

***In Situ* Reactive Compatibilization in Polymer Blends: Effects of Functional Group Concentrations**

M. SALEEM and W. E. BAKER, *Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6*

Synopsis

Polystyrene (PS) and polyethylene (PE), along with their reactive counterparts, i.e., polystyrene having oxazoline reactive groups (OPS) and polyethylene with carboxylic acid groups (CPE), were melt blended in a Rheomix mixer. These blends were prepared by mixing these polymers in various proportions under a variety of conditions. In an alternate procedure the OPS, CPE graft polymer (OPS-*g*-CPE) was prepared by melt blending these two polymers beforehand, and subsequently this grafted polymer was used as a compatibilizer for PS-PE blends. The effects of the addition of OPS and CPE, on the one hand, and OPS-*g*-CPE, on the other hand, on the compatibility of PS-PE blends were investigated. The morphology of these blends was examined with a scanning electron microscope (SEM) and related to their tensile properties. The PS-PE blends are found to have the typical coarse morphology of incompatible blends and poor tensile properties while their reactive counterparts, OPS-CPE blends, have fine grain microstructure and show improved tensile strength throughout the range and improved elongation in the PE-rich blends. Relatively low concentrations of the reactive pair, oxazoline and carboxylic acid, are shown to be necessary to produce improved compatibility. The preblended graft copolymer OPS-*g*-CPE imparts compatibility to PS-PE blends also but not as effectively. This suggests that the addition of OPS and CPE during melt mixing of PS and PE forms OPS-*g*-CPE polymer at the interface and that these ingredients act as "*in situ* reactive compatibilizers" which improve physical properties.

INTRODUCTION

Two main methods of preparing functionally compatible blends of incompatible pairs of polymers have been developed. The first, and relatively older method, is based on the use of graft or block copolymers having identical or similar block or graft segments as the blend components. These copolymers are termed emulsifiers or compatibilizers, and influence the compatibility by acting as "interfacial agents."¹ The effects of PS-*g*-PE graft and block copolymer emulsifier on the compatibility and mechanical properties of PS-PE blends have been investigated in considerable detail,²⁻¹¹ and improvements in properties are reported in both these cases. The particular role of diblock copolymers such as poly(styrene-*b*-hydrogenated butadiene) and other polymers was discussed in length more recently,¹² and it was pointed out that the structure and length of block segments play a key role in optimizing the properties of the resulting blends. Although the above-mentioned method is effective, it requires well-controlled polymerization procedures to prepare block and graft copolymers of specific structures for particular applications.

In recent years compatible polymer blends have been produced by a second technique involving *in situ* reactive processes in the melt. The method is

based on the blending together of chemically interactive polymers. Functionalized polymer pairs having coreactive chemical groups including polyamide/rubber,^{13,14} polyolefin/rubber,¹⁵ polystyrene/polyethylene,^{16,17} and polystyrene/rubber¹⁸ have been the subject of investigations. In all these cases changes in morphology as well as improvements in mechanical properties were achieved and are attributed to the chemical reaction between the reactive polymers. The resulting graft, block, or crosslinked polymer imparts compatibility on the blend, probably because this newly created material forms primarily at the interface between the otherwise incompatible polymers. Hence it behaves somewhat like an "*in situ* emulsifier or compatibilizer." In previous work,^{16,17} it was found that, during the melt mixing of OPS and CPE, chemical reaction between the oxazoline and carboxylic acid results in a graft polymer having amido-ester linkages. The maximum reaction took place at an OPS-CPE weight ratio of 3 : 2, and this reacted blend was thought to be a potential compatibilizer. In this work both this prereacted blend and its constituents were evaluated as compatibilizers for PS-PE incompatible blends. In addition to using this premade graft material as a compatibilizer a number of additional blends were made in which the reactive OPS and CPE were added simultaneously to their nonreactive analogues, PS and PE, in blends, in order to develop the preferred process sequences as well as the optimum concentrations of OPS and CPE. Compatibility was evaluated by investigating the morphology and tensile properties of these blends. Since the reaction between these two reactive polymers was found to be rather slow, zinc chloride was tested as a catalyst for this reaction and its effect on the overall properties of the blends was examined.

EXPERIMENTAL

Materials

Polystyrene (PS) (Styron 685), low density polyethylene (PE) (polyethylene 746), reactive polystyrene (OPS) (XUS 140056.01), and reactive polyethylene (CPE) (Primacor 1430) were obtained from the Dow Chemical Co. Pellets of these polymers were used without any further purification or treatment. CPE is reported to contain 9 wt% acrylic acid with the corresponding carboxylic acid functionality and OPS 1 wt% vinyl oxazoline with the corresponding oxazoline functionality. Irganox 1010, a high molecular weight phenol antioxidant (AO), was used in the blend to prevent any possible degradation.

Procedures

All the blends were melt-blended on a Haake-Buchler Rheomix mixer Model 600, with roller blades. The mixing variables were controlled through the System 40 microcomputer. Prior to the preparation of these blends, torque measurements were made on each individual polymer in the mixer to assess their relative viscosity characteristics at the processing conditions used in this study with the technique developed by Favis and Chalifoux.¹⁹ The polymers

were selected to have torque viscosity ratios close to unity as follows:

$$\frac{\text{CPE}}{\text{OPS}} = 1.8, \quad \frac{\text{PE}}{\text{PS}} = 0.69, \quad \frac{\text{CPE}}{\text{PE}} = 1.15, \quad \frac{\text{OPS}}{\text{PS}} = 0.67$$

The blends were prepared by dry-blending pellets of the required polymers in the desired proportions and then charging 40 g into the mixer. The mixer was set at the required time and mixing speed before hand. All blends were prepared at 235°C. Once the polymer was melted, 0.1% antioxidant was added to the melt. After the completion of the prescribed melt fluxing, the blend was immediately removed from the mixer and cut into small pieces and used for characterization studies.

Various series of blends (A–J, X, Y) with different composition numbers (1–9), along with the conditions of their preparation are listed in Tables I and II. G40, an OPS-CPE(60/40) melt blend, was prepared under conditions described for series B and was subsequently used as a compatibilizer for the series of blends F, G, and H. Although the ratio of the G40 to the polymers varied in each sample, the overall ratio of PS to PE was retained at 30/70, 70/30, and 80/20 for series F, G, and H, respectively, in Table II. In order to reduce the mixing time and increase reaction rate, the blends in series J were prepared by adding 0.1% zinc chloride after 3 min of initial mixing at a roller speed of 200 rpm.

The morphology of the blends was examined on a scanning electron microscope, JEOL Model JSM 840. The melt blended samples were fractured under liquid nitrogen to obtain an exposed surface of about 10 mm². The samples were gold coated prior to the examination. Depending on the nature of the blends, representative micrographs were taken in the magnification range of 2,000–50,000.

Tensile samples of 20 × 2.0 × 0.02 cm dimensions were cut from hot-pressed sheets of uniform thickness. The measurements were made on an Instron Model 122, at an extension rate of 5 cm/min. At least five specimens of each

TABLE I
Conditions for the Preparation of OPS, PS, CPE, and PE Blends

Compositions (wt%)		PS-PE	OPS-CPE	OPS-CPE-PE	OPS-PS-CPE	OPS-PS-CPE-PE
No. in series	Series	A	B	C	D	E
	1		90/10	90/10	90/5/5	45/45/10
2		80/20	80/20			
3		70/30	70/30	70/15/15	35/35/30	35/35/15/15
4		60/40	60/40 ^a			
5		50/50	50/50	50/25/25	25/25/50	25/25/25/25
6		40/60	40/60			
7		30/70	30/70	30/35/35	15/15/70	15/15/35/35
8		20/80	20/80			
9		10/90	10/90	10/45/45	5/5/90	5/5/45/45

^aSample B4 is abbreviated as G40 and was used as a compatibilizer for the series of blends F, G, and H. All blends prepared at 100 rpm and 235°C for 30 min.

