Grafting Styrene onto a Polyethylene Surface: A Model Study of an Interfacial Reaction

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ABSTRACT: A model reactor system was assembled to study surface grafting reactions which would occur at the polymer interface in *in-situ* blend compatibilization using a vector fluid. The vector fluid's purpose is to convey a reactive ingredient to a blend interface and induce copolymer formation. Polyethylene (PE) was chosen as the polymer substrate, styrene monomer and/or dimethyl phthalate (DMP) as the vector fluid, and a peroxide initiator as the reactive ingredient. The free radical surface grafting reaction of styrene onto the PE surface was studied at melt processing temperature with a factorial experimental design involving the factors of time, temperature, initiator type and initiator concentration. It was found that styrene monomer was grafted at the PE substrate surface, forming a layer of PE-*g*-PS graft copolymer which was observed with attenuated total reflection Fourier transform infrared spectroscopy. The results indicated that the grafting reactions occurred not only at the immediate surface (2–3 μm), but also beneath the PE surface ($\sim$ 200 μm) due to the swelling of the PE by the styrene monomer. The reaction below the immediate surface could be significantly reduced by the presence of DMP, a nonsolvent of PE; but the surface reaction was not affected. Explanations for the reaction behavior of the two different vector fluids are proposed based on the experimental results. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 427–440, 1998

Key words: styrene; surface grafting; vector fluid; interfacial reaction; blend compatibilization

INTRODUCTION

A new approach is under investigation to compatibilize immiscible polymer blends using a vector fluid system. This technique is an *in-situ* reactive approach which aims at forming compatibilizing copolymer at the blend interface with the addition not of any new polymeric materials but rather of low-molecular-weight components. The vector fluid system usually consists of two parts, as follows: a liquid that is immiscible or miscible in either blend component, and a reactive ingredient that is miscible in this liquid (Fig. 1). The reactive ingredient would be a highly reactive compound that would preferably induce coupling reactions at the interface to form block or graft copolymer. Addition of the vector fluid to the polymer blends aims to reduce the usage of the premade reactive polymers or copolymers while resulting in equally efficient compatibilization, as is obtained with other blend compatibilization strategies. The concept of the vector fluid was first suggested in a polyethylene–polyamide (PE–PA) reactive blending system.[1] Liquid maleic anhydride (MA) (0.1%) and peroxide (0.05%) dissolved in the MA were added into the blend, and it was found that the elongation at break and impact strength of the blends were improved significantly with only a small amount of reactive ingredient in the system. It was proposed that because of the low solubility of MA in the PE, some of the MA tends to remain at the interface, thus retaining the dis-

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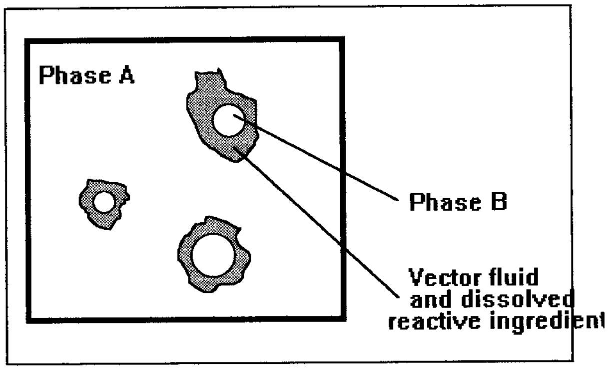


Figure 1 The behavior of the vector fluid in the melt.

solved peroxide. The grafting reaction of MA onto the PE backbone is triggered by the peroxide dissolved in MA. The coupling reactions between the functionalized PE and the terminal amines of PA occur at the interface to form PE–PA copolymers.

A number of vector fluids have been examined by Flaris et al.[2] and Sun et al.[3] in order to establish the criteria for selecting an effective vector fluid for immiscible PE–PS blends. It was found that if quite low-molecular-weight polymer was used as the new liquid in conjunction with peroxides, little PE–PS copolymer was formed in the system, possibly due to the low mobility of the polymeric vector fluid and the potential for it to form an independent dispersed phase. A significant degree of grafting of PS to the PE phase was achieved when the liquid phase was an immiscible organofunctional silane, which has a positive spreading coefficient.[4] This vector fluid is postulated to encapsulate the minor phase PE domains in the blends and consequently retains the peroxide at the interface, as illustrated in Figure 1. The ability of the silane to localize at the interface was confirmed theoretically using the spreading coefficient concept.[3] It was also observed that if the liquid used with the peroxide was styrene monomer, then PE-*g*-PS was also formed.[2] In this case, the liquid was miscible in both polymer phases at the blending temperature and the liquid could polymerize readily. It was not determined whether the grafted styrene groups originated from the monomer added or the original polystyrene. The mechanism of grafting *in-situ* at the interface is complicated.

The grafting reactions that occur at polymer melt interfaces have some relationship to grafting reactions that occur on a large, flat, well-defined polymer surface. Surface grafting is a versatile technique by which the surface properties of a polymer can be tailored through the choice of different monomers. For example, an effective way to prevent oxidation and degradation of polymer films is to graft ultraviolet (UV) stabilizers onto a polymer surface.[5,6] Polyethylene films[7–9] that have been surface-grafted with vinyl acetates, acrylic acid, and acrylamides show improved adhesion to other materials, making these materials suitable for the food packaging industry. The surface changes can be detected by using attenuated total reflectance Fourier transform infrared (ATR FTIR) spectroscopy.[10] The ATR technique has been utilized extensively in the surface analysis of polymeric materials.[11–15]

It is the objective of this study to demonstrate the reactions and behavior of a vector fluid on a polymer surface at elevated temperatures. A laboratory approach was designed to study these reactions under controlled conditions. The model system consisted of PE as the polymer substrate, styrene monomer as the vector fluid liquid, and a peroxide initiator as the reactive ingredient (see Fig. 2). The miscibility of the styrene in the PE substrate was also considered.

EXPERIMENTAL

Materials and Sample Preparation

The PE used was linear low-density polyethylene [Novacor PF-0118-B, Novacor Plastics Division, Calgary, Canada; $\bar{M}_w$ = 109 kg/mol, MFI = 1.0 g/10 min (ASTM, 190°C, 2.16 kg), ρ = 918 kg/m^3]. The styrene monomer (M_W = 104; boiling point = 142°C) used was received from Aldrich USA and inhibited with 15 ppm 4-*tert*-butylcatechol. The three peroxide initiators, 1,1-*di*-(*t*-butylperoxy)-3,3,5-trimethylcyclohexane (L231), *t*-amylperoxy-2-ethylhexanoate (L575), and *t*-amyl perbenzoate (tAPB) were supplied by Elf Atochem, King of Prussia, PA. The half-life times of these initiators at different temperatures are shown in Table I. Chloroform used in the extrac-

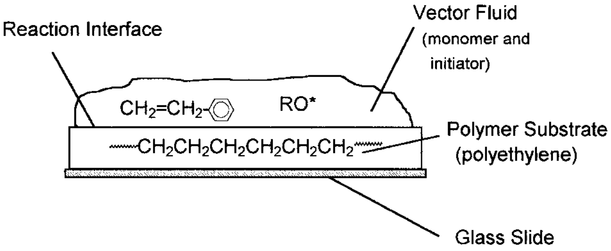


Figure 2 Simulation of the behavior of the vector fluid at the polymer surface.

