Chemical Modification of Polymer Blends by Reactive Processing: *In Situ* Reactions of Interlinking Agents in PS/EPDM Blends

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ABSTRACT: Polystyrene (PS) and the ethylene–propylene–ethylidene norbornene terpolymer (EPDM) were melt-processed in the presence of multifunctional interlinking agents, divinylbenzene (DVB) and trimethylolpropane triacrylate (TRIS), in an internal mixer to promote functionalization of the polymers and target *in situ* formation of the interpolymer product via coreaction of the functionalities. This approach leads to effective *in situ* compatibilization of the otherwise incompatible polymer components of the blends. The weight ratio of PS/EPDM and the concentration of the interlinking agents were kept constant at 70/30 and 5%, respectively. The effect of varying the concentration of the free-radical initiator (a peroxide) and the method of its addition during melt processing on the overall reaction outcome was also examined. Changes in torque during the melt-processing operation was monitored. Sequential extraction of the polymer blends was used to separate and characterize the insoluble fraction (interpolymer). Changes in the thermal behavior (shifts in glass transition temperatures) of both the polymer blends and their insoluble fractions was investigated together with an examination of the morphology and mechanical properties of the reactively processed blends. It was found that the use of mixed reactive interlinking agents in a one-step reactive blending process and the enhancement of PS reactivity via preinitiation before addition of the reactive agents led to an increase in the extent of the coupling reaction between the functionalized PS and EPDM. This results in the formation of an "across-phase" interpolymer with an optimum composition that is responsible for the significant changes observed in the morphology and associated improvements in the mechanical properties of the blend samples. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1933–1951, 1998

Key words: reactive processing; polymer blends; chemical modification; interlinking agents; PS/EPDM blends

INTRODUCTION

The production of polymer blends and alloys through the modification of existing commercial polymers rather than through the synthesis of new polymers is a cost-effective route to producing target polymer products. A major problem with polymer-blend preparation is the inherent thermodynamic immiscibility of the majority of polymer combinations; simple melt blending yields inherently weak and brittle multiphase systems because of high interfacial tension and poor adhesion between the phases. Enhanced performance of blends has been achieved by reducing the immiscibility between the polymer components,

maintaining a stabilized two-phase morphology with improved interphase adhesion.[1,2]

Polystyrene (PS)-based blends have received increasing commercial and scientific attention with regard to their use, recycling, and improvement of their physical and mechanical properties through compatibilization of the polymer components of the blends.[3–7] Two main approaches have been used to achieve the compatibilization of PS blends: The earlier "physical" approach involves the addition of block or graft copolymers which have similar segments to the blend components and, hence, act as solid-phase dispersants.[1,3,8–10] More recently, "chemical" approaches utilizing *in situ* compatibilization using reactive melt-processing strategies have been targeted to bring about compatibilization by promoting interfacial reactions and *in situ* production of a polymeric emulsifier which serves as an "interfacial agent."[2,11–15] Although the use of block or graft copolymers for blend compatibilization has been clearly demonstrated to lead to an improvement in the properties of the blend, this method is potentially expensive due to the need for an additional polymerization step and the control of the involved synthetic parameters required to produce a new copolymer for each polymer combination. The melt-reactive processing approach, on the other hand, is more versatile as it allows the achievement of the target interfacial reaction using the processing machine as a chemical reactor with consequent cost benefits.

Earlier, we successfully used multifunctional interlinking agents in reactive processing procedures to target specific reactions, for example, to functionalize hydrocarbon polymers for the grafting of antioxidant functions and to promote interfacial adhesion in polymer composites.[16–18] In this study, chemical modifications of polymer blends by reactive processing using multi-functional interlinking agents were carried out to achieve *in situ* interpolymer formation between immiscible polymers of PS/EPDM blends. The effect of the process parameters and nature of the modifying agents on the reaction outcome, the thermal behavior, morphological characteristics, and mechanical performance of the blends were investigated.

EXPERIMENTAL

Materials

The PS used was a low-flow extrusion grade (Huntsman PS Crystal 311) with a melt flow rate

(MFR) of 3.5 g/min supplied by Huntsman, UK. The ethylene–propylene–ethylidene norbornene terpolymer (EPDM) elastomer used was Vistalon 2504 (EXXON, UK) composed of 50% ethylene, 5-ethylidene-2-norbornene at 3.8%, and the remainder, of a propylene monomer. The interlinking agents, trimethylolpropane triacrylate (TRIS; Ancomer Ltd, UK) and a technical-grade divinylbenzene (DVB), a mixture of divinylbenzene (55%) and ethyl vinylbenzene (45%) both present as *meta* and *para* isomers (Aldrich Chemicals, UK), were used as received. The free-radical initiator (FRI) used was 2,5-dimethyl-2,5-bis-tertiarybutylperoxy hexane (Trigonox 101; T 101) kindly donated by AKZO Nobel, The Netherlands. Dichloromethane, toluene, and methanol used were laboratory-reagent grades (BDH, UK).

Processing Procedures and Sample Composition

All the PS/EPDM blend samples were melt-processed in a closed chamber (under restricted oxygen access) of an internal mixer (RAPRA-Hampden torque rheometer) using counterrotating rotors operated at 60 rpm for a total time of 10 min at 180°C. Changes in torque were monitored throughout the mixing period for each blend sample. Two reactive processing methods were used for preparing the blends. In all cases, the samples were prepared by initially dry blending the PS and EPDM pellets at a weight ratio of 70 : 30. For the simple addition of reagents, 35 g of the polymer mixture was charged into the chamber of the rheometer and mixed for an initial period of 3 min, after which the loading ram was raised and the required amounts of a mixture of the interlinking agents (TRIS and/or DVB) and the initiator (T101) were injected directly into the polymer melt during mixing. At the end of the addition of the reagents (addition period of 20 s), the ram was lowered down to reclose the chamber and the mixing was continued for a total of 10 min during which the torque was continuously monitored. In the case of an initiator preaddition, the same method above was used but with the additional use of a further small amount of peroxide which was mixed with the PS before melt processing. The processed blend samples were compression-molded into thin films (0.1–0.6 mm) at 180°C under a load of 150 kg/cm^2. Table I gives a summary of the composition of the polymer blend samples examined.