TABLE II
Composition of Blends of PS, PE, G40, OPS, and CPE

Mixing time (min)	← 10 →		200	ZnCl ₂		
	Mixing speed (rpm)	← 100 →				
		← None →				
	Polystyrene/polyethylene ratio (wt)					
	70/30					
	80/20					
Constituents	30/70		70/30		80/20	
	PS-PE-G40	PS-PE-G40	OPS-PS-CPE-PE	OPS-PS-CPE-PE	PS-PE-G40	PS-OPS-PE-CPE
Series No. in series	F	G	X	Y	H	J
1	0/70/30	65.5/27/7.5	—	—	77/18/5	78.5/1.5/19/1
2	24/66/10	56.5/21/22.5	—	—	74/16/10	77/3/18/2
3	12/58/30	—	—	—	71/14/15	74/6/16/4
4	—	47.5/15/37.5	22.5/47.5/15/15	—	68/12/20	71/9/14/6
5	0/50/50	38.5/9/52.5	—	—	—	68/12/12/8
6	—	—	—	15/65/10/10	65/10/25	65/15/10/10
7	—	—	—	—	59/6/35	57.5/22.5/5/15

TABLE III
Tensile Strength (MPa) and Elongation at Break (%) within parentheses, for Various OPS, PS, CPE, and PE Blends

Series ^a No. in series ^a	A	B	C	D	E	F	G	X	Y	H	J
1	24.8 (1.6)	34.3 (2.0)	31.5 (1.8)	34.5 (2.0)	36.5 (2.4)	8.7 (4.4)	11.7 (1.2)			23.1 (1.8)	21.9 (1.6)
2	19.1 (1.5)	26.7 (1.7)				6.1 (2.4)	11.4 (1.3)			26.3 (2.0)	21.3 (1.6)
3	15.6 (1.5)	26.5 (2.5)	18.0 (1.6)	32.5 (3.0)	16.9 (1.5)	4.9 (1.7)				24.7 (1.9)	23.6 (1.9)
4							21.6 (2.0)	24.6 (2.0)		29.0 (2.1)	23.5 (1.8)
5	7.4 (1.2)	14.7 (10.)	16.7 (3.0)	15.1 (6.0)	16.5 (3.1)	10.8 (3.1)	24.8 (2.0)				26.8 (2.0)
6	9.9 (3.2)	15.6 (48.5)									31.3 (2.2)
7	8.9 (5.1)	16.7 (97)	12.5 (41)	18.0 (100)	12.8 (46)				36.4 (2.5)	30.6 (2.1)	31.4 (2.2)
8	8.9 (16)	16.9 (162)								34.3 (2.4)	23.6 (2.5)
9	3.3 (91)	20.7 (427)	12.6 (184)	15.3 (194)	12.0 (160)						

^aSeries and number in series are the same as given in Tables I and II.

sample were used and average values of tensile strength at break and ultimate elongation were obtained. The tensile results were not intended as a replacement for instrumented impact results but only as a first indication of a change in the mechanical response of these systems. Tensile strength and elongation at break (in parenthesis) values for all the blends are given in Table III.

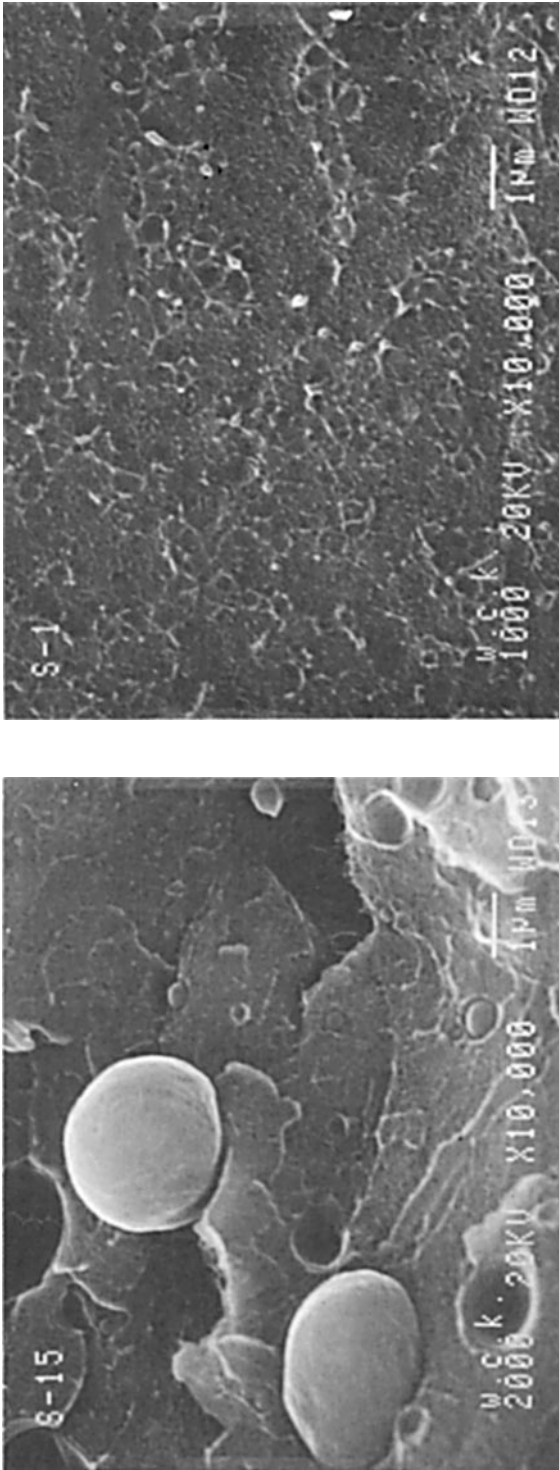
RESULTS AND DISCUSSION

In our previous studies,^{16,17} it was found that, by mixing reactive polystyrene having oxazoline groups (OPS) and a reactive polyethylene having carboxylic acid groups (CPE), reaction occurred between the OPS and the CPE resulting in a reactively coupled blend. The evidence for the reaction during the melt mixing process was obtained from torque increases. Further evidence for chemical reaction was obtained when the subsequent blends were characterized by Fourier transform infrared spectroscopy and differential scanning calorimetry and further substantiated using scanning electron microscopy. It was also found that OPS-CPE reactive blends had better elongation than the unreactive PS-PE blends. In this work attempts were made to (1) use OPS and CPE in smaller quantities to make PE and PS compatible in an *in situ* compatibilization process (series C, D, E, J, X, Y), (2) use a prereacted optimum combination of OPS and CPE as an "add-in compatibilizer" (series F, G, H), and (3) determine whether the reactive coupling process can be accelerated using $ZnCl_2$ and modified processing conditions (series J).

In Situ Reactive Compatibilization

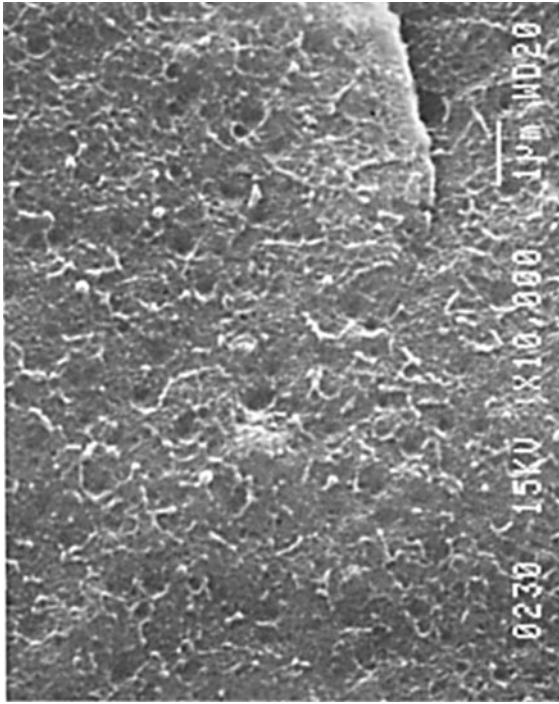
As shown in Table I, series A and B refer to unreactive PS-PE and reactive OPS-CPE blends, respectively. PS-PE blends, as expected, are incompatible in the whole composition range, whereas OPS-CPE blends have fine morphology as can be seen for blends A1 and B1 in Figure 1. In Figure 2 ultimate tensile properties of these two sets of blends are compared; an overall trend shows that reactive blends have higher tensile strengths, though comparable elongations when compared to the unreactive blends. There are differences in the tensile properties of the starting polymers, but the deviation from a linear prediction of tensile properties is less for the reactive blends than for the unreactive blends. The much finer morphology of blend B1 compared to A1 in Figure 1 did not, however, result in dramatic tensile improvement. In this region the failure mechanism would be primarily crazing [6]. The use of these *in-situ* compatibilizers has, as seen in Fig. 1 modified the domain size from 2-10 μ range down to approximately 0.1 to 0.5 μ . Apparently the domain size has been reduced below the optimum suggested by Buchnall²⁰ and the failure mechanism has gone from insufficient crazes (large domains) to too many small interacting crazes which results in major crack growth and continuing low ductility.

