O^{\bullet} + P \rightarrow R'OH + P^{\bullet}$
graft initiation	$P^{\bullet} + M \rightarrow PM^{\bullet}$
graft propagation	$PM_n^{\bullet} + M \rightarrow PM_{n+1}^{\bullet}$
homopolymer initiation	$R'O^{\bullet} + M \rightarrow R'OM^{\bullet}$
thermal initiation	$2M \rightarrow AH$
	$AH + M \rightarrow M^{\bullet} + A^{\bullet}$
	$A^{\bullet} + M \rightarrow AM^{\bullet}$
	$M^{\bullet} + M \rightarrow M_2^{\bullet}$
propagation	$M_n^{\bullet} + M \rightarrow M_{n+1}^{\bullet}$
termination	$PM^{\bullet} + P^{\bullet} \rightarrow$ graft copolymer
	$P^{\bullet} + P^{\bullet} \rightarrow$ crosslinked PE
	$P^{\bullet} + M_n^{\bullet} \rightarrow$ graft copolymer
	$M_n^{\bullet} + M_n^{\bullet} \rightarrow$ homo PS

In the above scheme M is the monomer, AH is a Diels–Alder adduct, $R'OOR'$ is the initiator, and P is the PE. Note that graft copolymer can be formed by the graft propagation and termination reaction between $P^{\bullet}$ and $M_n^{\bullet}$.

As stated above, dicumyl peroxide is capable of abstracting hydrogen from the PE to form reactive sites. Therefore, crosslinking is a primary concern. All of the reaction products completely dissolved in the hot xylene, indicating that they were not highly crosslinked. Figure 5 gives molecular weight distribution curves of the LDPE and purified graft copolymer. The graft copolymer shows broader molecular weight distribution than LDPE and a low and high molecular weight tail in the GPC curve. This means that dissociation of C—C bonds can occur simultaneously with crosslinking. In the peroxide modification of PE in the melt, PE is exposed not only to high temperature and shear forces, but also to the influence of oxygen. The degradation of PE is caused by thermooxidative degradation.[25]
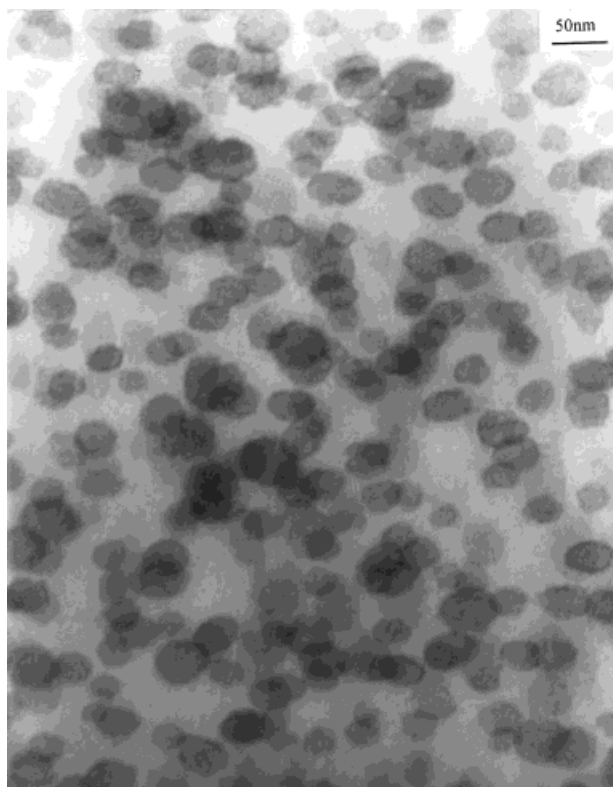
Figure 4 TEM micrograph of the purified reaction product.