Sequential Extraction of Blend Samples

Sequential Soxhlet extraction of the soluble fractions of the blend samples was carried out to de-

Table I   Composition of 70/30 PS : EPDM Blend Samples

	Sample Composition			
	Interlinking Agent (ILA)		Free-radical Initiator (FRI)	
Sample Code	Type	Amount (% w/w)	FRI : ILA (Molar Ratio)	FRI Preaddition (% w/w)
C1	None	Nil	Nil	Nil
T1	TRIS	5	0	0
T2	TRIS	5	0.001	0
T3	TRIS	5	0.01	0
T4	TRIS	5	0.001	0.07
D1	DVB	5	0	0
D2	DVB	5	0.001	0
D3	DVB	5	0.01	0
TD1	TRIS + DVB	2.5 + 2.5	0.001 + 0.01	0
TD2	TRIS + DVB	2.5 + 2.5	0.001 + 0.01	0.06

Samples processed in an internal mixer at 180°C for 10 min.

termine the amount and probable composition of the resulting interpolymer. Films (about 0.2 mm thick) of the blend samples were first Soxhlet-extracted in dichloromethane (DCM) for 3 h (DCM is a good solvent for PS and a nonsolvent for EPDM) in order to determine the amount of "free" (i.e., soluble) PS. Soxhlet extraction was then continued in toluene for another 3 h to determine the amount of "free" EPDM. The residual insoluble fraction after each solvent extraction was assayed, and from the proportion of each soluble component, the composition of the insoluble gel fraction was derived. The composition of the gel and results of the analysis by FTIR and DSC (see later) carried out on thin films of each blend and their extracted residues (gel fractions) were used to assess the extent of the reactive modification and the likelihood of interpolymer formation.

Thermal Characterization

A Perkin–Elmer DSC7 differential scanning calorimeter was used to characterize the thermal behavior of the blend samples. Small sample discs (7–10 mg) cut from pressed films of PS/EPDM compositions were crimped in aluminum pans and a temperature range from −100 to +150°C was scanned at a heating rate of 10°C per minute. Glass transitions were determined from heat-capacity curves using data-station software.

Tensile Testing

Tensile tests were performed with a computer-controlled Instron, Model 4301, series IX testing station with a dedicated routine program to collect the data and report a statistical analysis of the important tensile parameters from five replicates per film sample. Flat grips with a 4-bar compressed air clamp pressure were used in a 0.1-kN test cell. The grip separation rate was set at 10 mm/min for the specified strain rate of 0.1 min^{-1} with a gauge length of 100 mm (ASTM D882). The tensile strength, tensile modulus, percent elongation, and toughness factor were calculated. The latter was obtained by normalizing the energy to break under the tensile curve to the specimen volume.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to view the fracture surfaces from the tensile testing of the blend samples for comparative assessment of the blend morphology, using a Cambridge Instrument Stereoscan 90 scanning electron microscope. All samples were coated with a gold film using an Emscope SM300 coater set at 20 mA for 2 min.

RESULTS AND DISCUSSION

In situ chemical modification of the polymer components of the 70 : 30 PS : EPDM polymer blend

samples was targeted during the reactive processing procedures. The di- and trifunctional interlinking agents (DVB and TRIS) were used either separately or together during processing in the presence of the FRI, T101, in order to bring about chemical modification of the polymers and to promote an interfacial reaction between the modified polymer components of the blend samples. The effects of the type of the reactive modifier, the concentration of the FRI, and the method of addition of the initiator on the yield and composition of the interpolymer formed and on the nature and extent of undesirable competitive reactions were examined (see Table I for composition of the different blend samples examined).

Effect of Initiator Concentration on Interpolymer Yield Composition in the Presence of the Trifunctional Interlinking Agent TRIS and the Overall Reaction Outcome

The polymer components of the blend were initially melt-processed for 3 min followed by direct injection into the melt of the appropriate amounts of the FRI (T101) and the interlinking agent (TRIS) and processing was continued for a total time of 10 min. Figure 1(a) shows clearly that the torque changes were influenced significantly by varying the initiator concentration. In all cases, the torque was recovered to levels above their 3-min reference point (the point of addition of agents) and remained above the control (physical blend curve, sample C1). However, although the rate of the post-addition torque rise was higher at higher peroxide concentration [see Fig. 1(b), sample T3], the maximum torque peak was achieved with the sample containing an intermediate peroxide concentration (sample T2); this sample also gave the highest final torque value [see Fig. 1(c)]. These observations suggest a greater level of *in situ* reactions in this sample (sample T2).

Results from sequential Soxhlet extraction of these reactively processed samples, carried out to determine the amount and probable composition of the resulting interpolymer, showed that a considerable amount of gel was formed [up to 18%; samples T1–T3; see Fig. 1(d)]. Similar extraction and analysis of a control sample (i.e., a physical blend melt-processed under the same conditions) showed that both PS and EPDM were extremely soluble; only 0.3% insoluble residue was found. Although the total gel content of sample T3 (obtained using a higher peroxide concentration) appears to be the same as that present in sample T2 (obtained with a lower peroxide concentration), it is believed that a certain proportion of the gel in sample T3 does not represent a "real" interpolymer. A part of this gel is almost certainly due to a partial self-polymerization of TRIS (poly-TRIS, which is also insoluble under the extractive conditions used). This conclusion is supported by the inhomogeneous appearance of T3 films and the presence of a small amount of hard white insoluble material, typical of poly-TRIS. It is estimated that the contribution of poly-TRIS in this sample accounts for about 17% w/w of the total measured gel; hence, the amount of the gel representing the formation of an interpolymer is expected to be lower than that present in sample T2 [see Fig. 1(d) dotted line]. In the case of sample T2, on the other hand, the total gel measured is attributed entirely to the formation of an interpolymer since no evidence was found to support the presence of poly-TRIS (the sample appeared fully homogeneous). Furthermore, the involvement of TRIS in the interpolymer was clearly evidenced from FTIR analysis of the gel fraction of this sample (T2) which confirmed the significant presence of linked-TRIS moieties (strong saturated carbonyl absorption at 1739 cm^{-1}). The lower amount of "real" interpolymer formation in sample T3 may explain the lower torque peak observed for this sample [Fig. 1(c)], whereas the rapid initial post-addition torque rise [Fig. 1(a,b)] must be due to the concurrence of both target grafting reactions and competing reactions involving the polymerization of the multifunctional interlinking agent.