An attempt to obtain more suitable domain sizes was made by reducing the concentration of reactive oxazoline and carboxylic acid groups as seen in series C, D, and E. Blends in series C have the CPE component diluted 50% with PE and blends in series D have the OPS component diluted 50% with PS. Blends in series E have each reactive component diluted 50% with its nonreactive analogue. The morphological features of PS rich blends within series A, B, C,

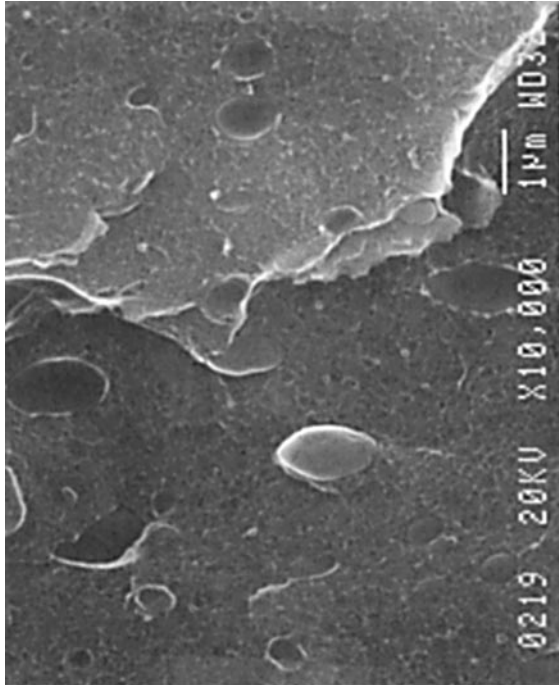


(A) SEM micrograph of polystyrene-polyethylene (90/10) blends showing the effect of 50% replacement of reactive polymer with unreactive polymer: (A) A1 PS-PE (90/10); (B) B1 OPS-CPE (90/5/5); (C) C1 OPS-PS-CPE (45/45/10).

(B)



(D)



(C)

Fig. 1. (Continued from the previous page.)

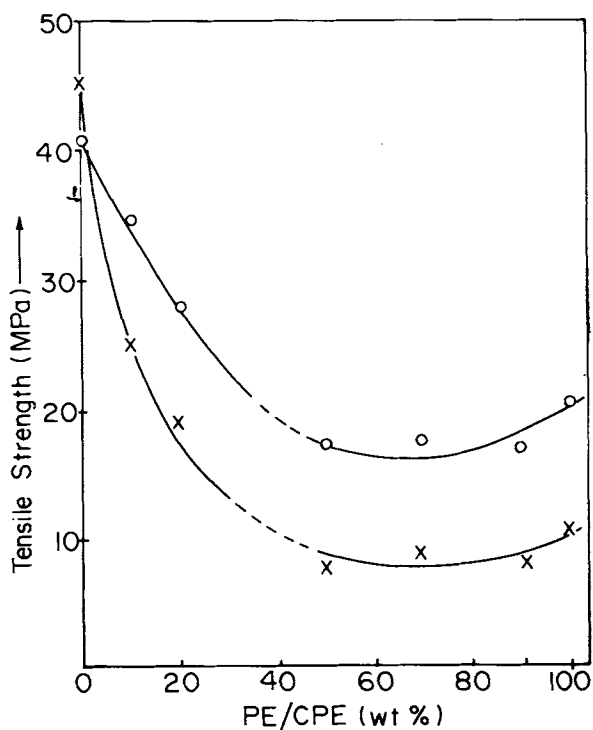


Fig. 2. Tensile strength vs. composition of OPS-CPE and PS-PE blends. (○) OPS-CPE blends; (X) PS-PE blends.

and D are compared in Figure 1. Compared to the large difference in morphology between blends A1 and B1, blend C1, with partial substitution of CPE with PE has intermediate domain sizes with tensile strength slightly less than the reactive blend B1 but considerably higher than the nonreactive blend A1. On the other hand, replacement of 50% of the OPS with PS (blend D1) does not result in any significant change from B1 in morphology and tensile properties. This suggests that there is more than enough oxazoline for reaction and its dilution does not appear to imbalance the stoichiometry of the interfacial grafting reaction. Furthermore, intermediate domain sizes have not been obtained which could lead to more ductile failure in the tensile test.

Figure 3 shows the morphology of some of the blends in series E in which both the OPS and CPE constituents have been diluted with their nonreactive analogues. Highly PS-rich blend E1 as well as PE-rich blend E9 both display fine morphology. Only blend E3 shows fairly large dispersed phase domains with smooth surfaces, indicating less than optimum compatibilization. The tensile strength and elongation of this blend is also lower than for blend D3. With the exception of blend E1, all the other blends of series E do not appear to give improvements in tensile strength or elongation over the corresponding blends in series B, C, and D. However, they are all superior to the nonreactive blends, and hence the concept of using these reactive ingredients, OPS and CPE, in reduced concentrations as "*in situ* reactive compatibilizers" may have