Grafting Behavior

Figure 6 shows the effect of the reaction time on conversion, degree of grafting, and grafting efficiency. Conversion and degree of grafting increased with increasing time. Grafting efficiency
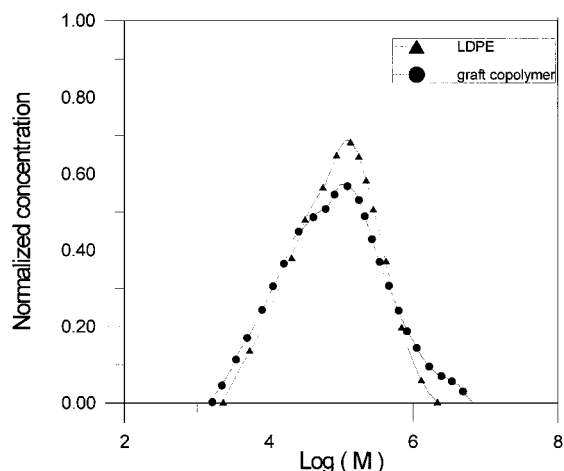
increased with time up to a maximum value and then decreased a little. This result might have been caused by the variation of morphology of the mixture during polymerization.

When the styrene was fed into the mixer, it became a continuous phase and coated the PE melt. Because styrene is miscible in the PE melt, the amount of styrene dissolved in the PE melt increased with increasing reaction time. Therefore, the grafting efficiency increased with increasing time up to 4 min. Continued polymerization caused phase separation. PE became the continuous phase and the PS formed the dispersed phase, separating as monomer-laden droplets. This caused a decrease in grafting efficiency. These observations were in agreement with the results obtained by analyzing the average molecular weight of PS homopolymer in Figure 7. The molecular weight of PS homopolymer increased with increasing time until 10 min and then decreased slightly. Note that in multiphase systems of polymers having different solubility parameters, solubility aspects may play an important role in the partition and reaction of the peroxide. The solubility parameter of the peroxide taken from Hogt[26] and calculated at 140°C using 9.5×10^{-4}/K for the coefficient of thermal expansion was 14.83 $(J/cm^3)^{1/2}$. Solubility parameters of LDPE and PS at 140°C were calculated from Krevelen,[27] and were 14.54 and 18.2 $(J/cm^3)^{1/2}$, respectively. Therefore, relatively more peroxide was partitioned in the PE phase, which corresponded to the

Figure 5 Molecular weight distribution curves for virgin LDPE and purified graft copolymer.
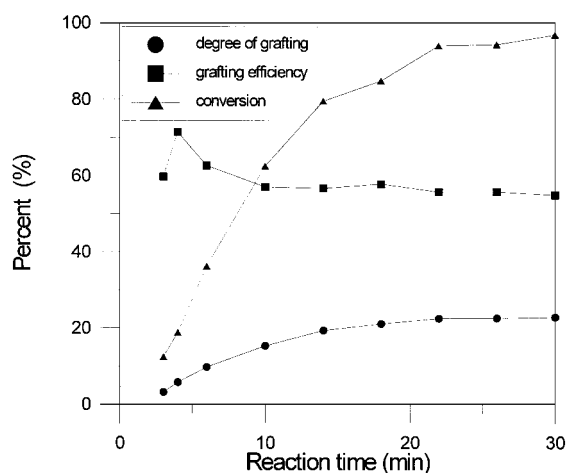

Figure 6 Degree of grafting, grafting efficiency, and conversion versus reaction time; dicumyl peroxide concentration, 0.05 mol/L; feed composition of styrene, 30%; and reaction temperature, 140°C.
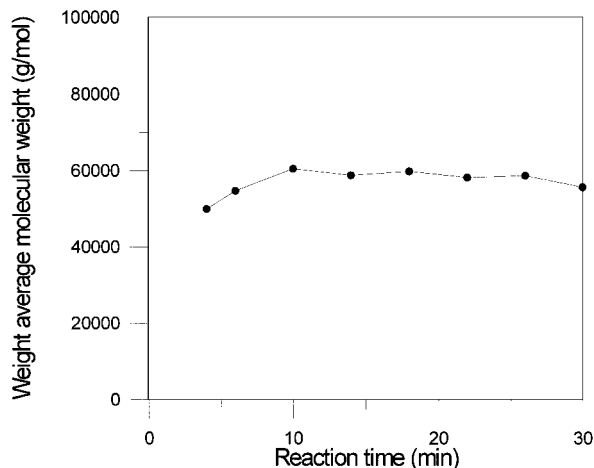
Figure 7 Weight average molecular weight of PS homopolymer versus reaction time; dicumyl peroxide concentration, 0.05 mol/L; feed composition of styrene, 30%; and reaction temperature, 140°C.