Further examination of the composition of the gel for these samples revealed that, at all peroxide concentrations, the gel was dominantly based on EPDM, with only a minor, although increasing contribution, of PS-based gel [see Fig. 2(a)]. Based on these findings in the blend samples, and the behavior of the individual polymer components when modified separately with TRIS under similar conditions,[19] a simplified schematic representation was constructed to illustrate the effect of initiator concentration on the overall reaction outcome of the modification of the blends with the trifunctional interlinking agent, TRIS [Fig. 2(b)]. The conditions of the mechanochemical initiation (e.g., sample T1) gave rise to a limited availability of reactive acrylate radicals (from TRIS). The expected reaction routes of initiated TRIS, under these conditions, is that of addition to the free unsaturation in EPDM (Scheme 1, reaction 2) and, to a much lesser extent, of the self-
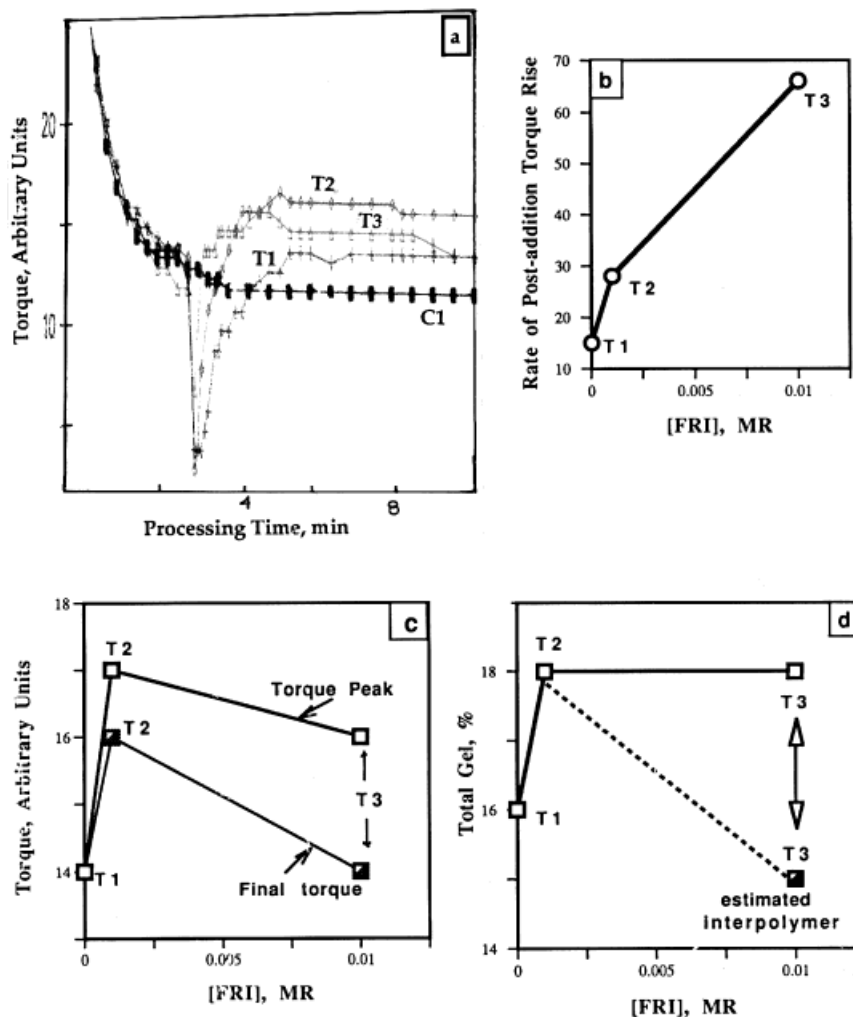
Figure 1 (a–c) The torque behavior of a physical blend (control: C1) and reactively processed blend samples containing 5% TRIS and different FRI : TRIS molar ratios; see Table I. The total insoluble gel (c) is also shown.

polymerization of TRIS (Scheme 1, reaction 3). This limited source of acrylate radicals and the low level of initiation would have a particularly negative impact on the generation of polystyryl radicals, which accounts for the lower degree of the PS reaction [Fig. 2(b)] and its minor contribution (13% only) to the gel composition [Fig. 2(a)]. However, the addition reaction of initiated TRIS on the pendant unsaturation in EPDM seems to be a facile one even under these low initiation levels, reflecting the higher degree of EPDM reaction [Fig. 2(b)]. The ease of EPDM modification must be responsible for the high level of TRIS-modified EPDM present in the gel [Fig. 2(a)].

At higher peroxide concentrations (e.g., Sample T3), the polystyryl radical generation increases, both due to the presence of a higher con-

centration of the FRI and the increased presence of the initiated acrylate moieties (Scheme 2, reaction 1), leading to a slight increase in the PS contribution to the interpolymer gel fraction [see Fig. 2(a); although the overall gel is still dominated by the EPDM contribution]. However, no overall benefit was gained from this enhanced reaction of PS at the highest initiation level (sample T3) due to the increasing importance of the self-polymerization of TRIS (Scheme 2, reaction 4), which becomes the predominant competing side reaction, hence compromising the "true" interpolymer yield [see Fig. 1(d) and Fig. 2(b)]. Sample T2 processed in the presence of an intermediate concentration level of the initiator, therefore, gave a maximum amount of the interpolymer gel, which is believed to be an intimate mixture of "within-
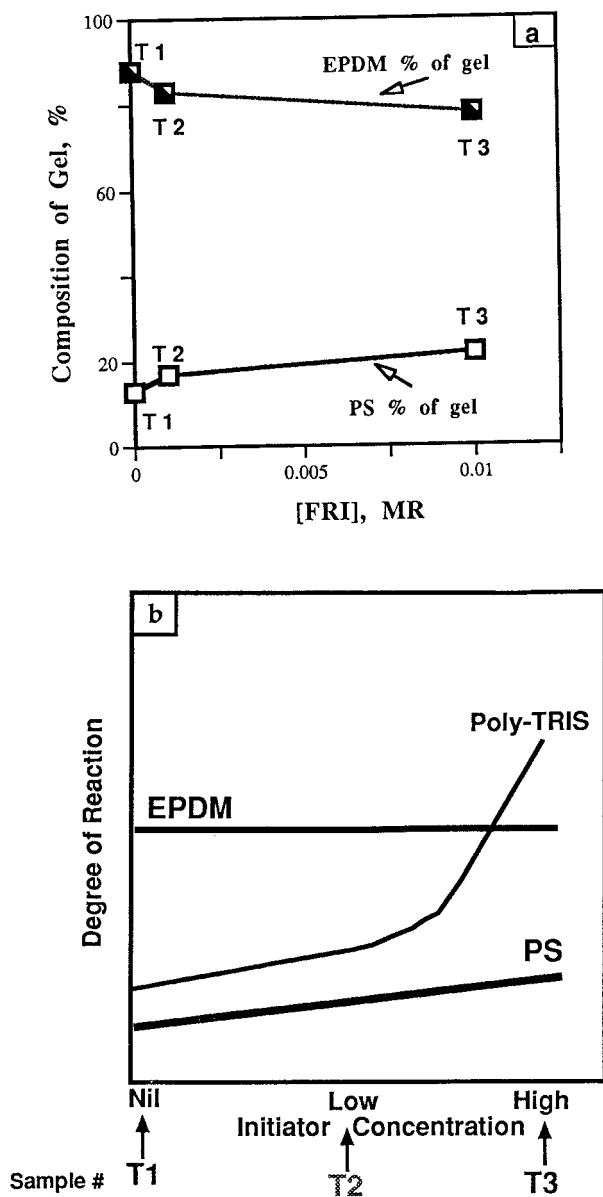
Figure 2 (a) Composition of insoluble gel in blend samples containing 5% TRIS and different FRI : TRIS molar ratios. (b) Simplified schematic representation illustrating the effect of initiator concentration on the reaction outcome of the components of TRIS-modified PS : EPDM blends.