Table I Calculated Half Lives and Time-Dependent Decomposition of the Initiators

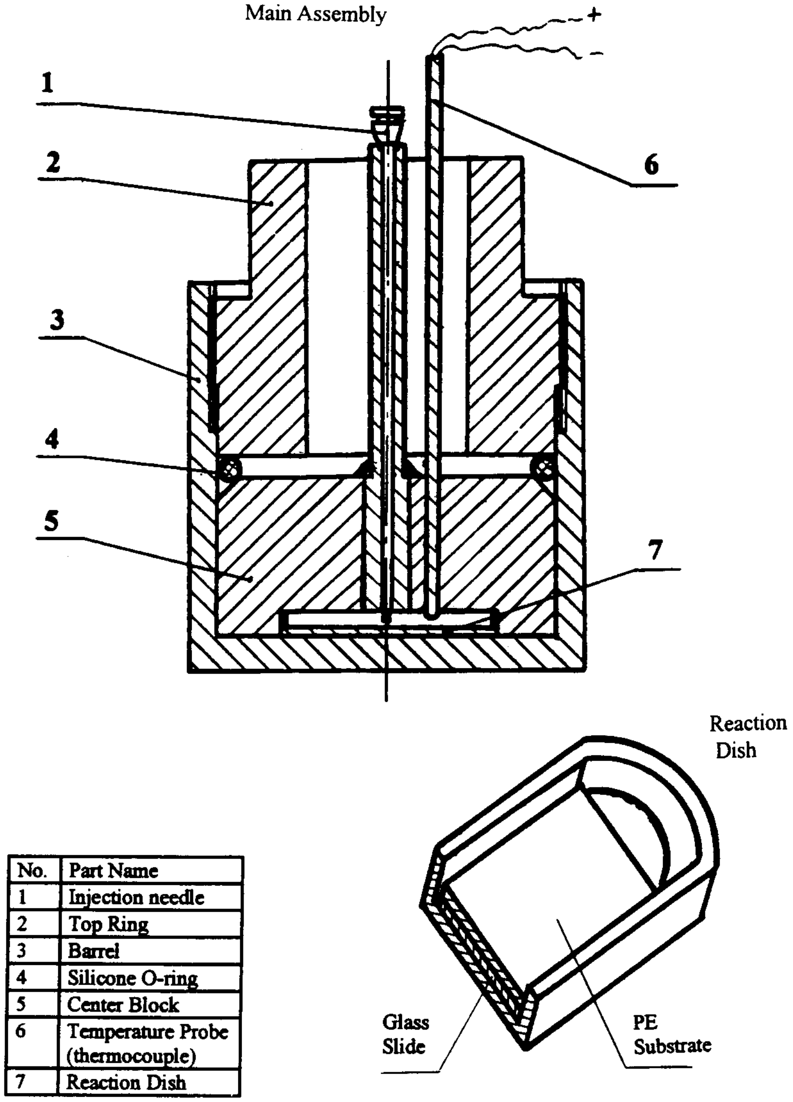
Initiator	*t*APB	Lupersol 231	Lupersol 575
Half-lives at various temperatures (minute)			
150°C	3.6	1.3	0.09
160°C	1.5	0.5	0.04
170°C	0.65	0.2	0.015
Fraction of residual initiator (at 150°C) after a reaction time of			
4 min	0.46	0.12	0[a]
10 min	0.15	0.005	0
16 min	0.05	0.0002	0
Fraction of residual initiator (at 160°C) after a reaction time of			
4 min	0.16	0.004	0
10 min	0.001	9.5×10^{-7}	0
16 min	6.1×10^{-4}	0	0
Fraction of residual initiator (at 170°C) after a reaction time of			
4 min	0.014	9.5×10^{-7}	0
10 min	2.3×10^{-5}	0	0
16 min	3.9×10^{-8}	0	0

[a] Numbers are less than 10^{-10}.

tion was reagent grade solvent from BDH USA. Dimethyl phthalate (DMP) ($M_W = 194$; boiling point = 292°C) used as the insoluble vector fluid component was from Kodak USA.

The PE substrate was made by pressing PE pellets to form a 1 mm thick sheet using a hydraulic compression machine at 170°C. The PE specimens (58 × 38 × 1 mm) were melted onto a clean glass slide (58 × 38 × 0.9 mm thick) at 170°C and then cooled down to room temperature. The reactive ingredients were prepared by mixing styrene monomer and, in some cases, DMP, with different amounts of peroxide initiators. When the DMP was used, the DMP to styrene ratio was always 1 : 1. The surface grafting reactions were carried out in a pressure-resistant, stainless steel reactor that was designed specifically for this study (Fig. 3). After the reactor was heated to the set temperature (150, 160, 170°C), it was maintained at that temperature for 1 h and then quickly disassembled. The PE sample was placed into the reaction dish, and the reactor was reassembled and sealed promptly. After three minutes had passed to allow the PE sample enough time to melt and the inside chamber temperature of the reactor to come back to the starting temperature, 6 mL of the reactive ingredient was injected onto the reaction dish inside to cover the PE sample surface. After a prescribed time (4, 10, or 16 min), the reactor was disassembled again, and the PE sample was taken out and quenched to stop the reaction by immersing it in methanol. There was a temperature drop (about 10°C) after the cold reactive ingredient was first injected onto the reaction dish. However, as the reaction was undergoing, the inside chamber temperature came back to the set point in about 15 s and then remained at that point within ±1–2°C.

The PE sample was then thoroughly extracted with chloroform in a Soxhlet tube for 48 h. Two tests were done to confirm that all of the PS homopolymer had been thoroughly removed by the chloroform from the PE substrate after 48 h of extraction. One test was to monitor the concentration of PS homopolymer extracted in the chloroform solvent with UV spectrometer. It was observed that after 48 h, another 24 h of extraction resulted in the further extraction of 0–0.0002 g of PS. The second test was to determine if there was any free PS homopolymer that had not been extracted and was left inside the PE substrate. Several already extracted PE samples were cut into small pieces (1 mm in diameter) and then further extracted with chloroform for another 48 h. No measurable weight loss of the PE sample was observed in this test. Therefore, both tests indicated that the further extraction was not necessary, and the first 48 h extraction was satisfactory.



No.	Part Name
1	Injection needle
2	Top Ring
3	Barrel
4	Silicone O-ring
5	Center Block
6	Temperature Probe (thermocouple)
7	Reaction Dish

Figure 3 Reactor design.

A two-level, four-factor complete factorial design was chosen as the basis of this research; and the following four factors (experimental conditions) were studied: reaction temperature, reaction time, initiator concentration, and initiator decomposition rate (Table II).

ANALYSIS

The amount of grafting (AG) is defined as the weight percentage of the styrene bound to the original PE substrate. The amount of styrene monomer grafted to the PE substrate is denoted as AG_{st}. Because the mass of each sample could be measured precisely with an analytical balance, the AG_{st} was determined by the following equation:

$$AG_{st} = \frac{WS_{after} - WS_{original}}{WS_{original} - WS_{slide}} \times 100\% \qquad (1)$$

where WS_{after} is the weight of the sample and glass slide after surface grafting and extraction, $WS_{original}$ is the weight of the sample and glass slide before the surface grafting reaction, and WS_{slide} is the weight of the glass slide after extraction.