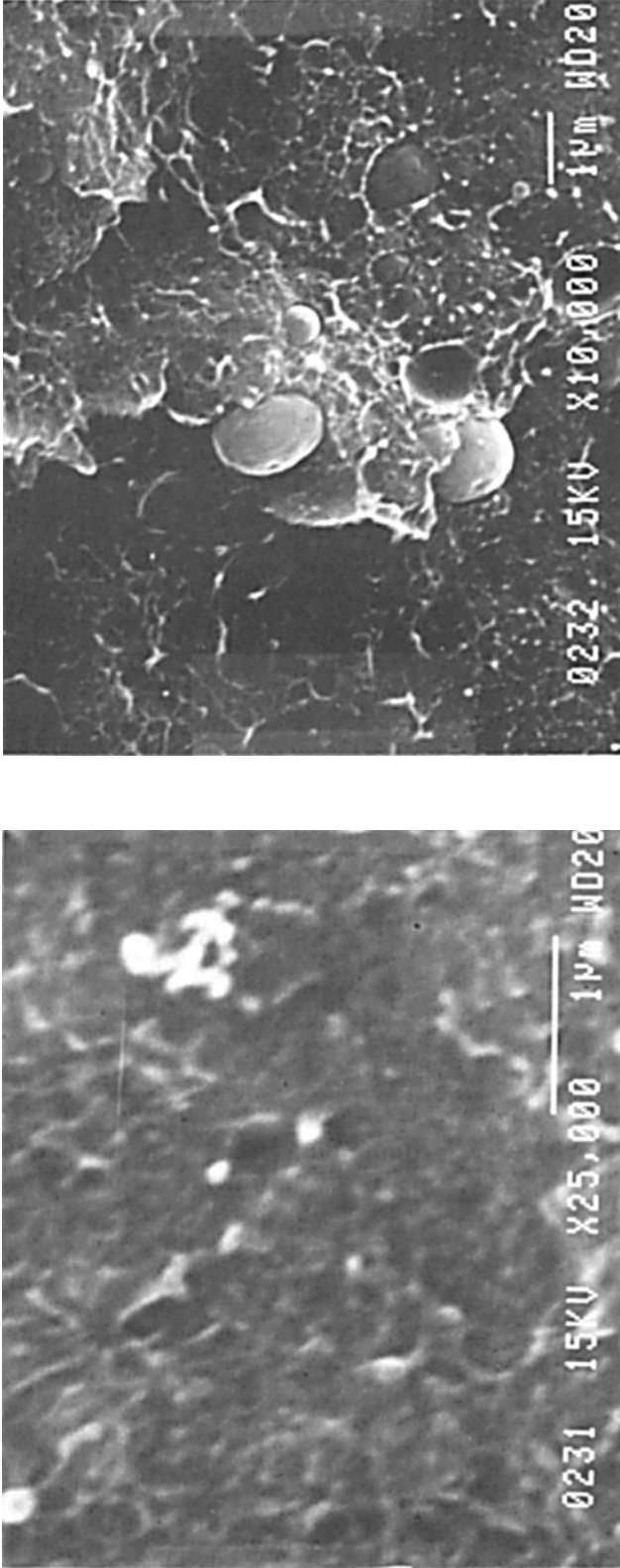
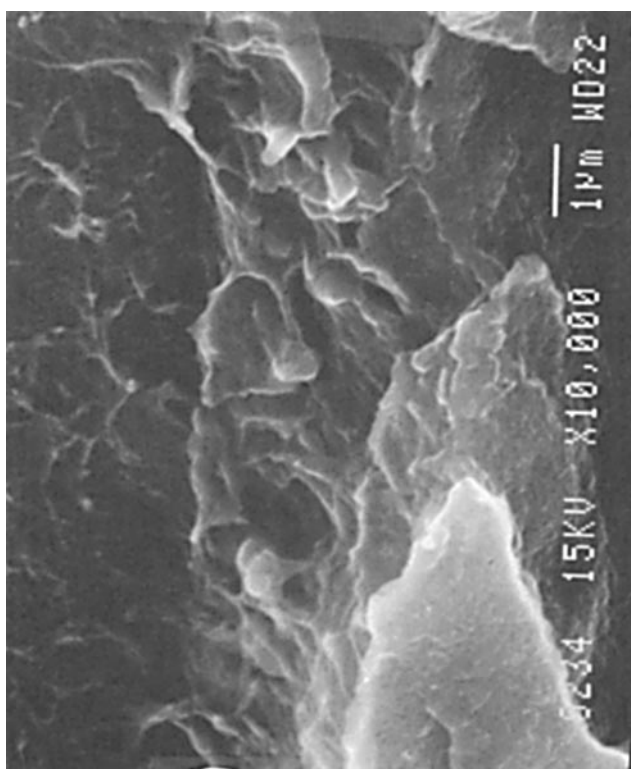
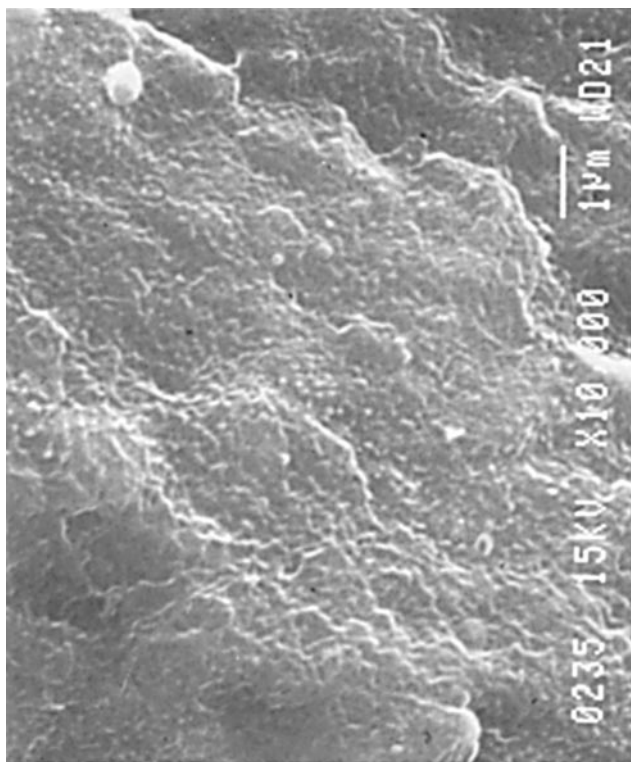


Fig. 3. SEM micrographs of series E blends prepared by replacing 50% of both of the reactive polymers with the corresponding unreactive polymer: (A) E1 OPS-PS-CPE-PE (45/45/5/5); (B) E3 OPS-PS-CPE-PE (35/35/15/15); (C) E7 OPS-PS-CPE-PE (15/15/35/35); (D) E9 OPS-PS-CPE-PE (5/5/45/45).



(C)



(D)

Fig. 3. (Continued from the previous page.)

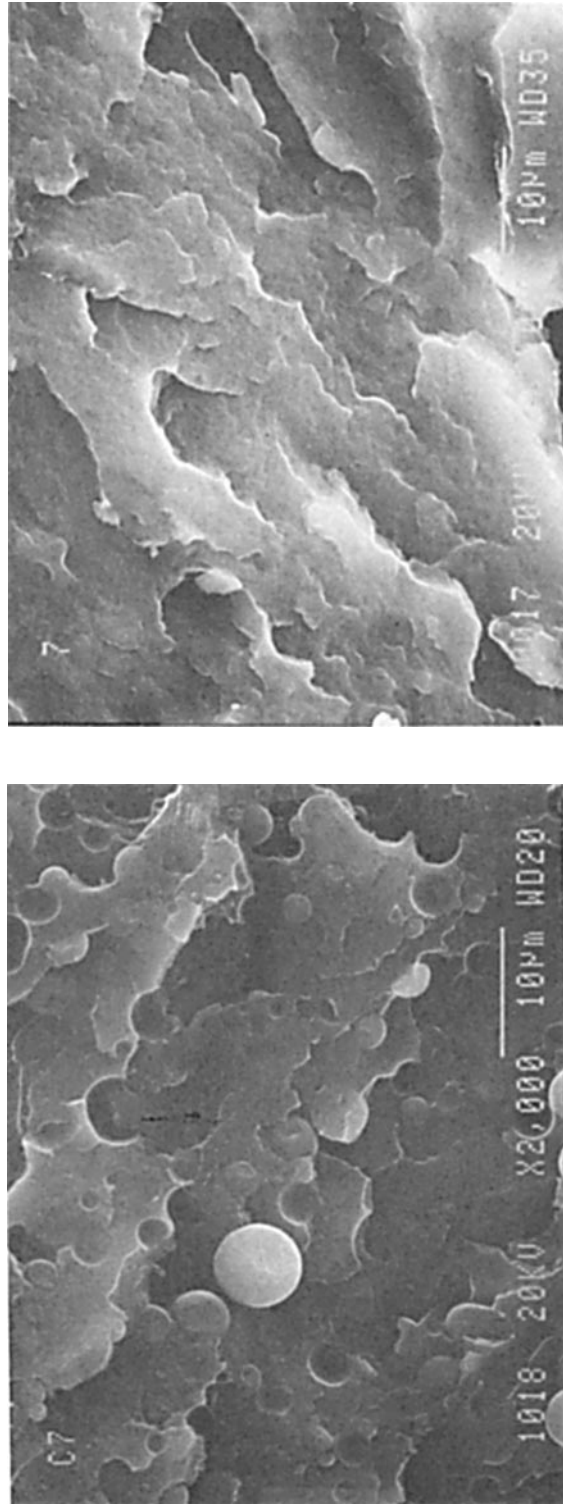
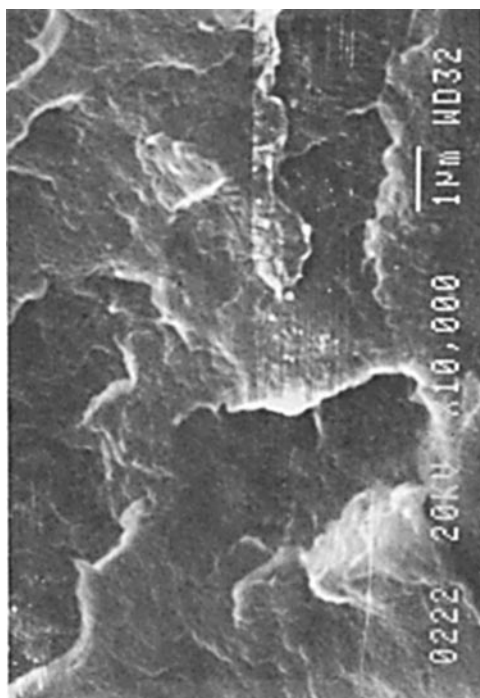
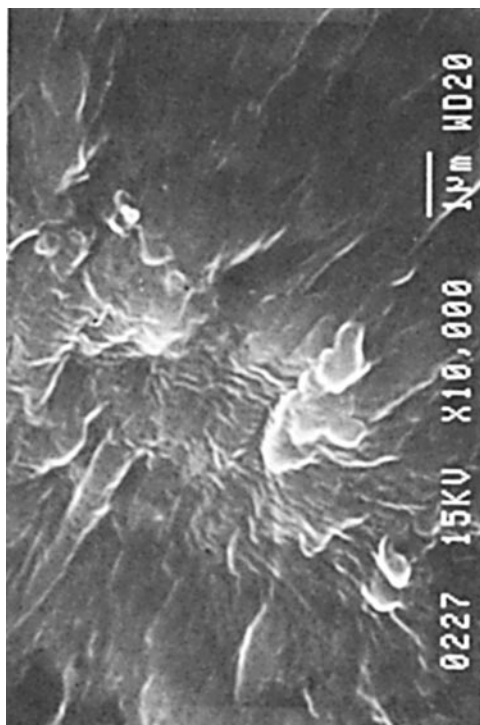