phase" modified polymers, mainly TRIS-modified EPDM with a low contribution of TRIS-modified PS (see Schemes 2, reactions 2 and 3).

Approaches to Enhance the Reactivity of PS

It is clear from the above results that a combination of factors including the inherent "inertness"

of PS and the presence of the more readily reactive EPDM, together with the addition of an easily polymerizable interlinking agent, are responsible for the low degree of the PS reaction and lack of its incorporation in the interpolymer. Two approaches which attempt to increase the *in situ* reactivity of PS during melt processing with an interlinking agent were therefore examined. The first involves preinitiation of the PS radicals before addition of the interlinking agent, and the second relies on the use of a modifier which is structurally similar to PS.

Effect of Preinitiation of PS Radicals on Interpolymer Formation and Reaction Outcome

A preinitiation of polystyryl radicals was targeted via the addition of a small concentration of peroxide to the polymer before processing and the addition of the reactive agents (e.g., TRIS). This method was applied to PS alone and the grafting of TRIS on PS was shown to be significantly increased[19]—hence, the further use of this approach in the PS/EPDM blend samples (e.g., sample T4, see Table I). Comparison of the characteristics of sample T4 produced by the preinitiation method and modified with TRIS with that of an identical blend sample but which was processed without the preinitiation step, sample T2, shows that the torque peak in the case of sample T4 is higher, suggesting a greater level of *in situ* reactions [Fig. 3(a)]. More importantly, the composition of the interpolymer in sample T4 was completely reversed so that the major contribution is now based on PS: 80% PS-containing gel, in contrast to just over 20% in the case of sample T2 [see Fig. 3(b)]. The strategy of preinitiation appears to have successfully shifted the degree of the PS reaction upward, as depicted in the modified schematic plot of the reaction outcome [Fig. 3(c)], and this is responsible for the observed increase in the PS-graft reactions reflected in its major contribution to the composition of the gel [Fig. 3(b)]. A possible mechanism for this upward shift in the degree of PS reaction is that the polystyrene macroradicals generated during the premixing become available for increased cross reaction with EPDM and the active unsaturation of TRIS, thus reducing the extent of the self-reaction of acrylate radicals (no significant formation of poly-TRIS was observed). The cross reaction between the functionalities on PS and EPDM appears, therefore, to play an important role in the case of sample T4. This is reflected in the observed swelling of this sample dur-
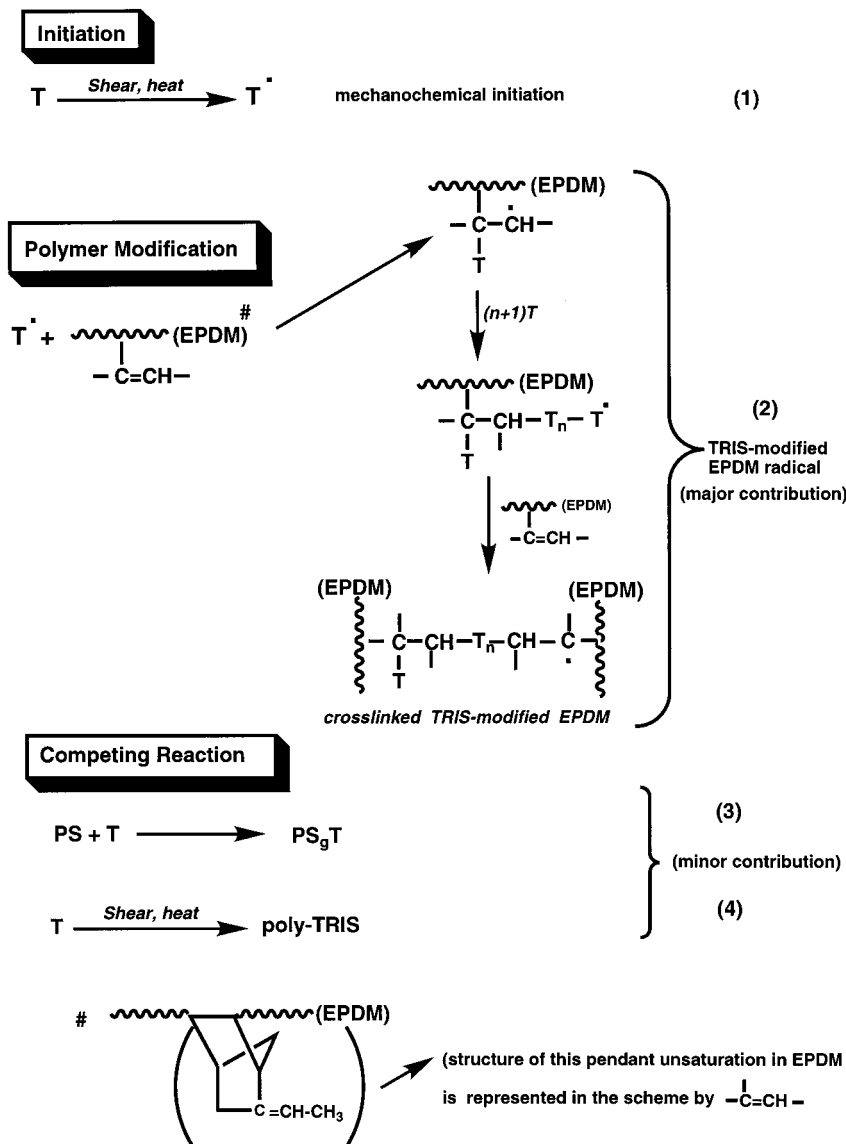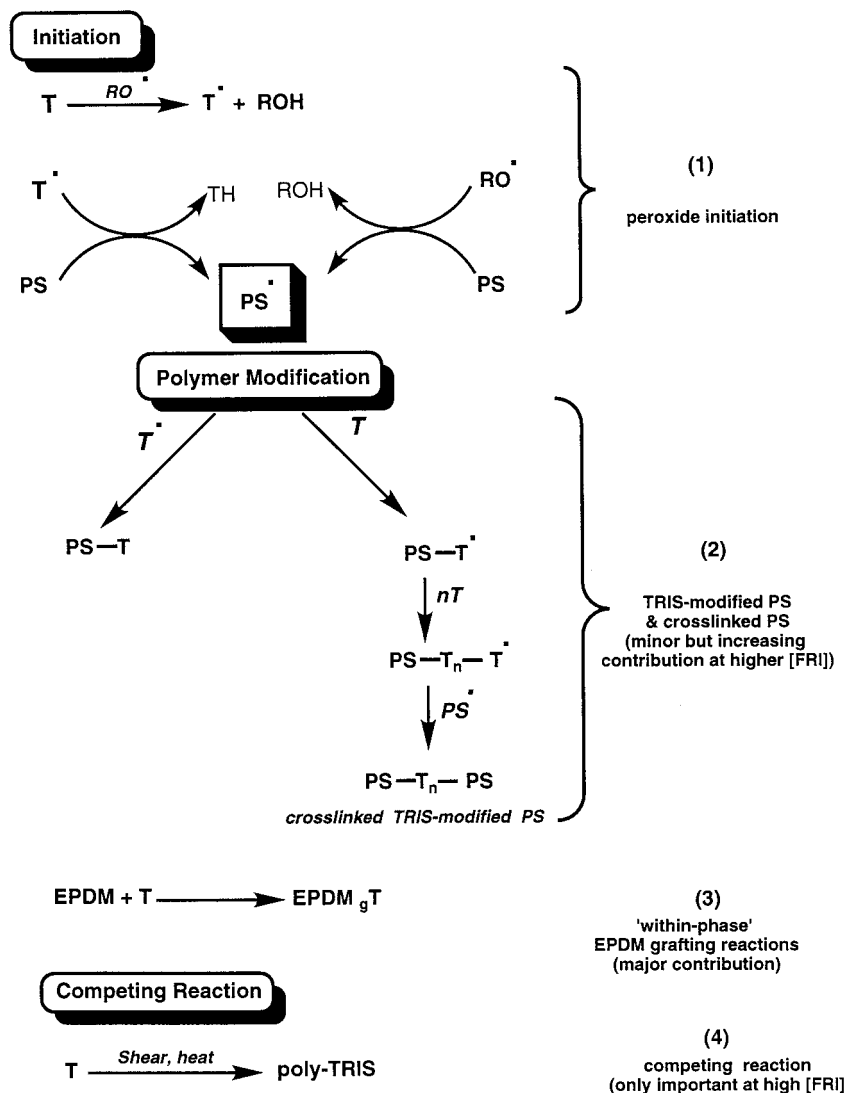
Scheme 1 Mechanochemically initiated reactions involved during melt-reactive processing of PS : EPDM (70 : 30 w/w) blends containing TRIS (T), for example, **T1**.