A BOMEM MB-series FTIR spectrometer and a Spectra Tech Model 301 ATR attachment were used for the ATR FTIR analysis. ATR FTIR spectra were usually measured with a resolution of 2

Table II Conditions for Factorial Design and Observed Results

					PS Surface Concentration		
Run	X1/Temp	X3/Min	X2/$\times 10^3$ mol/100 g	X4/Speed	Gravimetric (wt %)	ATR FTIR (wt %)	PS Number Average M_W ($\times 10^{-4}$ g/mol)
1	−1/150°C	−1/4	−1/0.48	−1/slow	−1.4	6	0.3
2	1/170°C	−1/4	−1/0.48	−1/slow	1.5	6	2.0
3	−1/150°C	1/16	−1/0.48	−1/slow	6.3	4	1.1
4	1/170°C	1/16	−1/0.48	−1/slow	3.6	14	3.5
5	−1/150°C	−1/4	1/2.88	−1/slow	14.4	14	2.2
6	1/170°C	−1/4	1/2.88	−1/slow	12.3	11	1.9
7	−1/150°C	1/16	1/2.88	−1/slow	14.3	22	2.9
8	1/170°C	1/16	1/2.88	−1/slow	9.1	14	3.0
9	−1/150°C	−1/4	−1/0.48	1/fast	−4.3	4	0.5
10	1/170°C	−1/4	−1/0.48	1/fast	−0.3	6	1.0
11	−1/150°C	1/16	−1/0.48	1/fast	−1.4	4	0.4
12	1/170°C	1/16	−1/0.48	1/fast	0.5	6	1.9
13	−1/150°C	−1/4	1/2.88	1/fast	5.6	16	0.3
14	1/170°C	−1/4	1/2.88	1/fast	15.2	12	0.8
15	−1/150°C	1/16	1/2.88	1/fast	5.4	10	0.4
16	1/170°C	1/16	1/2.88	1/fast	7.8	8	2.6

cm^{-1} after 10 scans by using a KRS-5 IRE crystal that has a refractive index of 2.38. The calibration curve was obtained by measuring the peak ratio of 719 cm^{-1} (PE) versus 696 cm^{-1} (PS) in a series of melt blends of PE–PS with known PS content.

Gel permeation chromatography (GPC) (Waters Associates liquid GPC Model 244) was used to determine the molecular weights of extracted PS homopolymer in the chloroform. The instrument ran at room temperature using THF as the solvent. The GPC was calibrated using polystyrene standards, and the flow rate to the machine was set to 1 ml per minute. Samples containing 0.1% PS by weight were prepared using THF. The modified PE substrate was also fractured in liquid nitrogen to form a freshly broken surface of the cross section. The sample was then gold-coated, and scanning electron microscopy (SEM) (Joel 840 at 10 kV) images of both the cross section and the grafted surface were obtained. The surface images of these cross sections were obtained with an optical microscope (Olympus) using a polarized beam as the source light.

RESULTS AND DISCUSSION

The route to a PE–PS graft involves the peroxide decomposing and abstracting hydrogen from the backbone of the PE, yielding macroradicals. The macroradicals then react with the styrene monomer resulting in monomer grafted onto PE. The grafted styrene monomer may continue to react with other free monomer molecules, resulting in propagation from the graft site. The chain propagation reaction leads to an increase in molecular weight of the grafted PS and finally an increase of the amount of the grafting on the PE surface.

The surface ATR FTIR spectrum of a PE substrate having undergone a surface grafting reaction with styrene is shown in Figure 4(b). The spectrum contains the PE peaks at 1472, 1462 (CH_2 and CH_3 bending), 719, and 729 cm^{-1} (CH_2 rocking, shift due to the crystallinity), which are the same as the characteristic peaks of pure PE shown in Figure 4(a). The styrene contributions in Figure 4(b) are 1451, 1492 (C—H bending), 1600 (aromatic C=C stretch), and 696 cm^{-1} (out of phase ring deformation for monosubstituted aromatic ring), which are the same peaks in a pure PS FTIR spectrum [Fig. 4(c)]. The ATR FTIR spectrum indicates that after the surface grafting reaction, a new material, possibly the grafted PS, has been formed at the surface of the PE substrate. It is speculated that since all of the formed PS homopolymer, unreacted styrene monomer, and any undecomposed peroxide initiator were thoroughly extracted with chloroform, the PS signal in the ATR FTIR spectrum [Fig. 4(b)] could be attributed to the styrene that was bound to the