Fig. 4. SEM micrographs of polystyrene-polyethylene (30/70) blends showing the effect of 50% replacement of reactive polymer: (A) A7 PS-PE (30/70); (B) B7 OPS-CPE (30/70); (C) C7 OPS-CPE-PE (30/35/35); (D) D7 OPS-PS-CPE (15/15/70).



(C)



(D)

Fig. 4. (Continued from the previous page.)

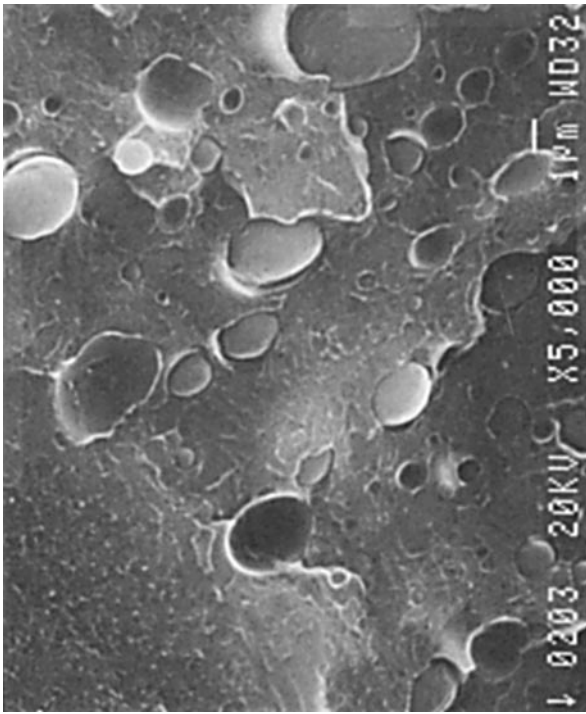
merit. The required concentration to obtain optimum particle sizes, however, may be difficult to obtain in this blend system.

Figure 4 shows the micrographs for a PE-rich system containing 70% PE overall. The change in morphology between the incompatibilized A7 and the compatibilized B7, C7, and D7 is striking. The 50% dilutions of reactivity in each of the phases, blends C7 and D7, compared to B7 do not change the morphology again suggesting that the oxazoline and carboxylic acid groups in B7, C7, and D7 exceeds that required for compatibilization. At this PE/PS ratio (70/30) the failure mechanism in the tensile test is likely shear yielding and the effect of the compatibilizers on tensile strength and elongation (Table III) are very noticeable. The absence of a visible dispersed phase may suggest some type of partially crosslinked network.

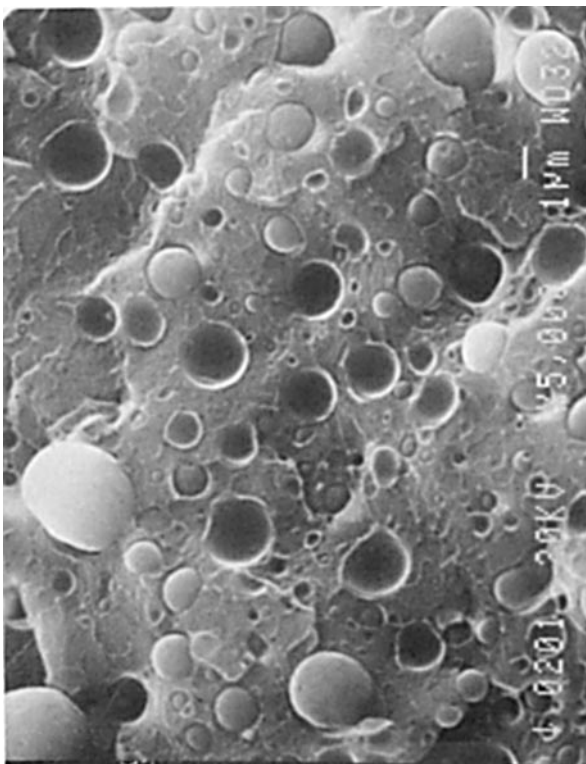
In these reactive group dilution studies it has been assumed that the OPS and PS (and CPE and PE) were miscible in each other and no significant immiscibility exists that would affect the morphology observed. This seems reasonable for OPS which contains only 1 wt% oxazoline and hence has very similar chemistry as well as viscosity as the PS. Films made from melt blends of CPE and PE form a continuous progression of physical properties, suggesting at least reasonably good miscibility. Processing times of 30 min provide ample time for the PS and OPS (PE and CPE) to form one phase. The micrographs of systems C7 and D7 compared to B7 in Figure 4 support this.

Addition of a Premade Compatibilizer

In an earlier study,^{16,17} it was observed that a (60/40) OPS-CPE blend displayed maximum interpolymer reaction. This particular reacted blend, G40, was prepared in a separate first step and used as a potential compatibilizer for PS-PE blends. Three series of blends F, G, and H having overall PS/PE proportions 30/70, 70/30, and 80/20, respectively, were prepared using different amounts of G40. In each series total PS-PE ratio in these blends was kept constant by replacing the appropriate amount of PE and PS with G40. The increasing number within each series corresponded to an increasing proportion of G40 as shown in Table II. Figure 5 shows the SEM micrographs of fractured surfaces of PS-PE (80/20) blends, series H. There is a reduction in the average size of the PE domains with the addition of G40. It indicates that G40 is compatible with both the phases and acts as a compatibilizer for the PS-PE blends. Similar compatibility was observed in series F in which PS is the dispersed phase. Despite this gradual improvement in compatibility with G40, it is hard to ascertain what role G40 plays at the interface to improve adhesion. Nevertheless, this compatibilization effect is strongly manifested in the tensile properties of the PS rich blends, series G and H. In Figure 6 the changes in tensile strength of these three blends are plotted against the amount of G40 in the blend. For comparison the tensile strength of the corresponding blends of pure reactive ingredients is quoted in the right-hand side. The maximum improvement in tensile strength is observed in the PS-rich blend of 80/20 composition. A blend with 35% G40 (H7) has 80% higher tensile strength than the corresponding PS-PE blend and 28% higher tensile strength than the corresponding OPS-CPE blend. The tensile improvement from about 20 to 30 MPa is similar to that increases observed by Coumans