ing dichloromethane extraction (no such swelling was observed in the case of sample T2).

Thermal Characteristics of Blend Samples T2 and T4. To further understand the factors responsible for the observed differences in the behavior of samples T2 and T4 affected by the PS preinitiation approach, the thermal characteristics of both the blend samples and their insoluble fractions were examined by DSC using a temperature range of −100 to +150°C which allows the identification of both the EPDM and PS glass transition temperatures (T_g). Table II and Figure 4 show

the T_g values and the first-derivative DSC scan traces for blend samples T2 and T4 and that of their respective insoluble gel fractions. The physical blend control (# C1) gave glass transition temperatures of −52.9 and +101.6°C for the EPDM and PS components, respectively (Table II).

In the case of sample T2 (no preinitiation of PS), the glass transitions (T_g) of the component polymers in the blend sample show higher-temperature shifts compared to that observed in the the physical blend. Similarly, the glass transitions of the components in the gel fraction of sample T2 show higher-temperature shifts compared

Initiation

$$T \xrightarrow{RO\cdot} T\cdot + ROH$$

(1)

peroxide initiation

Polymer Modification

PS—T   PS—T·   (2)

$$\downarrow nT$$

PS—T$_n$—T·

$$\downarrow PS\cdot$$

PS—T$_n$—PS

crosslinked TRIS-modified PS

**TRIS-modified PS
& crosslinked PS
(minor but increasing
contribution at higher [FRI])**

$$EPDM + T \longrightarrow EPDM\,_gT$$

(3)
**'within-phase'
EPDM grafting reactions
(major contribution)**

Competing Reaction

$$T \xrightarrow{Shear,\ heat} poly\text{-}TRIS$$

(4)
**competing reaction
(only important at high [FRI])**

Scheme 2   Free-radical (peroxide)-initiated reactions involved during melt-reactive processing of PS : EPDM (70 : 30 w/w) blends containing TRIS (T), for example, **T2** and **T3.**

to the component's glass transition temperatures of the reactively processed blend sample. This increase in the component's T_g, particularly in the gel fraction, indicates some degree of homopolymer modification for both PS and EPDM, leading to the formation of substantially "within-phase" grafting of TRIS to each of the blend components but with a major contribution from EPDM reactions [see also Fig. 3(b)].

The thermal behavior in the case of the reactively processed blend sample T4 in which PS preinitiation was targeted before the addition of the interlinking agent shows that the glass transitions of both blend components shift to lower temperatures (by up to about 2°C) compared to that

of the physical blend (# C1) [Fig. 4(b) and Table III]. Furthermore, the gel fraction of this sample has shown two other important thermal characteristics: First, the EPDM transition has significantly increased in both magnitude and temperature (by around 6°C) compared to the corresponding transition in the blend sample, and, second, a more profound change is the absence of a measurable PS glass transition [see Fig. 4(b)] in the gel fraction of this T4 sample (monitored up to a 150°C final test temperature and further confirmed by replicate testing of fresh samples).