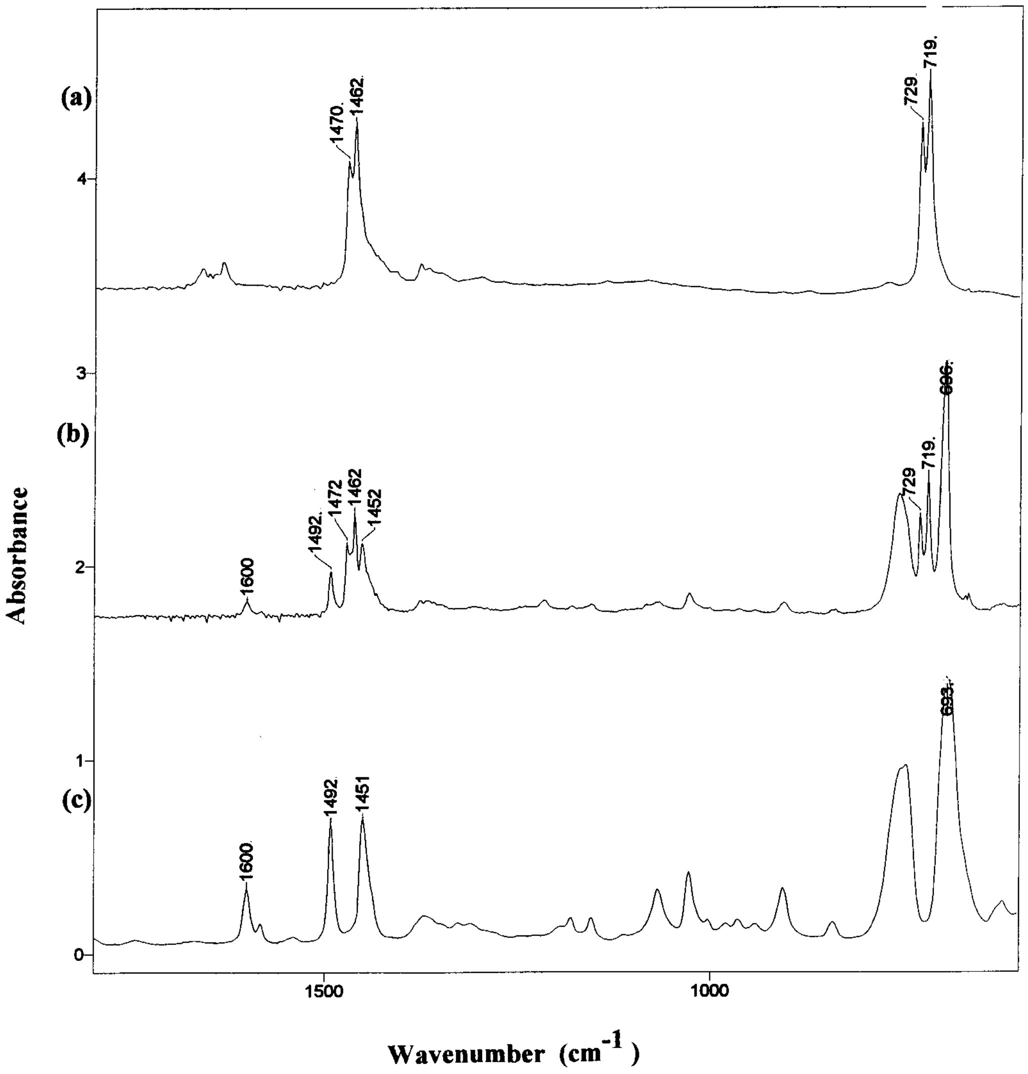


Figure 4 ATR FTIR spectra of surfaces of (a) PE, (b) modified PE substrate, and (c) PS.

PE substrate surface. Hence, the formation of PE-*g*-PS graft is confirmed by comparing the spectra of the reacted PE substrate to the pure PE substrate. Further evidence of grafting was observed gravimetrically. As shown in Table II, up to a 15 wt % increase (runs 5, 7, 14; Table II) was obtained after the surface grafting reaction, supporting the existence of the PE-*g*-PS copolymer.

An analysis of the results in Table II can be seen in Figures 5 and 6 and Table III. Figure 5 shows the main effects on the amount of PS grafted on and through the PE substrate (determined gravimetrically), while Figure 6 shows the main effects on the PS concentration on the PE surface only (ATR FTIR). Of the four factors investigated, the most significant effect (Figs. 5 and 6; Table III) is the reaction time that is supported by both characterization methods. One possible explanation for the time effect may be from the gel effect of the highly viscous system. The grafting reaction occurred mainly beneath the PE surface (as discussed below), and the viscosity of PE that was swollen by styrene monomer was extremely high at the experimental temperature. At high concentrations of polymers (both PE and PS), it became exceedingly difficult for the growing PS chain ends to move through the entangled mass of polymer chains. It was easier for a monomer molecule to diffuse through the reaction mass. Thus, the rate of the termination reaction was limited by the rate at which the PS macroradicals could diffuse together, with termination by combination of growing chains being relatively unlikely. This lowers the effective termination rate con-

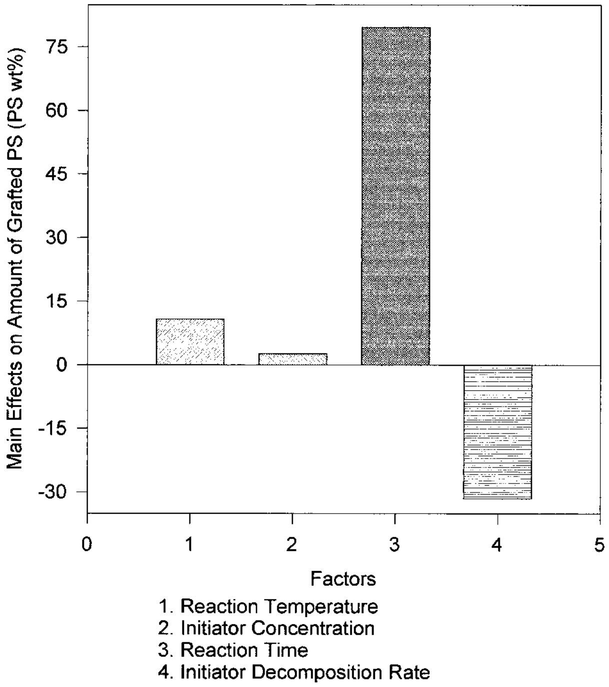


Figure 5 Main effects on the amount of PS grafted in the PE substrate.

stant. Therefore, the longer the time, the more the styrene monomer could diffuse into the PE phase; and the net effect was to increase the molecular weight of the grafted PS chains, leading to an increase in the total mass of styrene grafted.

The initiator decomposition rate was found to be the second most significant, having a negative effect on the amount of grafting. It is obvious that if the initiator decomposition rate is very high, the initiator may not have enough time to migrate out of the styrene monomer to the PE surface before it decomposes into free radicals. These free radicals are more likely consumed in styrene homopolymerization than in forming PE macroradicals, which lead to the grafting of styrene monomer onto PE molecules. The other two main effects, reaction temperature and the concentration of the peroxide initiator, are positive and relatively small. Increasing the temperature increases the mobility of the PE macromolecules and the diffusion rate of the initiator. The more the initiator that diffuses to the PE substrate, the greater probability that grafting may occur. However, increasing temperature may significantly accelerate the initiator decomposition rate. As discussed above, the higher rate of decomposition results in a negative effect on the yield and reduces the amount of grafting. Therefore, raising temperature does increase the amount grafting but not very significantly, suggesting these competing factors may be roughly in balance. Increasing the concentration of the peroxide should increase the concentration of formed free radicals in the system and subsequently increase the total amount of grafting. A small amount of air is in the reaction chamber when the styrene monomer is injected into the system. It can be suggested that peroxy moieties can be formed on the polymer surface in contact with air. A control run, however, with styrene injected only, without peroxide, showed no grafting.

In order to compatibilize two immiscible polymers with graft or block copolymer in the blend, it should be noted that the grafted chain must be long enough to allow for entanglement of the molecules, which is believed to "knit" the separated polymer phases together. Kramer and coworkers[16–18] found that the minimum degree of polymerization of PVP for entanglement, N_e, is 255. Computer simulation[19] of entangled polymer chains using a local knot model estimated that the critical entanglement degree of polymerization for generic polymer molecules is about 230, which translates into a critical entanglement molecular weight, M_c of about 2.4×10^4 g/mol for PS. The goal of studying the effects on the PS homopolymer molecular weight is to determine what experimental factors lead to high-molecular-weight PS grafted on the PE backbone. The molecular

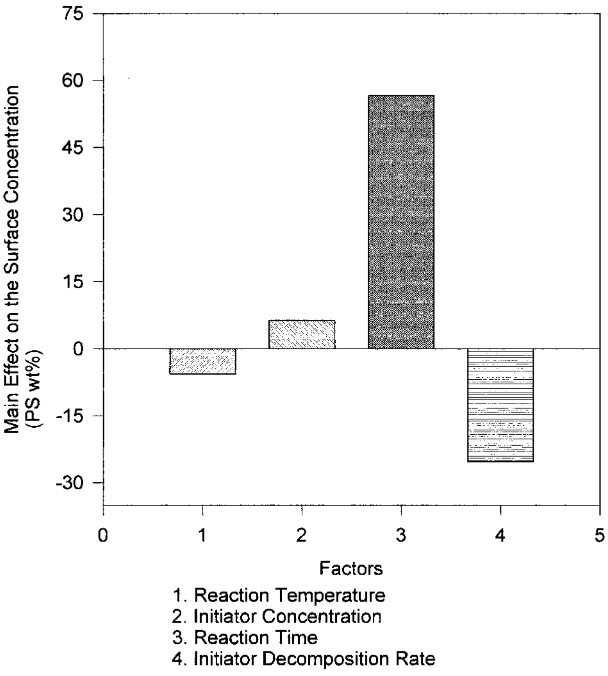


Figure 6 Main effects on the amount of PS grafted on the PE surface.