Figure 9 Weight average molecular weight of PS homopolymer versus dicumyl peroxide concentration; feed composition of styrene, 30%; reaction time, 10 min; and reaction temperature, 140°C.

smaller difference between the solubility parameters of the peroxide and that of PE as compared with that of PS. As a result, the concentration of dicumyl peroxide was higher in the PE phase than in the PS phase. During the final stages of polymerization, very short PS chains were produced as the monomer became depleted.

Figure 8 shows the effect of dicumyl peroxide concentrations on conversion, degree of grafting, and grafting efficiency. The conversion increased with an increasing concentration of dicumyl peroxide, and the degree of grafting increased
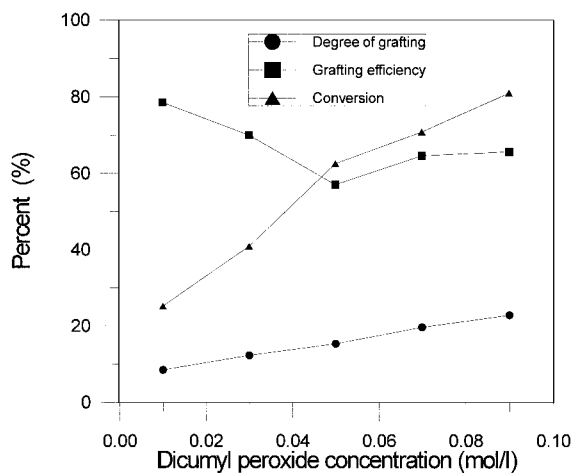

Figure 8 Degree of grafting, grafting efficiency, and conversion versus dicumyl peroxide concentration; feed composition of styrene, 30%; reaction time, 10 min; and reaction temperature, 140°C.
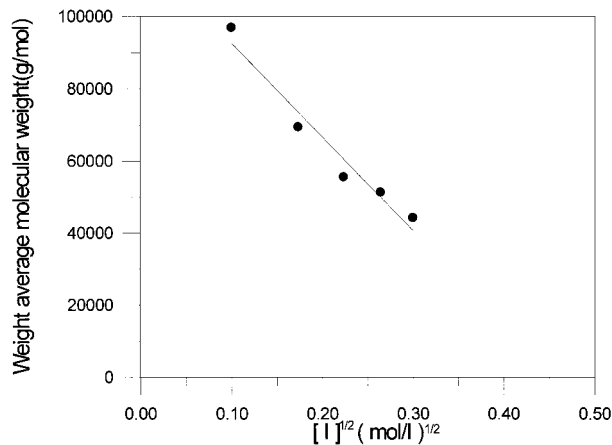
slightly with an increasing concentration of dicumyl peroxide. The grafting efficiency decreased with dicumyl peroxide concentration up to a minimum value and then increased. Generally the effect of raising the initiator concentration is to decrease the grafting efficiency.[28] Note that when the grafting efficiency was over the minimum value, the amount of PE radical, PS radical, and graft copolymer radical increased with the increasing concentration of dicumyl peroxide, which increased the possibility of interaction of the PE radical and PS radical; therefore, the grafting efficiency was increased.

Figure 9 shows the effect of dicumyl peroxide concentration on the molecular weight of PS homopolymer. The effect of raising the initiator concentration was to increase the rate of initiation. Therefore, the average molecular weight of the PS homopolymer decreased with increasing initiator concentration.