These characteristic glass transition shifts, particularly in the gel, and the loss of PS-Tg, as well as the broadening of the EPDM transition peak, in
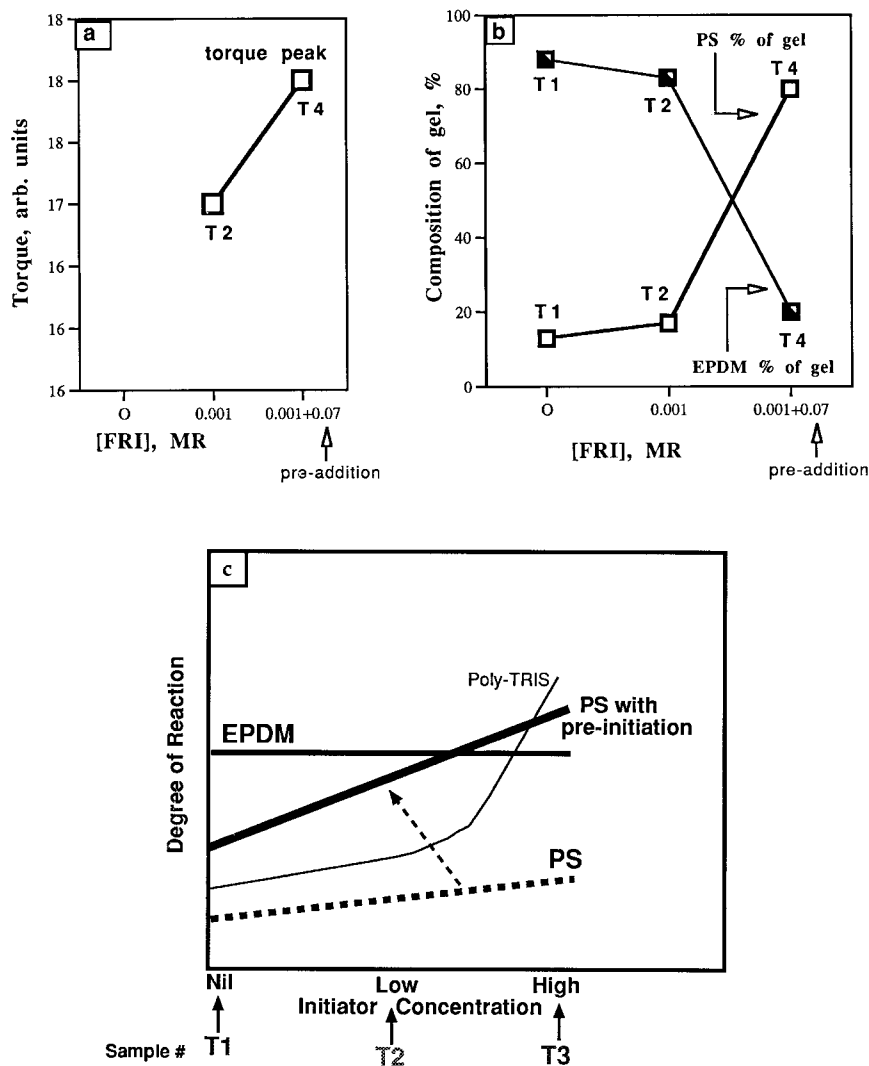
Figure 3 Effect of methods of addition of the FRI on (a) torque peak and (b) gel composition of blend samples containing 5% TRIS and various FRI : TRIS molar ratios. (c) A modified schematic plot of the reaction outcome is also shown.

sample T4 is, therefore, indicative of the occurrence of a coupling reaction between the modified PS and EPDM to the extent that a substantial PS content must have been effectively grafted throughout the interpolymer as microdomains below the scale at which an independent glass transition would be discernible by DSC, leading to an "across-phase" PS and EPDM interpolymer formation.

Effect of Using a Modifier with Structural Similarity to PS on Composition of Interpolymer

The second approach adopted to increase the reactivity of PS was to use a more compatible interlinking agent—hence, the choice of DVB, which

is structurally similar to PS. Figure 5 shows the effect of the initiator concentration on the processing behavior and amount and composition of the gel formed in the blend samples modified with DVB. Torque changes for the blend samples modified with DVB in the absence of an initiator (sample D1, see Table I for composition) show that the torque level does not recover after the addition of the reagents, rising only slightly from the minimum and remaining well below the torque level of the control (physical blend) sample (C1). However, increasing the initiator concentration (samples D2 and D3) leads to an increase in the final torque to above that of the control. The total amount of the insoluble gel was also shown to

Table II   Glass Transition Temperatures of PS and EPDM Components in Blend (B) Samples and in Their Insoluble Gel (G) Fractions Obtained from Sequential Solvent Extraction Followed by DSC Analysis

	Component's T_g (°C)							
	Contribution from EPDM				Contribution from PS			
			Shifts in EPDM T_g (°C)				Shifts in PS T_g (°C)	
Sample Code	Blend T_g B	Gel T_g G	T_g B $- T_g$ C1	T_g B $- T_g$ G	Blend T_g B	Gel T_g G	T_g B $- T_g$ C1	T_g B $- T_g$ G
C1 control	−52.9 (T_g C1)	No gel	—	—	101.6 (T_g C1)	No gel	—	—
T2	−51.8	−50.8	+1.1	+1.0	104.3	108.0	+2.7	+3.7
T4	−54.8	−48.9	−1.9	+5.9	100.6	No PS T_g	−1.0	—
D2	−50.7	−49.7	+2.2	+1.0	104.9 and 116.3	108.8	+3.3	+3.9
TD2	−54.8	−48.7	−1.9	+6.1	98.3	No PS T_g	−3.3	—
EPDM	−52.9							
PS	+101.6							

Shifts in T_g values of blend components with respect to that of the control (physical blend) and the insoluble gel fractions are also shown.

increase with increasing initiator concentration [see Fig. 5(b)].

Figure 5(c) also shows that at a low initiation level (samples D1 and D2) the gel is composed of almost entirely PS. This argues strongly for the specificity of DVB as a modifier for PS so that preferential partitioning of DVB in PS takes place to the extent of almost total exclusion of EPDM (solubility parameters of DVB and PS are quite similar, 10.8 and 9.2 cal$^{1/2}$ cm$^{3/2}$, respectively; the latter was estimated using Small's method.[20] This similarity in the solubility parameters could also explain the extreme plasticizing effect, reflected by the limited torque development, shown in sample D1 (and to a lesser extent in D2) after the addition of DVB during melt processing of the blends in the absence (or presence of very small concentration) of an initiator [see Fig. 5(a)].