Table III The Calculated Effects and Their Significance

Factors	Effects on the Total PS Grafted (Gravimetric)	Significance (tESD = ±1.24)	Effects on the Surface Concentration (ATR)	Significance (tESD = ±0.55)
X1 temperature	10.8		−6	
X2 initiator concentrate	2.6		6	
X3 time	79.7		57	
X4 initiator decomposition rate	−31.5		−25	
IE[a] of X1X2	−17.8		7	
IE of X1X3	−1.4		−32	
IE of X1X4	25		−0.3	XXX[b]
IE of X2X3	−24.4		−5	
IE of X2X4	−10.5		−29	
IE of X3X4	−0.6	XXX[b]	−5	
IE of X1X2X3	−2.7		−13	
IE of X1X2X4	−0.7	XXX[b]	−3	
IE of X2X3X4	1.9		−14	
IE of X1X2X3X4	−7.7		18	

[a] IE is the interaction effect.
[b] Nonsignificant effect.

weight of PS homopolymer that was extracted from the PE substrate was used to estimate the molecular weight of grafted PS chain.

It has been observed that the reaction time has the most significant effect on the molecular weight of PS homopolymer (Table IV and Fig. 7). This observation does not conform to one's expectation from the kinetics of free radical polymerization in which the time is not a significant factor. There are several possibilities in this study which may explain the time effect. At a longer reaction time, the generation rate of free radicals has dropped significantly. However, the polymerization of styrene monomer could still proceed and grow to high molecular weight because of the decrease of the free radical concentration and the impeded termination reaction. It should be noted that the molecular weights of PS homopolymer at the PE surface and beneath the immediate surface might be quite different. The PS homopoly-

Table IV Effects on the Molecular Weight of the PS Homopolymer

Factors	Effects on Molecular Weight ($\times 10^{-4}$)	Significance (tESD = ±1.6)
X1 temperature	−2.2	
X2 initiator concentration	−7.6	
X3 time	14.9	
X4 initiator decomposition rate	−8.8	
IE[a] of X1X2	4.8	
IE of X1X3	−1.4	XXX[b]
IE of X1X4	1.5	XXX
IE of X2X3	−3.4	
IE of X2X4	−2.5	
IE of X3X4	−1.1	XXX
IE of X1X2X3	−2.7	
IE of X1X2X4	−0.3	XXX
IE of X2X3X4	1.3	XXX
IE of X1X2X3X4	−0.7	XXX

[a] IE is the interaction effect.
[b] Nonsignificant effect.

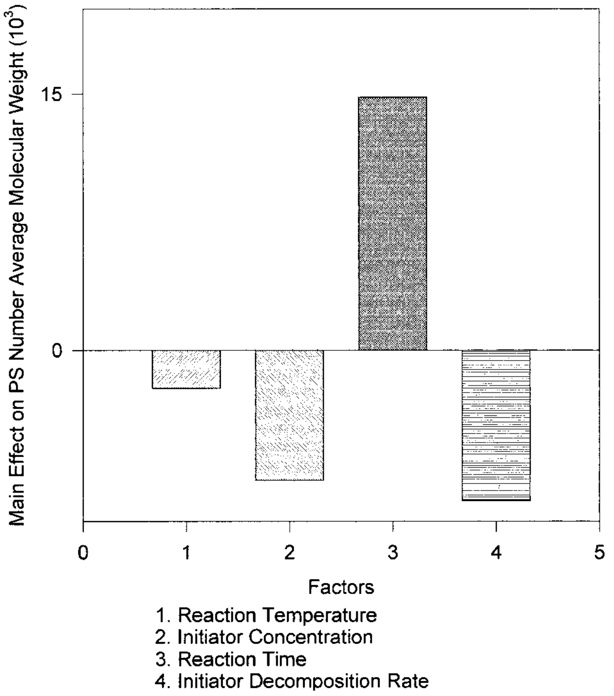


Figure 7 Main effects on the number-average molecular weight of the PS homopolymer.

mer formed inside the PE substrate might have much higher molecular weight than the PS formed in styrene monomer on the surface due to the gel effect, as discussed above.

The effects of initiator decomposition rate and initiator concentration can be explained by studying the kinetic chain length, ν, in a radical chain polymerization, which is defined as the average number of monomer molecules consumed (polymerized) per each free radical, which initiates a polymer chain. This quantity is given by eq. (2), as follows:

$$\nu = \frac{k_p[M]}{2(k_d k_t[I])^{1/2}} \tag{2}$$

where k_p is the rate constant of propagation, $[I]$ is the initiator concentration, k_d is the rate constant of initiator decomposition, k_t is the rate constant of termination, and $[M]$ is the monomer concentration.

$$k_d = \frac{0.639}{t_{1/2}} \tag{3}$$

where $t_{1/2}$ is the half-life time of the initiator.

Equations (2) and (3) show very significant characteristic of radical chain polymerizations. The kinetic chain length is inversely dependent on the radical concentration or the initiator decomposition rate. Any attempt to increase the polymerization by increasing the radical concentration and increasing the initiator decomposition rate leads to a low-molecular-weight polymer. This is supported by the negative effects observed for the initiator concentration and initiator decomposition rate in Table III and Fig. 5.

The slightly negative effect from the reaction temperature showed that an increase of the experimental temperature would not result in an increase of the molecular weight of PS homopolymer formed above the PE surface in the experimental temperature region studied. The polymer chain length should depend on the ratio of $k_p/(k_d k_t)^{1/2}$, as indicated in eq. (2). The temperature effects on the rate constants in this ratio appear to result in little molecular weight change.

A comparison of the data obtained from the two characterization methods (gravimetric and ATR FTIR) is shown in Table V. Using the gravimetric approach, there is a 12.8% weight increase after the grafting reaction compared to the original sample. If the grafted PS was assumed to locate only at the surface, a pure PS layer formed, if possible, at the PE surface would be 114 μm thick. Since the detection depth of ATR FTIR is only 3.9 μm, there should not be any PE signal in the ATR FTIR spectrum. However, both PS and PE signals can be clearly seen in the ATR FTIR spectra, indicating that there is a large amount of grafted PS that is located below the PE surface as well on the surface.

It is evident that the grafting reaction must contain the following two steps: the swelling of PE by styrene monomer, and the grafting of PS onto the PE. There is no pure PS layer at the PE substrate surface, but rather a layer of PE–PS copolymer. Some unreacted styrene and initiator may diffuse down into the PE bulk, only plasticize the PE substrate, and then be extracted with the chloroform due to the fact that no PE crosslinking was observed in this study. Similar results were observed in the studies of Tazuke et al. and Tazuke and Kimura.[20,21] Different solvents were used for the grafting of acrylamide onto the surface of polyethylene and polypropylene films, and extensive grafting of acrylamide occurred when the solvent used could diffuse into the polymer film.