Figure 10 shows the effects of reaction temperature on grafting behavior. Conversion and degree of grafting increased with temperature until 160°C and then decreased at 170°C. The conversion increase was caused by an increase in the polymerization rate. The decrease in conversion at 170°C can be explained by the concentration of the initiator. The half-life of dicumyl peroxide at 170°C is about 1 min. The set temperature of 170°C resulted in an actual temperature of the reaction mixture of about 180°C due to shear heating. As a result, most of the initiator was decomposed in the early reaction period. Grafting effi-
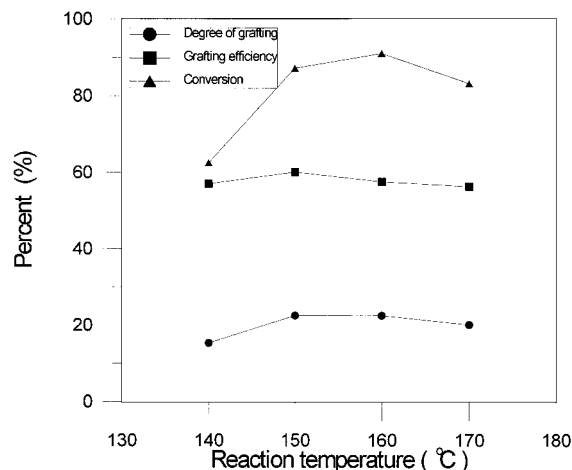
Figure 10 Degree of grafting, grafting efficiency, and conversion versus reaction temperature; dicumyl peroxide concentration, 0.05 mol/L; feed composition of styrene, 30%; and reaction time, 10 min.

ciency increased with temperature up to a maximum value and then decreased, but its variation was very small. It could be expected that a temperature rise results in an increase in grafting efficiency because the activation energy of the graft initiation reaction is larger than that of homopolymer initiation. This observation can be explained by the thermal polymerization of styrene. In Figure 11 we can see that thermal polymerization proceeded rapidly. Therefore, a rise in the temperature causes an increase in the graft initiation rate and at the same time thermal polymerization rate. Figure 12 shows the effect of temperature on the molecular weight of the PS homopolymer. Because a rise in the temperature causes an increase in the decomposition rate of the initiator, the average molecular weight of the PS homopolymer decreased with temperature.

Because the variation of reaction parameters did not result in a large increase in grafting efficiency, another way to achieve a high degree of grafting might be to increase the feed composition of styrene.

Table I shows the graft polymerization characteristics observed at 30 min of reaction time for several styrene compositions. Degree of grafting increased with increasing feed composition of styrene, whereas grafting efficiency decreased. This result can be explained by the morphology variation of the mixture of PE and styrene. Figure 13 gives the relationship between the torque and the reaction time as a function of feed composition of styrene.

As the styrene concentration increases, the time required for the torque to rise increases. When styrene forms the continuous phase in the low torque region, styrene is homopolymerized for some time, which results in a large decrease in grafting efficiency.

The molecular weights of PS homopolymers (Table I) extracted from the reaction product were larger than that of pure PS polymerized at the same condition without PE, because the effective dicumyl peroxide concentration was reduced in the PS-rich phase as mentioned earlier with the presence of the PE melt. The molecular weights of the graft copolymers were larger than that of pure PE due to the branched PS chain.

Preliminary Evaluation of Compatibilizing Effect of PE-*g*-PS Copolymer

Investigation of the capability of the graft copolymer prepared in this study to behave as a compatibilizer for HIPS/PE blends was performed. The copolymer had a degree of grafting of 22.8%, a PS homopolymer content of 13.1%, and an M_w of PS homopolymer of 55,622.