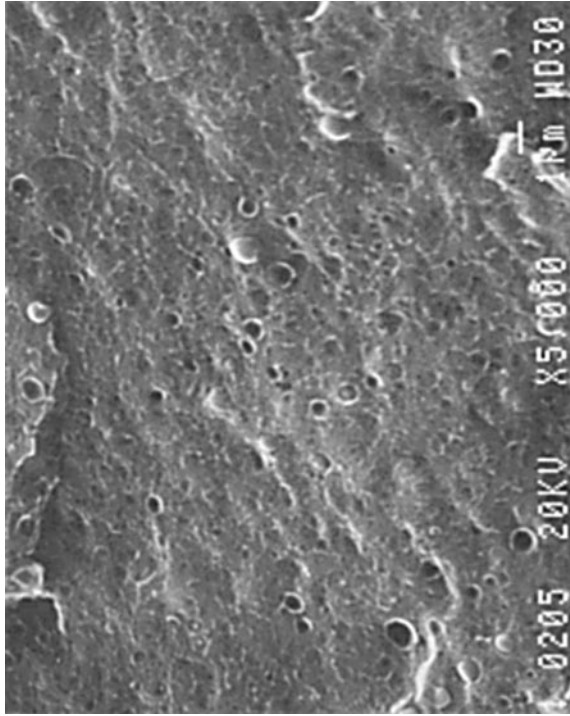


(B)

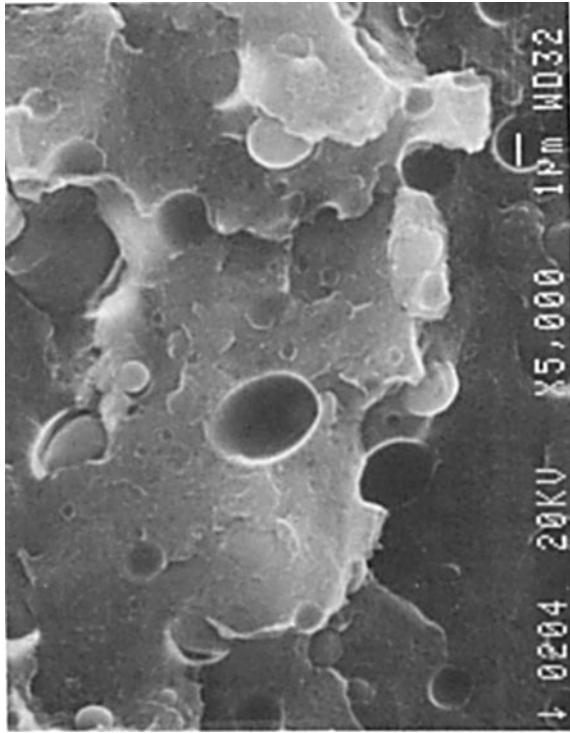


(A)

Fig. 5. SEM micrographs of polystyrene-polyethylene (80/20) blends containing different amounts of G40: (A) H2 PS-PE-G40 (74/16/10); (B) H4 PS-PE-G40 (68/12/20); (C) H6 PS-PE-G40 (65/10/25); (D) H7 PS-PE-G40 (59/6/35).



(D)



(C)

Fig. 5. (Continued from the previous page.)

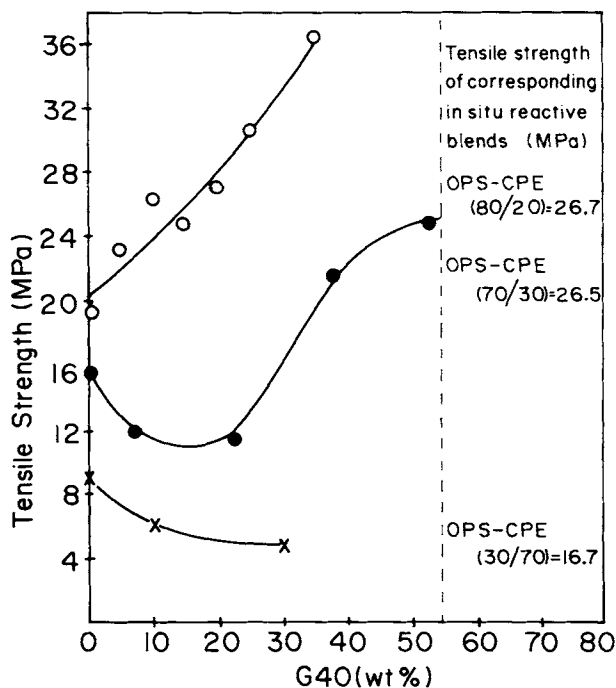


Fig. 6. Effect of G40 concentration on tensile strength of PS-PE-G40 blends: (○) PS-PE (80/20); (●) PS-PE (70/30); (×) PS-PE (30/70).

et al.⁶ in 15% 1dPE system using a hydrogenated diblock copolymer of PS and polybutadiene as a compatibilizer. In that study higher elongations between 2.5 and 4% were observed. This tensile premium is not evident in systems containing more polyethylene and is not as effective as the earlier discussed *in situ* compatibilization. This tensile premium displayed by H7 supports the use of this type of premade compatibilizer in certain systems however. Nonreactive PS-PE-rich blends have domain size of up to 5 μm and generally low tensile properties, whereas OPS-CPE blends have very fine morphology (see Fig. 1) and higher tensile strengths. In the case of blend H7 an intermediate morphology is seen. Domains of about 1 μm are clearly visible (Fig. 5), which are closer to the optimum size suggested by Buchnall. This seems to suggest that smaller proportions of the two reactive "*in situ*" compatibilizers may be required than premade block or graft copolymers to give the same morphology. An intermediate domain size morphology has resulted in an increase in the tensile strength of this particular blend but only minor increases in elongation.

Parallel to the series of blends G and H where the pregrafted polymer G40 was used as a compatibilizer, two blends X4 and Y6 were prepared to match blend G4 and H6, respectively. In both the cases the ratio of OPS to CPE was 3:2, the only difference being that in series G and H the compatibilizer G40 was prepared before hand and then mixed with PS and PE, whereas in blends X4 and Y6 the blends were prepared by mixing all the four polymers simultaneously. It can be seen from Table III that both X4 and Y6 have higher tensile strength than the G4 and H6, respectively. This increase may be

attributed to an *in situ* grafting reaction and mixing, resulting in a better distribution of the grafted polymer at the interface. This suggests that although the premade compatibilizer technique is effective, in some cases the chemically reactive "*in situ*" technique can also be effective if the types and amounts of chemical functionality can be optimized.

In the earlier work of Heikens et al.²⁻⁵ and the recent work of Fayt et al.¹² the block copolymers have been well documented as premade compatibilizers for emulsifying incompatible polymer blends. These linear polymers with carefully designed block lengths have much better controlled structure than the OPS/CPE melt reacted blend G40. Hence the relatively larger amounts of compatibilizer required in the study (25–35%) compared to the diblock copolymer approach (2–10%) is understandable. However the use of carefully designed "*in situ*" reactive compatibilizers has merit and is being pursued further.

Rate Considerations

Results for the OPS–CPE system showed that the reaction between oxazoline and carboxylic acid functional groups is rather slow.¹⁷ The slow nature of this reaction was also confirmed during the study of model compounds of the same functionality.¹⁶ Obviously, long mixing times are undesirable for reactive extrusion, though there is a possibility of reducing reaction time through more intense and efficient mixing in a twin screw extruder. To address this, zinc chloride was used as a catalyst in the hope that it would act as a Lewis acid to open oxazoline ring and hence reduce the reaction time. As an experiment OPS–CPE (90/10) blends were prepared with and without 0.1% zinc chloride. It can be seen from time–torque plots of these blends (Fig. 7) that there is a pronounced increase in torque for the blend with the catalyst, curve b, compared to that for the blend without catalyst, curve a. This indicated that this catalyst is effective in reducing the reaction time to about 10 min.