Now it is possible to explain why rising temperature has a positive effect on the total amount of styrene grafted throughout the specimen but a negative effect on the surface concentration of PS,

Table V Comparison of Extent of Grafting by Weight Measurement and by ATR Analysis[a]

Condition	Gravimetric	ATR Detection
Before reaction	2.3145g pure PE	PE signals only
After reaction and extraction	2.6098g PE grafted with PS	Both PS and PE signals
g-PS concentration	12.8% overall	13%
Nature of PE surface after grafting and extraction	If all PS is at the PE surface, a thickness of 114 μm is calculated	<3.9 μm, both PS and PE signals

[a] The data point is the center point.

as shown in Table III. Increasing the temperature increases the mobility of the PE molecules and allows more styrene monomer to permeate below the surface of the substrate.[22,23] This facilitates more grafted PS being formed inside the PE substrate. Low temperature is beneficial to increase the amount of PS at the surface because the lower the temperature, the lower the mobility of the PE, and the harder it is for styrene monomer to diffuse into the substrate. Hence, a higher amount of grafted PS is observed on the surface.

The further evidence that a layer of PE–PS copolymer formed at the PE substrate surface can be clearly seen from the scanning electron microscope (SEM) image of the fracture surface of the cross section of the PE substrate in Figure 8(a). The SEM picture shows that the cross section of the PE substrate has two distinct layers. The darker and thinner layer, which is about 200 μm thick, is the PE-*g*-PS copolymer layer. The thicker layer is the PE layer, which is about 1000 μm thick, containing rapidly diminishing amounts of grafted PS. It is observed that there is no hole or porous structure at the fractured surface. The image suggests that little PS homopolymer, which was formed during the grafting, coalesced inside the PE substrate, to be subsequently extracted with chloroform leaving a hole behind. This can be proven further by observing the optical microscope image [Fig. 8(b)], which was taken using a beam of polarized light. The different layers of polymers reflect the polarized light differently due to their different refractive indices so that two separate layers can be observed in the picture. The PE-*g*-PS layer is bright and thin, and the PE portion is dark.

The image of the reaction surface is shown in Figure 8(c). The surface morphology shows that a significant number of round holes reside at the surface. An explanation may be that both the grafted PS and the PS homopolymer were formed during the surface grafting reaction, but the PS homopolymer, which preferentially located at the surface, was extracted with chloroform; and round holes were left at the PE surface.

Effect of a Nonsolvent Vector Fluid

Dimethyl phthalate (DMP), which was proven to be nonreactive to the PE by ATR FTIR, was chosen to be the solvent to reduce the diffusion of the styrene monomer. It was observed in Table VI that the addition of DMP to the grafting system significantly reduced the total amount of grafted styrene in the PE substrate, but the surface concentration of grafted PS was maintained as detected with ATR FTIR. A possible reason for the consistently low levels of PE-*g*-PS graft to PE in the presence of DMP may be that the diffusion of styrene monomer into the PE substrate was greatly reduced by the DMP, which has much lower solubility and diffusion coefficient in PE than does the styrene, as shown in Table VII. As discussed above, the styrene monomer that was dissolved in the DMP was hindered from penetrating the PE surface because of its preferred solubility in DMP. Thus, the grafting reaction of styrene onto PE occurred only at the interface between the PE and the DMP solution. The surface concentrations in the presence of DMP were about 80% of those without the DMP as detected with ATR FTIR. The diffusion of styrene monomer into the PE substrate was greatly reduced due to the reduced solubility and diffusion coefficient of DMP–styrene solution (Table VII). Most of the styrene monomer underwent homopolymerization to form PS homopolymer within the DMP, while some of the styrene molecules and free radical initiators reached the PE surface, resulting in the grafting of styrene onto PE surface. However, there was little or no styrene monomer and initiator that could diffuse below the PE surface. The thickness of the formed PE-*g*-PS layer on the PE substrate was too thin to be observed by micros-

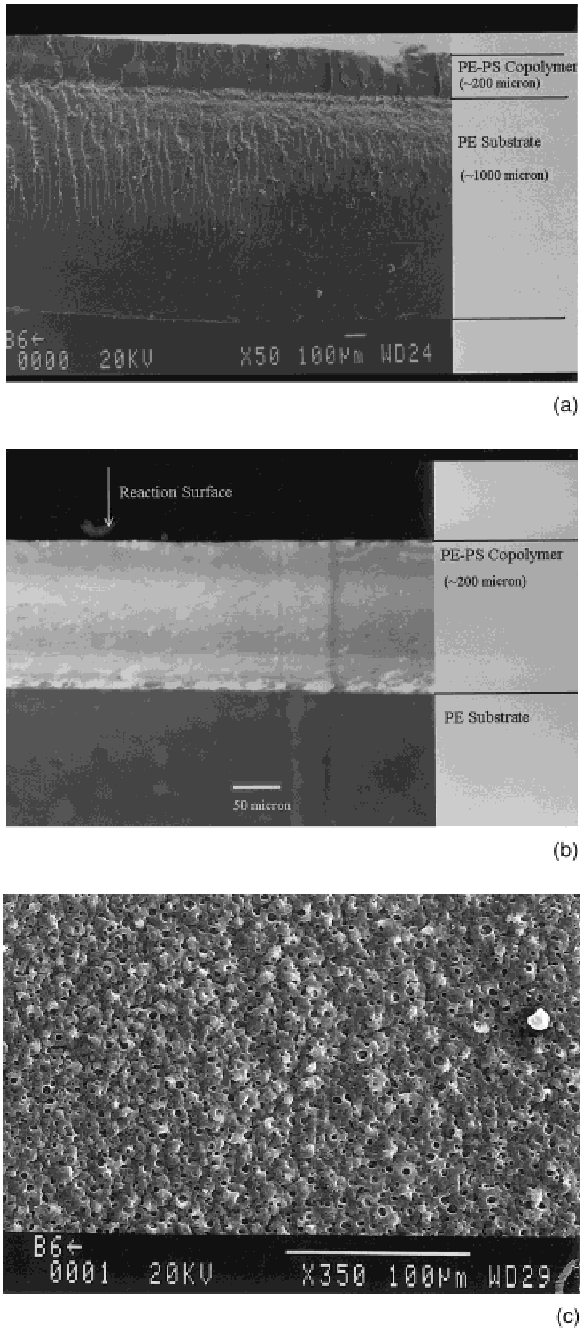


Figure 8 (a) SEM image of a cross section of the PE substrate; (b) optical microscopy image of the cross section of the PE substrate; and (c) SEM image of the PE substrate surface after grafting and extraction.

copy. Therefore, the total amount of styrene grafted was reduced considerably; but the surface reaction was not significantly affected, as detected with ATR FTIR. A similar observation was obtained in the studies of Tazuke et al. and Tazuke and Kimura.[20,21] When a nonsolvent of polyethylene and polypropylene was chosen for the grafting for the acrylamide, the grafting reaction was retained only at the surface of polymer film with a small amount of grafting. However, if a good solvent for the polymer was used, the homogeneous grafting occurred below the polymer surface. Hence, to confine grafting to the polymer surface, the solvent must not swell the base polymer excessively.