However, it appears that above a critical degree of initiation, for example, in sample D3, the reaction between DVB and EPDM becomes predominant as reflected in the changeover in the composition of the gel for this sample (D3), giving rise to a much higher EPDM contribution in the gel [Fig. 5(d)]. It is also clear from Figure 5 that sample D3 shows the greatest rate of postaddition torque rise. It is possible, therefore, that, at suffi-

cient peroxide concentration, the rate of radical initiation exceeds the rate of DVB diffusion into the PS phase, allowing competition between nonspecific reactions, so that facile addition of initiated DVB to unsaturation in EPDM becomes the dominant process—hence, the high EPDM and reduced PS proportions in the gel. No evidence for DVB self-reaction was observed at all peroxide concentrations used and all processed blend samples were homogeneous and contained no solid deposits.

Effect of Using a Combination of Two Interlinking Agents Together with PS Preinitiation on the Yield and Composition of Interpolymer and the Thermal Characteristics of the Blends

The results described so far have demonstrated clearly that there are problems associated with both approaches discussed above in spite of the fact that the reactive processing methods used have been largely successful in functionalizing and, in some cases, promoting coupling reactions in the PS−EPDM blends examined. In the case of modification of the blends with the trifunctional agent TRIS, problems due to different reactivities of the components in the blend system has led to
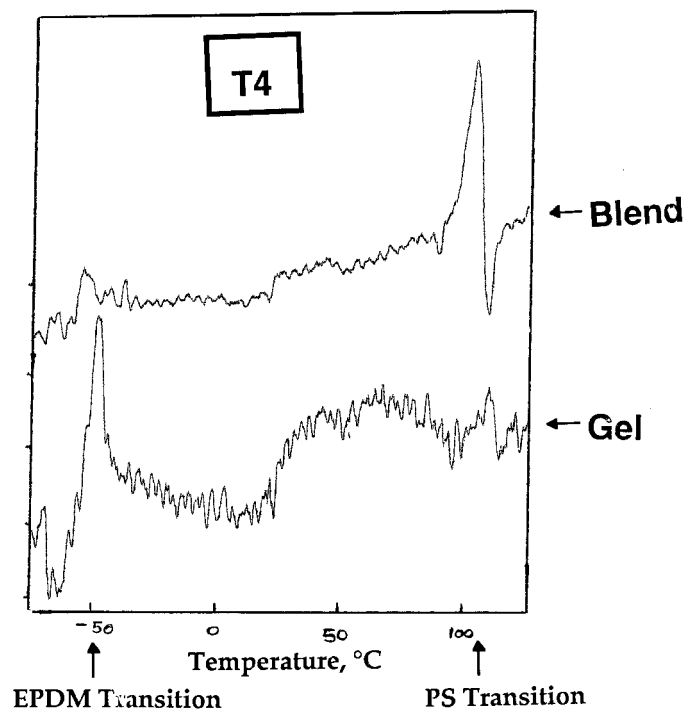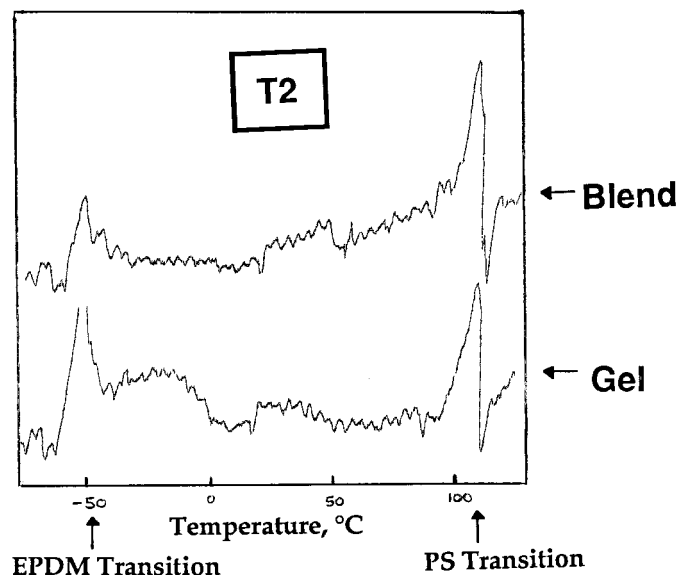
Figure 4 First-derivative DSC scan traces for blend samples containing 5% TRIS and FRI added without (T2) and with preinitiation (T4) and for their respective insoluble gel fractions.

a major contribution from reactions of one or the other of the blend components—in this case, the predominance of EPDM and TRIS (i.e., formation of poly-TRIS) reactions. On the other hand, although approaches used to increase the effectiveness of PS modification (either via its preinitia-

tion or by using DVB) have led to the desired "across-phase" coupling reactions, this appears to have taken place without achieving the optimum composition of the interpolymer—hence, the domination of reactions of only one of the polymer components of the blend samples. In all cases, the

Table III   Tensile Properties of Blend Samples Containing Different Interlinking Agents

Sample Code	Elongation to Break (%)	Tensile Strength (MPa)	Toughness Factor (×100 Mpa)
TD2	2.8	9.8	17.8
T4	1.9	10.7	11.6
D2	1.5	9.6	9.3
T3	1.1	8.3	5.0
C1	1.5	9.2	9.0

See Table I for sample compositions.

contribution from the competitive side reactions becomes important at high initiation levels.

With the aim of optimizing the target interpolymer formation, conditions were chosen which aimed at achieving the "equalization" of reactivities of the different components and the minimization of excessive competitive processes involving both "within-phase" reactions of blend components and self-reactions of the multifunctional interlinking agents. The effect of combining the two interlinking agents, TRIS and DVB, together with the preinitiation of PS, in one reactive processing step, was therefore explored with the intention of targeting a simultaneous *in situ* modification of the two polymers, each with a "favored" ILA, and to further promote an interfacial coupling reaction between the functionalities of the modified polymers.

Figure 6 shows a comparison of the gel composition of a blend sample prepared in this way (with mixed interlinking agents and PS preinitiation, sample TD2) with that of two controls, each reactively processed with only one of the two interlinking agents using the optimum initiator concentration, samples T2 and D3 (see Table I for compositions). The major reaction process in the case of both control samples (T2 and D3) which led to a gel dominated by EPDM graft reactions has significantly changed in the case of sample TD2 to give a gel composition of near equal proportion of each of the two blend polymer components [Fig. 6(a)]. This would suggest that a state of the balanced contribution from reactions of each of the blend components has been achieved.