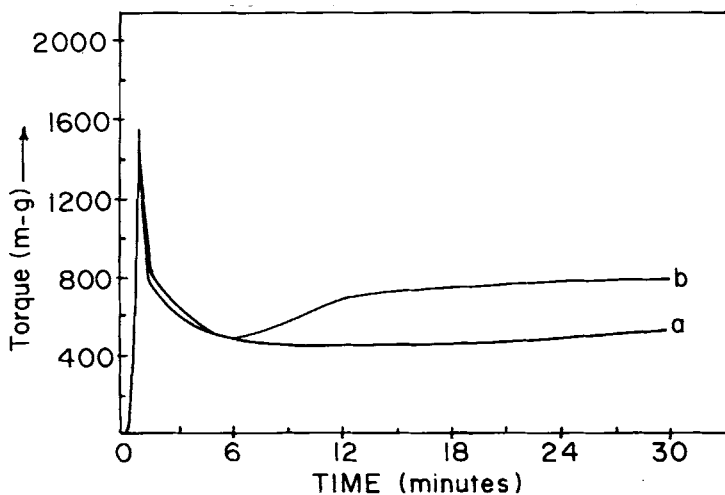


Fig. 7. Mixing torque-time for OPS–CPE (90/10) blend showing the effect of zinc chloride as a catalyst: (a) without zinc chloride; (b) with 0.1 wt % zinc chloride.

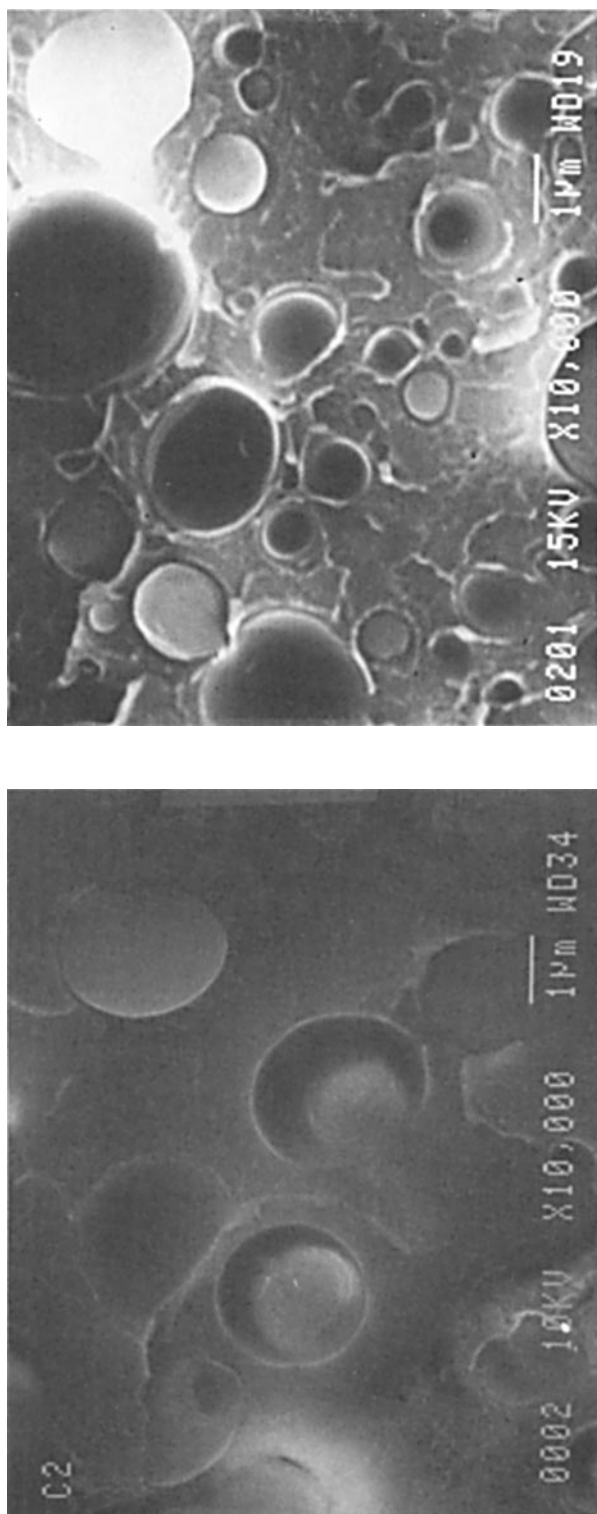
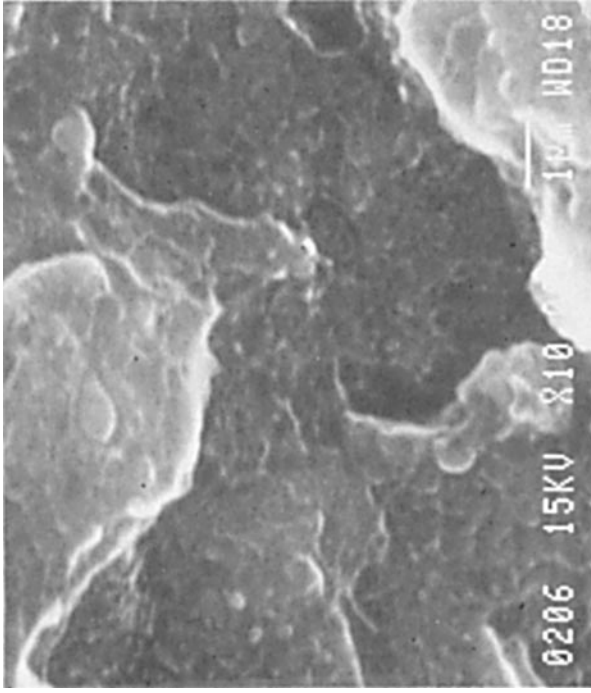
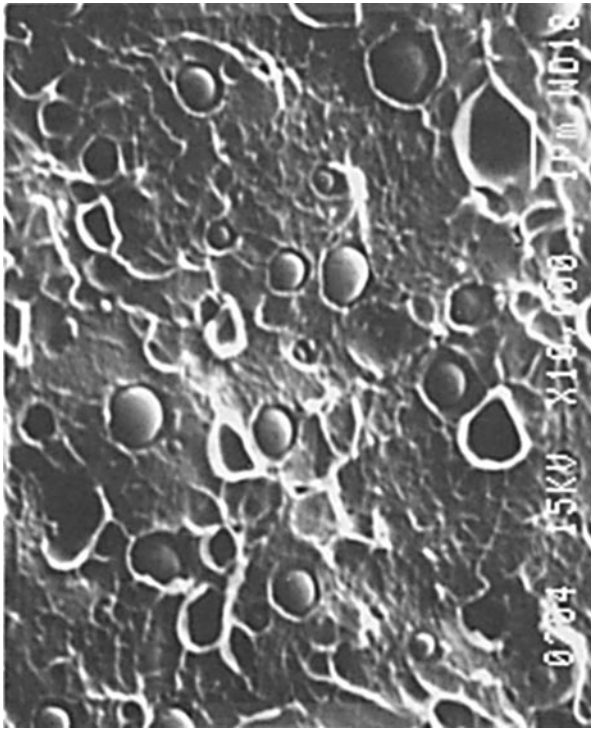


Fig. 8. SEM micrographs of polystyrene-polyethylene (80/20) blends showing the effect of addition of small amounts of OPS and CPE: (A) A2 PS-PE (80/20); (B) J1 PS-OPS-PE-CPE (78.5/1.5/19/1); (C) J4 PS-OPS-PE-CPE (71/9/14/6); (D) J6 PS-OPS-PE-CPE (65/15/10/10).



(D)



(C)

Fig. 8. (Continued from the previous page.)

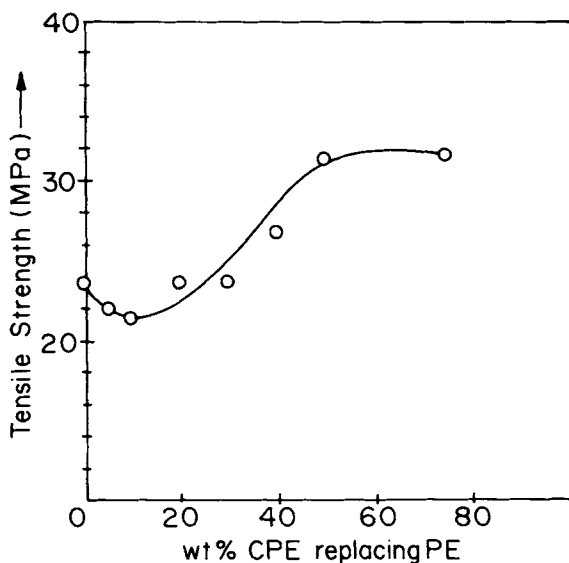


Fig. 9. Changes in the tensile strength of PS-PE (80/20) blends with the replacement of PE with CPE and PS with OPS. Ratio of OPS to CPE is 3:2.