Discussion of Vector Fluid Behavior in Melt Blend Systems

The effectiveness of a vector fluid to compatibilize an immiscible polymer blend can be attributed to (1) its ability to reach the interface, (2) the amount of the copolymer that forms and remains at the interface, and (3) the conformation the copolymer may have at the interface. The location of the vector fluid, which contains the reactive ingredient in a polymer melt, should depend on many physical parameters such as the solubility of the reactive ingredient in the polymer melt and the vector fluid, the solubility of the vector fluid in the polymer melt, the surface tension between the vector fluid and the polymers, and the relative viscosity of the vector fluid and polymers.

Vector fluids can be divided into the following two classes: soluble and insoluble in the blend components. If a vector fluid is soluble in the blend components, such as styrene, which is soluble in both the PS and PE phases, the vector fluid, carrying the free radical initiator, may not reside solely at the interface of the polymer blend. Rather, it can diffuse into the blend components with the reactive ingredient initiating a crosslinking reaction inside the polymer phases. Therefore, a monomer must be chosen as the vector fluid to reduce the undesirable crosslinking. The monomeric vector fluid still has the ability to diffuse into its soluble polymer phases but forms copolymer and homopolymer inside the soluble phase(s) as described in Figure 9. As in the PE–PS–styrene–initiator case, the styrene swells the PE melt phase at high temperature; and at the same time, the grafting of styrene onto PE and the homopolymerization reaction of styrene are initiated by the thermal decomposition of the free radical initiator dissolved in the styrene liquid phase. Some of the styrene monomer may also diffuse into the PS phase to form PS homopolymer because PS is also soluble in the styrene. During *in-situ* compatibilization, more and more new interfaces can be generated with the mixing equipment. The formation of PS homopolymer at the interface may not only interpenetrate the PS

Table VI The Role of DMP in the Surface and Substrate Grafting

Experimental Conditions	DMP, Peroxide, and Styrene		Styrene and Peroxide Only	
	Gravimetric (% grafted)	ATR FTIR (% grafted)	Gravimetric (% grafted)	ATR FTIR (% grafted)
150°C, 4 min, 0.48×10^{-3} mol/100 g St, tAPB	0	4.7	−1.4	6.0
150°C, 16 min, 2.88×10^{-3} mol/100 g St, tAPB	1.7	12.6	14.3	22.4
170°C, 4 min, 0.48×10^{-3} mol/100 g St, L575	0.1	5.7	−0.3	6.1
170°C, 16 min, 2.88×10^{-3} mol/100 g St, L575	0.6	8.5	7.8	7.7
160°C, 10 min, 1.68×10^{-3} mol/100 g St, L231	1.3	9.1	12.8	13.3

phase but also intermingle with the PE-*g*-PS at the interface. As the styrene portion of the PE-*g*-PS copolymer coexists readily in the PS, intermingling between the two phases can occur.

On the other hand, if a vector fluid is soluble in neither of the blend components, a different situation exists. If the surface tension of the vector fluid is carefully selected, it can encapsulate the minor polymer phase. The criteria for this is a position spreading coefficient.[3,4] The vector fluid then tends to reside at the polymer interface and a suitable reactive ingredient must be selected to form copolymers *in-situ* without crosslinking the blend components. The reactive ingredient may be simply a peroxide initiator, which may result in the formation of graft or block copolymer at the interface.[2,3,26,27] It should be noted that without the vector fluid, the PE polymer tends to be crosslinked in the presence of the peroxide initiator because the reagents may easily penetrate blend phase(s) rather than being retained at the interface. An appropriate vector fluid must be used so that the coupling reaction is restricted to the interface of the blend components as illustrated in Figure 10. The vector fluid must dissolve the reactive ingredient much more easily than the polymer melt so that little reactive ingredient can diffuse into the polymer phase(s), and it is therefore retained at the interface. If the reactive ingredient in the vector fluid consists of a monomer and an initiator, both the grafting and homopolymerization reaction may occur; but only the surface of the minor phase polymer particles, which is surrounded with the vector fluid, can be grafted with the monomer. In this case, the graft copolymer formed should locate right at the interface and possibly entangle with the other blend component at the polymer–polymer interface. If the ingredient is the initiator only, an interfacial grafting reaction between blend components and crosslinking of each phase may both occur.

CONCLUSIONS

Styrene can be grafted onto a polyethylene surface with peroxide, a free radical initiator, at high temperature, without any crosslinking of polyeth-

Table VII Parameters of Different Vector Fluid Components[a]

Parameter	DMP	Styrene	DMP to Styrene (1 : 1)
δ Solubility parameter $(\mathrm{cal/cm^3})^{1/2}$($\delta$ of PE = 7.9)	10.7	9.3	9.6
Density ($\mathrm{g/cm^3}$)	1.19	0.89	
	10.9	NA	
Permeability through PE ($\mathrm{g \times mm/m^2 \times d}$) @73.9°C	Nonsolvent of PE	Solvent of PE ≫6000[c]	NA
Diffusion coefficient through PE ($\mathrm{cm^2/s}$) @150°C[b]	1.7×10^{-6}	4.4×10^{-5}	1.4×10^{-6}
Boiling point (°C)	292	142	

[a] See Duda et al.,[22] Seong-UK Hong,[23] and Brandup and Immergut.[24]
[b] See Zielinski and Duda[25] and Teh and Rudin.[26]
[c] Taken from data for ethyl benzene.

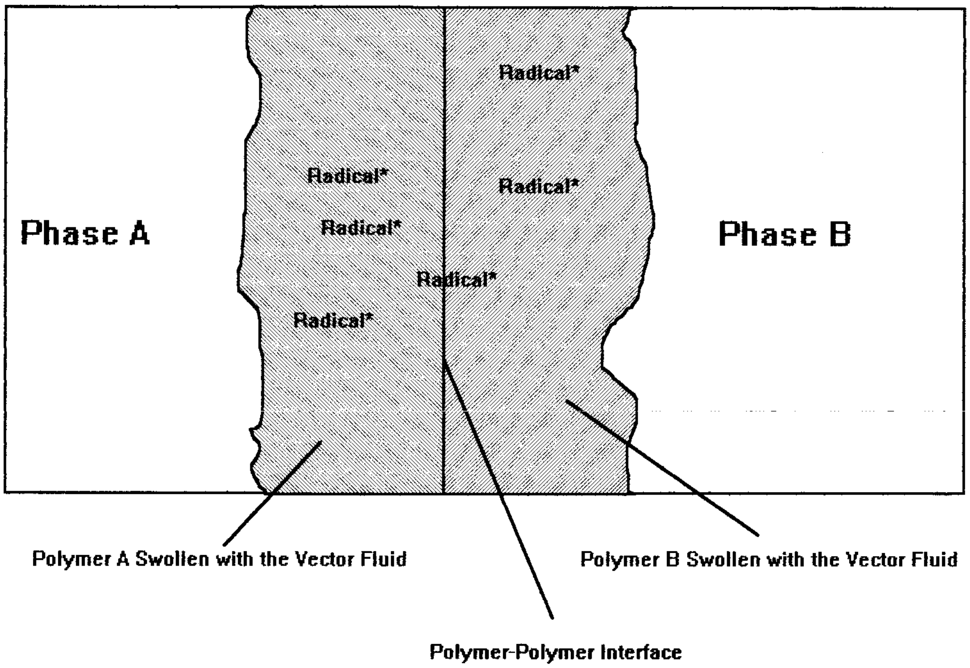


Figure 9 Behavior of a vector fluid that is soluble in the polymer phases.