The morphology of the blends was investigated using SEM of the impact fracture surfaces. The morphology of the polymer blends was primarily affected by two factors: interfacial tension and rheological properties.[2] Particle size increased as the interfacial tension increased and as the viscosity ratio deviated from unity. In the present case
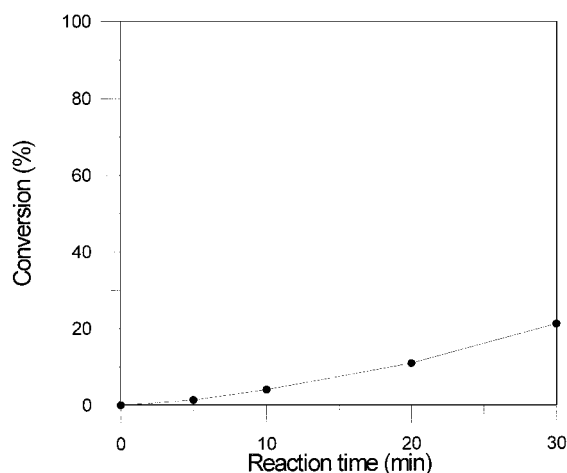

Figure 11 Conversion versus reaction time in thermal polymerization; feed composition of styrene, 30%; without dicumyl peroxide; and reaction temperature, 160°C.
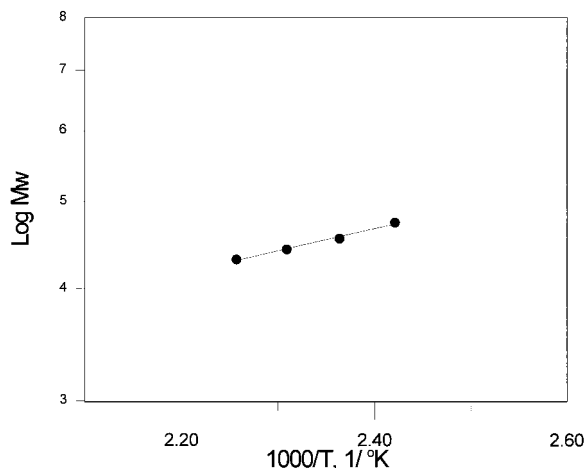
Figure 12 Weight average molecular weight of PS homopolymer versus reaction temperature; dicumyl peroxide concentration, 0.05 mol/L; feed composition of styrene, 30%; and reaction time, 10 min.

Figure 13 The relationship of torque and time as a function of feed composition of styrene; dicumyl peroxide concentration, 0.05 mol/L; and reaction temperature, 140°C.

the viscosity ratio of LDPE to HIPS was 1.3 at the shear rate of 100 s^{-1}: furthermore, interfacial tension between PE and PS was reported to be high: 5.1 mN/m at 180°C.[29] As a result, coarse phase dispersions were observed in the HIPS/LDPE blend at the 70/30 composition. These coarsely dispersed phases displayed no adhesion with the matrix [Fig. 14(a)]. Upon addition of the graft copolymer, emulsification of LDPE and HIPS took place, leading to a much finer dispersion and improved interfacial adhesion. The beneficial effect of the graft copolymer on the disper-
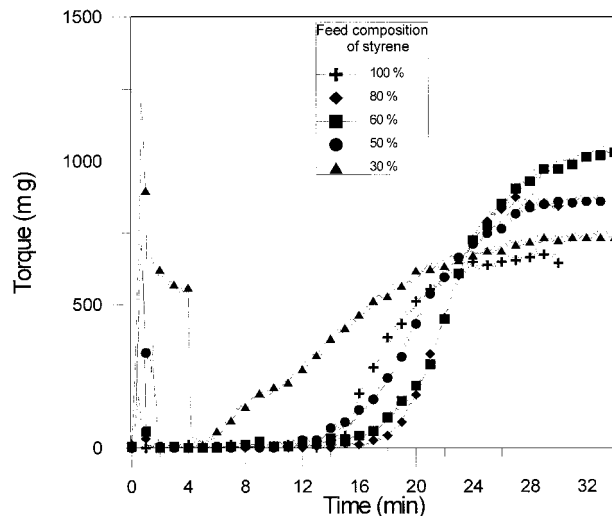
sion and interfacial adhesion of HIPS/LDPE blends was examined by the investigation of the impact strength of the blends. Figure 15 shows the effect of graft copolymer on the Izod impact strength of HIPS/LDPE blends. The Izod impact strength, which had a low value for the blend without compatibilizer, increased significantly as the amount of the graft copolymer was increased. For instance, the impact resistance of the 70 HIPS/30 LDPE blend increased from 5.3 to 12.7