Stoichiometry Considerations

Following this, blends of series J containing a constant 20% of polyethylene components were prepared using 0.1% zinc chloride and mixing conditions of 10 min at 200 rpm. The blends in this series contained increasing amounts of the reactive components, OPS and CPE. The morphology of these blends is compared with the unreactive blend of the same composition in Figure 8. With an increase in the amount of the reactive components, there is a gradual decrease in the domain size of the dispersed phase until, at 50% replacement of PE with CPE, a blend with fine morphology results. A corresponding increase in the tensile strength of these blends can be seen in Figure 9.

These results are analyzed further by making an estimate of the mole percent of reactive pairs which would be available to react in the blend based on the molar concentrations of the vinyl oxazoline and acrylic acid in the starting reactive polymers. Also the percent increase in tensile strength of the reactive blends in series J are determined relative to the nonreactive system A2. These data are shown in Table IV and the percent increase in tensile strength is plotted against the estimated mol % of reactive pairs in Figure 10. The improvement in tensile strength appears to level off in the range of 0.15–0.225% reactive pairs. A review of the percent improvements in tensile strength in series B–E also show several cases where low concentrations of reactive pairs give major improvements in tensile strength (B9, D5, D7, D9, and E5). This suggests that if reactive compatibilizers with higher concentration of reactive sites (than the 1% oxazoline in OPS) were used much lower concentrations of these reactive compatibilizers may be feasible.

One of the underlying problems of the reactive *in situ* compatibilization is the potential for further interaction of the reactive components when they are

TABLE IV
Relationship between Reactive Pairs Concentration and Tensile Improvement

Blend no.	PS	Composition (wt %)			CPE	Estimated mol % reactive pairs	Tensile strength (MPa)	Percent improvement in tensile strength
		OPS	PE	PE				
A2	80	0	20	0	0	19.1	0	
J1	78.5	1.5	19	1	0.015	21.9	15	
J2	77	3	18	2	0.03	21.3	12	
J3	74	6	16	4	0.06	23.6	24	
J4	71	9	14	6	0.09	23.5	23	
J5	68	12	12	8	0.12	26.8	40	
J6	65	15	10	10	0.15	31.3	64	
J7	57.5	22.5	5	15	0.225	31.4	65	

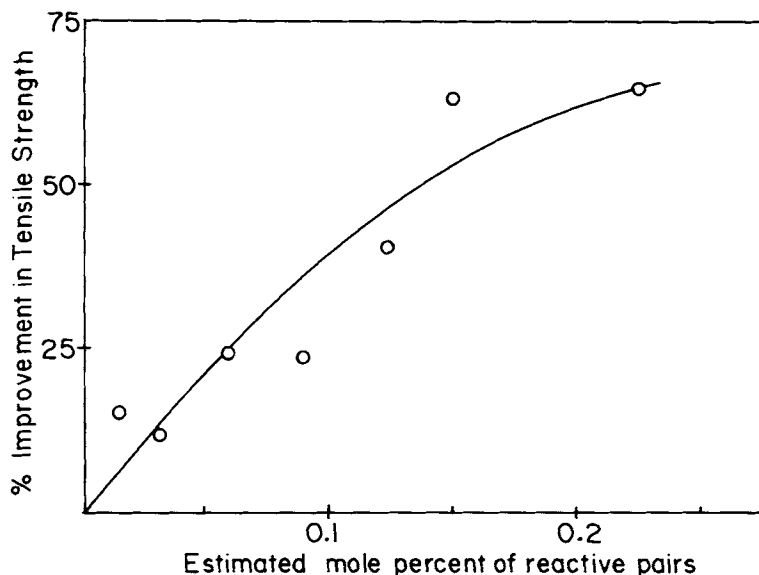


Fig. 10. Percentage improvement in tensile strength as a function of the concentration of reactive pairs used in "in situ" compatibilization.

again processed. Appropriate morphology and properties may exist after compounding but this may change in a subsequent extrusion or molding step to produce a less than optimal final product. The evidence presented here that relatively low concentrations of reactive components are sufficient to produce major property improvements in the first compounding stage is an encouraging signal that only minor further interactions may occur in a second processing step. If this technique is to gain wider acceptance the major interfacial grafting reactions will have to be isolated to this first compounding step.

CONCLUSIONS

Melt blends of reactive polystyrene and interactive polyethylene display fine morphology and improved tensile strengths compared to their non-reactive analogues. It has been shown that these two reactive polymers can be used to compatibilize a nonreactive PS/PE system in two ways. First, they can be prereacted in the melt and then added as a premade compatibilizer akin to earlier techniques. Second they can be added together in unreacted forms to a PS/PE melt where they react together to perform an "in situ reactive compatibilization" role. In this study the second technique has shown merit indicating that it can rival, in some cases, the traditional method of using a carefully designed diblock copolymer compatibilizer. In the 0–25% PE blends improvements in tensile strength were not accompanied by the higher elongations seen in toughened polystyrene. This is attributed to the smaller than optimum domain sizes which do not yield stable crazes. Further research is aimed at preparing larger dispersed domains.

For "in situ reactive compatibilization" to be optimized, the number of functional groups and the molecular weight of the coreactive compatibilizers

will have to be designed carefully, but relatively low concentrations of these compatibilizers should be possible.

References

1. D. R. Paul, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic, New York, 1978.
2. W. M. Barentsen and D. Heikens, *Polymer*, **14**, 579 (1973).
3. W. M. Barentsen, D. Heikens, and P. Piet, *Polymer*, **15**, 119 (1974).
4. D. Heikens and W. M. Barentsen, *Polymer*, **18**, 69 (1977).
5. D. Heikens, N. Hoen, W. M. Barentsen, P. Piet, and H. Laden, *J. Polym. Sci. Polym. Symp.*, **62**, 309 (1978).
6. W. J. Coumans, D. Heikens, and S. D. Sjoerdsma, *Polymer*, **21**, 103 (1980).
7. W. M. Barentsen, D. Heikens, and P. Piet, *Polymer*, **21**, 1469 (1980).
8. R. Fayt, R. Jerome, and Ph. Teyssie, *J. Polym. Sci. Polym. Lett. Ed.*, **19**, 79 (1981).
9. D. B. Cavanaugh and C. H. Wang, *J. Polym. Sci. Polym. Symp. Phys. Ed.* **19**, 1269 (1981).
10. R. Fayt, R. Jerome, and Ph. Teyssie, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 2209 (1982).
11. B. Baotern, Y. Pietrasanta, and T. Sarraf, *Angew. Makromol. Chem.*, **148**, 198 (1987).
12. R. Fayt, R. Jerome, and Ph. Teyssie, *Polym. Eng. Sci.*, **27**, 328 (1987).
13. S. Cimmino, L. D'Orazio, R. Greco, G. Maglio, M. Malinconico, C. Mancarella, E. Martuscelli, R. Palumbo, and G. Ragosta, *Polym. Eng. Sci.*, **24**, 48 (1984).
14. R. Greco, M. Malinconico, E. Martuscelli, G. Ragosta, and G. Scarinzi, *Polymer*, **28**, 1185 (1987).
15. A. Y. Coran and R. Patel, *Rubber Chem. Technol.*, **56**, 1045 (1983).
16. W. E. Baker and M. Saleem, *Polymer*, **28**, 2057 (1987).
17. W. E. Baker and M. Saleem, *Polym. Eng. Sci.*, **27**, 1634 (1987).
18. M. W. Fowler and W. E. Baker, *Polym. Eng. Sci.*, **28**, 1427 (1988).
19. B. D. Favis and J. P. Chalifoux, *Polym. Eng. Sci.*, **27**, 1591 (1987).
20. C. B. Buchnall, *Toughened Plastics*, Applied Science, London, (1977) p. 207.

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