ylene. The grafting reaction of styrene onto the PE surface under simulated melt blending conditions consists of the following two steps: the swelling of PE by the styrene monomer, and the grafting of styrene onto the PE backbone. The resulting PE-*g*-PS copolymer forms a relatively thick copolymer layer within the PE substrate rather than a thin surface layer on it. The amount of styrene grafted can be controlled by carefully manipulating various reaction factors such as reaction time, initiator concentration, initiator decomposition rate, and reaction temperature. The factorial ex-

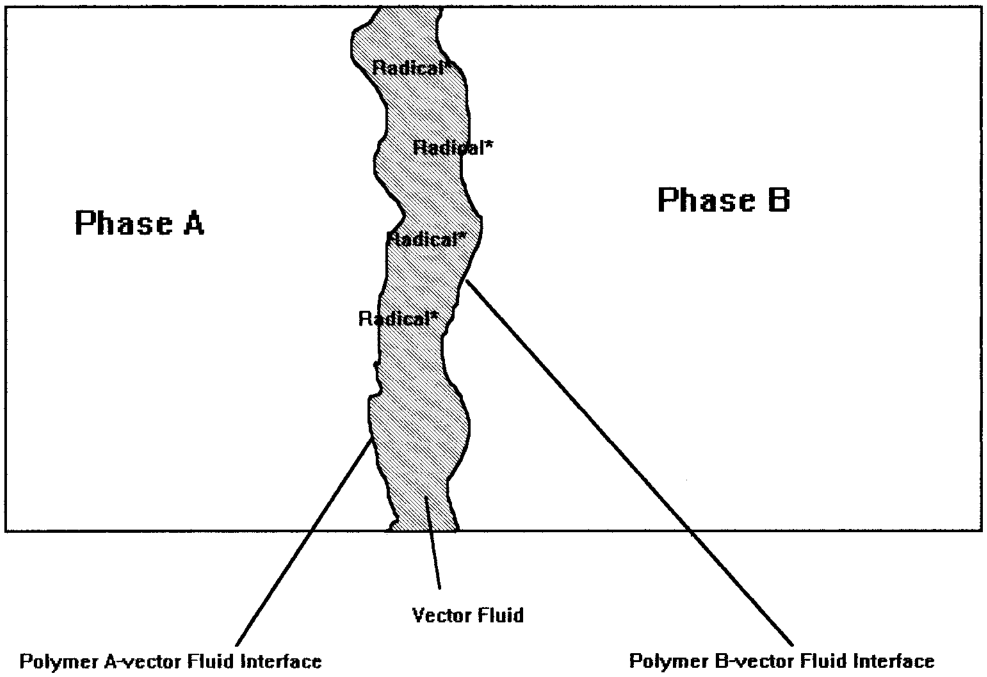


Figure 10 Behavior of a vector fluid that is not soluble in the polymer phases.

perimental design provides important information, such as the main effects and multilevel interaction effects of the experimental factors, and permits one to optimize the grafting reaction and increase the styrene grafting levels effectively. It was found that increasing the reaction time provided the most significant positive effect on the amount of grafting while increasing the initiator decomposition rate had the most significant negative effect.

The addition of a non-solvent to the reaction environment, namely dimethyl phthalate, permits one to reduce the diffusion of the styrene into the PE substrate and localize the reactions at the surface of the PE substrate.

This model system can be used to simulate the interfacial reactions in the *in-situ* compatibilization process. The ATR FTIR technique has proven to be a powerful technique that can be used to detect the changes at a polymer surface. The results can be used to explain the behavior of the different vector fluids in the compatibilization of polymer blends. Furthermore, the experimental technique provides a useful method to study reaction on polymer interfaces at elevated temperatures.

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REFERENCES

1. M. Seadan and M. Lambla, *Polym. Eng. Sci.,* **32,** 1677 (1992).
2. V. Flaris, W. E. Baker, and M. Lambla, *Polym. Networks Blends,* **6,** 29 (1996).
3. Y.-J. Sun, V. Flaris, and W. E. Baker, *Can. J. Chem. Eng.* submitted.
4. S. Y. Hobbs, M. E. J. Dekkers, and V. H. Watkins, *Polymer,* **29,** 1598 (1988).
5. K. Allmer, A. Hult, and B. Ranby, *J. Polym. Sci., Polym. Chem. Ed.,* **27,** 3405 (1989).
6. K. Allmer, A. Hult, and B. Ranby, *J. Polym. Sci., Polym. Chem. Ed.,* **27,** 3419 (1989).
7. B. Boutevin and J. J. Robin, *Eur. Polym. J.,* **26,** 559 (1990).
8. S. Yamakawa, *J. Appl. Polym. Sci.,* **20,** 3057 (1976).
9. S. Yamakawa, F. Yamamoto, and Y. Kato, *Macromolecules,* **9,** 754 (1976).
10. F. M. Mirabella Jr. and N. J. Harrick, *Internal Reflection Spectroscopy: Review and Supplement,* Harrick Scientific Corp., New York, 1985.
11. D. J. Carlsson and D. M. Wiles, *Can. J. Chem.,* **48,** 2397 (1970).
12. S. S. Blackwell, P. J. Degen, and F. D. Osterholtz, *Appl. Spectrosc.,* **32,** 480 (1978).
13. R. Iwamoto and K. Ohta, *Appl. Spectrosc.,* **38,** 359 (1984).
14. F. M. Mirabella Jr., *J. Polym. Sci., Polym. Phys. Ed.,* **22,** 1283 (1984).
15. F. M. Mirabella Jr., *J. Polym. Sci., Polym. Phys. Ed.,* **22,** 1293 (1984).
16. J. Washiyama, E. J. Kramer, C. Creton, and C. Y. Hui, *Macromolecules,* **27,** 2019 (1994).
17. J. Washiyama, E. J. Kramer, and C. Y. Hui, *Macromolecules,* **26,** 2928 (1993).
18. C. Creton, E. J. Kramer, C. Y. Hui, and H. R. Brown, *Macromolecules,* **25,** 3075 (1992).
19. K. Iwata, *J. Phys. Chem.,* **96,** 4111 (1992).
20. S. Tazuke, T. Matoba, H. Kimura, and T. Okada, ACS Symposium Series 121, American Chemical Society, Washington, DC, 1980, p. 217.
21. S. Tazuke and H. Kimura, *J. Polym. Sci., Polym. Lett.,* **16,** 497 (1978).
22. J. L. Duda, J. Vrentas, S. Ju, and H. T. Liu, *AIChE J.,* **28,** 279 (1982).
23. Seong-Uk Hong, *Ind. Eng. Chem. Res.,* **34,** 2536 (1995).
24. J. Brandrup and E. Immergut, *Polymer Handbook,* 3rd ed, John Wiley & Sons, New York, 1989.
25. J. M. Zielinski and J. L. Duda, *AIChE J.,* **38,** 405 (1992).
26. J. Teh and A. Rudin, *Polym. Eng. Sci.,* **31,** 1033 (1991).
27. J. Teh and A. Rudin, *Polym. Eng. Sci.,* **32,** 1678 (1992).