Table I Characteristics of Graft Copolymers as Function of Feed Composition of Styrene, Dicumyl Peroxide Concentration (0.05 mol/L), Reaction Time (30 min), and Reaction Temperature (140°C)

|	Feed Composition of Styrene (%)				
	30	50	60	80	100
Conversion (%)	96.80	92.15	95.78	91.23	
Degree of grafting (%)	22.80	28.00	38.92	51.04	
Grafting efficiency (%)	54.90	30.22	27.10	13.99	
PS homopolymer					
M_n	24,188	27,647	28,873	25,689	21,892
M_w	55,622	53,391	56,351	49,542	41,023
M_w/M_n	2.30	1.93	1.95	1.93	1.87
Separated LDPE and PE-g-PS mixture					
M_n	26,040	25,110	24,890	25,120	
M_w	269,100	285,800	331,700	303,000	
M_z	1,523,000	1,597,000	2,218,000	1,939,000	
M_w/M_n	10.33	11.38	13.32	12.06	
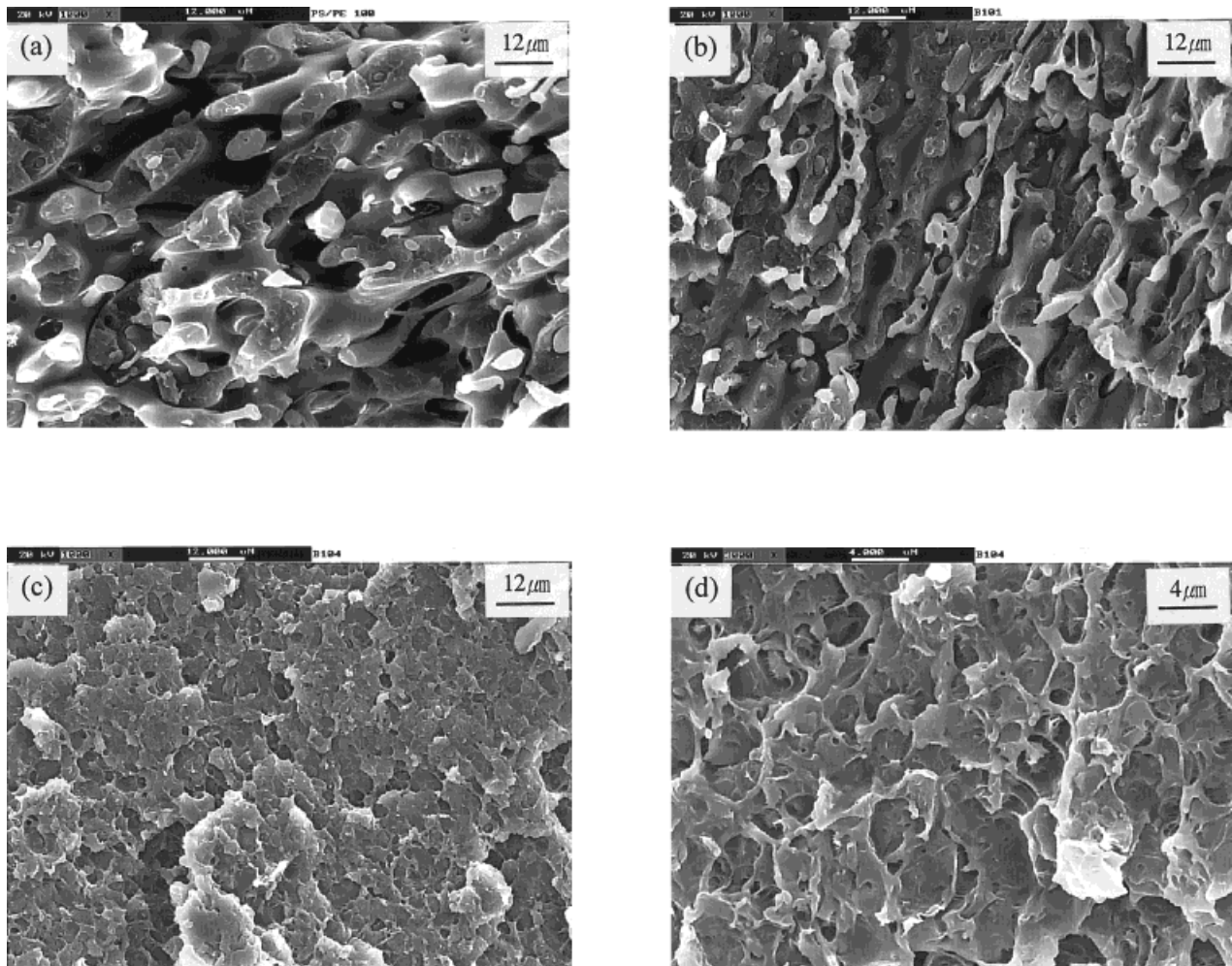
Figure 14   SEM photomicrographs of 70HIPS/30LDPE blends with the copolymers: (a) 0%, (b) 5%, (c) 10%, and (d) magnification of (c).

upon addition of the graft copolymer. This high impact strength was mainly attributed to finer phase dispersion and improved interfacial adhesion.

CONCLUSIONS

It was shown that PE-*g*-PS copolymer could be synthesized by the free radical graft copolymerization of styrene with dicumyl peroxide onto PE. The existence of grafted PS was proved by FTIR analysis and TEM observation.

Grafting efficiency increased with increasing reaction time up to a maximum value and then decreased due to the solubility of styrene in the PE melt and the phase separation of PS and PE.

The effect of increasing the concentration of dicumyl peroxide was a decrease in grafting efficiency up to a minimum value and then an increase due to the increased probability of interaction of the PE radical and PS radical. Grafting efficiency was little affected by the variation of reaction temperature because the increase in temperature caused an increase in the thermal polymerization rate of styrene. Grafting efficiency decreased largely with increasing feed composition of styrene due to the nonhomogeneous nature of the reaction medium.

The compatibilizing effect of the copolymer prepared in this study was preliminarily demonstrated by the morphology and mechanical properties of HIPS/LDPE blends.

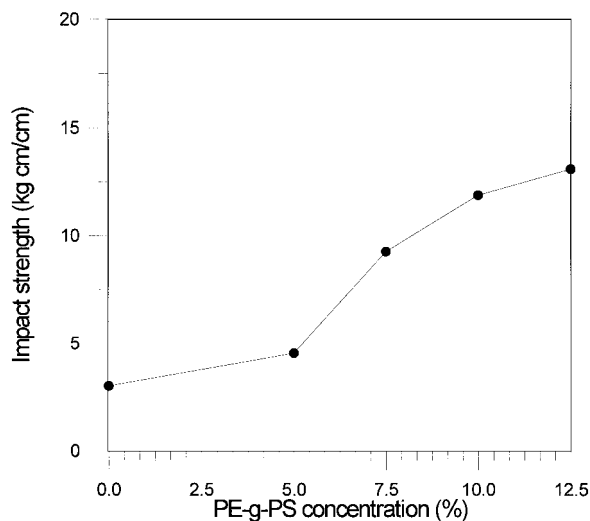The copolymer promoted the dispersion and in-

Figure 15 The relationship of Izod impact strength of 70HIPS/30LDPE blends and the graft copolymer concentration.

terfacial adhesion of phases and very significantly improved the impact strength of HIPS/LDPE blends.

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