The highest gel yield produced [Fig. 6(b)] and the highest torque peak [Fig. 6(c)] exhibited by this TD2 sample is a further indication of the major changes which have taken place in this

blend sample and which have been caused by a significant level of reactions of the various components of the blend. Furthermore, the thermal behavior of sample TD2 was quite different from that exhibited by the two controls. Figure 7 and Table II show negative T_g shifts of the blend components with respect to the physical blend, whereas in the gel fraction, the EPDM glass transition showed a large positive shift relative to the corresponding transition in the blend. These characteristic glass transition shifts, particularly in the gel of this sample (TD2), together with the absence of a glass transition attributable to PS and the broadening of the EPDM transition peak are, therefore, indicative of the occurrence of an effective "across-phase" coupling reaction between the modified polymer components of the blend.

Morphology, Compatibility, and Tensile Properties of Reactively Processed Blends

Reactive processing approaches of blends in which competing side reactions undermine the target interfacial "across-phase" reactions will not lead to the potential physical benefits expected from *in situ* compatibilized blends. Examples of such undesirable competing reactions in the case of the PS–EPDM blend samples discussed in this work are, first, the localized "within-phase" modification reactions which become dominant when using a single interlinking at a low level of initiation (samples T2 and D2) and, second, the self-reaction of the multifunctional interlinking agent when used at a high level of initiation (e.g., sample T3).

In the latter case, the predominance of the polymerization reaction of TRIS during the reactive modification of PS–EPDM must have been responsible for the lack of enhancement in compatibility reflected by the similarity in the morphology of this sample (T3) with that of the physical blend control (C1). In both cases, the scanning electron micrographs of the tensile fracture surfaces show that both PS and EPDM existed as semicontinuous planar and rather large domains, in the order of 10–20 microns, characterized by smooth phase interfaces typical of weak adhesion between the two phases (see Fig. 8). As a consequence, there was no enhancement in the physical properties of this blend; in fact, the tensile properties (elongation to break, stress to break, and toughness factor) in this case were slightly reduced compared to the phys-
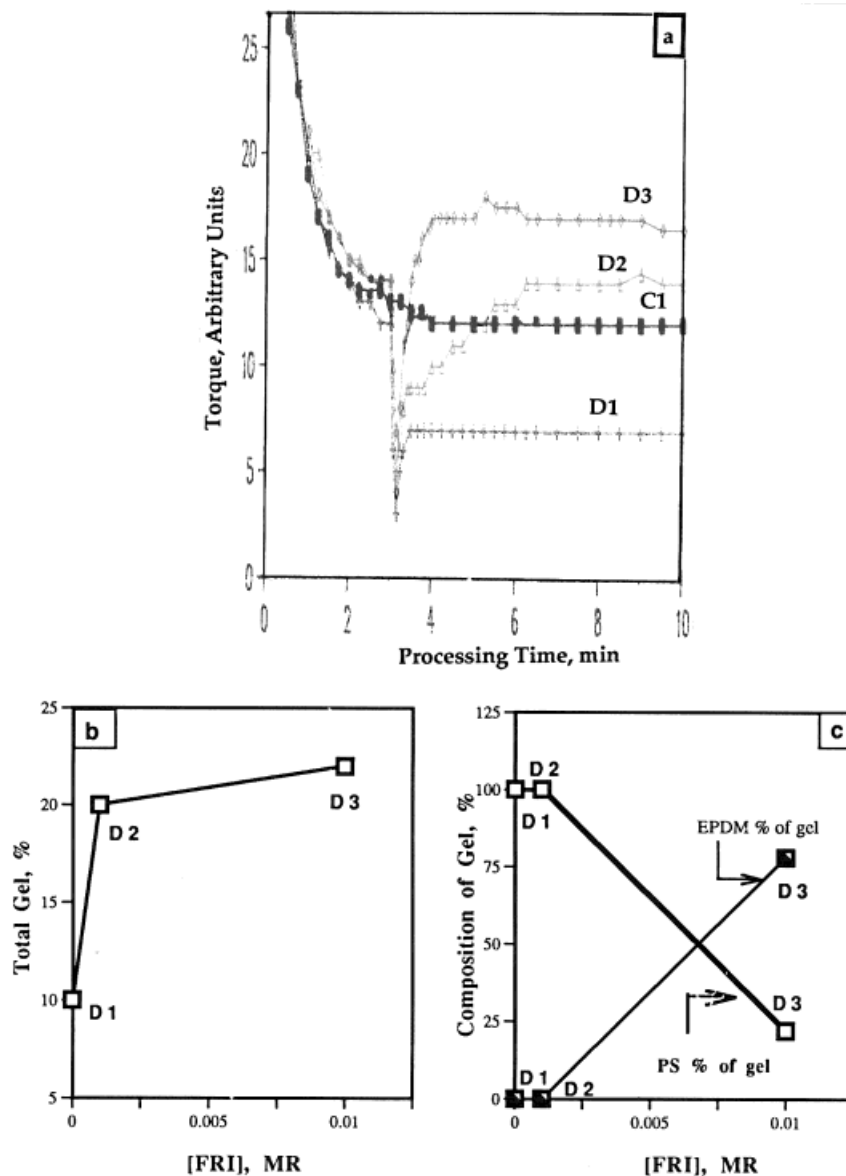
Figure 5 Effect of initiator concentration on the processing behavior, amount, and composition of the gel formed in blend samples modified with 5% DVB.

ical blend. This may be due to stress concentration and failure due to the presence of the resulting large amounts of incompatible poly-TRIS solid particles observed in this sample.

In the case where "within-phase" reactions have predominated (mainly EPDM modification for sample T2 and almost exclusively PS modification in sample D2), the evidence from the scanning electron micrographs (Fig. 9) suggests that the compatibility of these blend samples has been enhanced and this is reflected in the considerable reduction in domain size (especially in sample D2) and the appearance of a well-dispersed sec-

ond phase. However, this partial compatibilization did not lead to a gain in the tensile properties of these samples when compared to that of the physical blend control.

Reactive modification of the PS–EPDM blends which are suitably targeted to optimize the formation of the desired interpolymer and minimize the extent of the competitive reaction processes should give rise to enhanced compatibility and produce improved blend characteristics. This was achieved in this work, to varying extents, through preinitiation of the less reactive PS together with polymer modification via
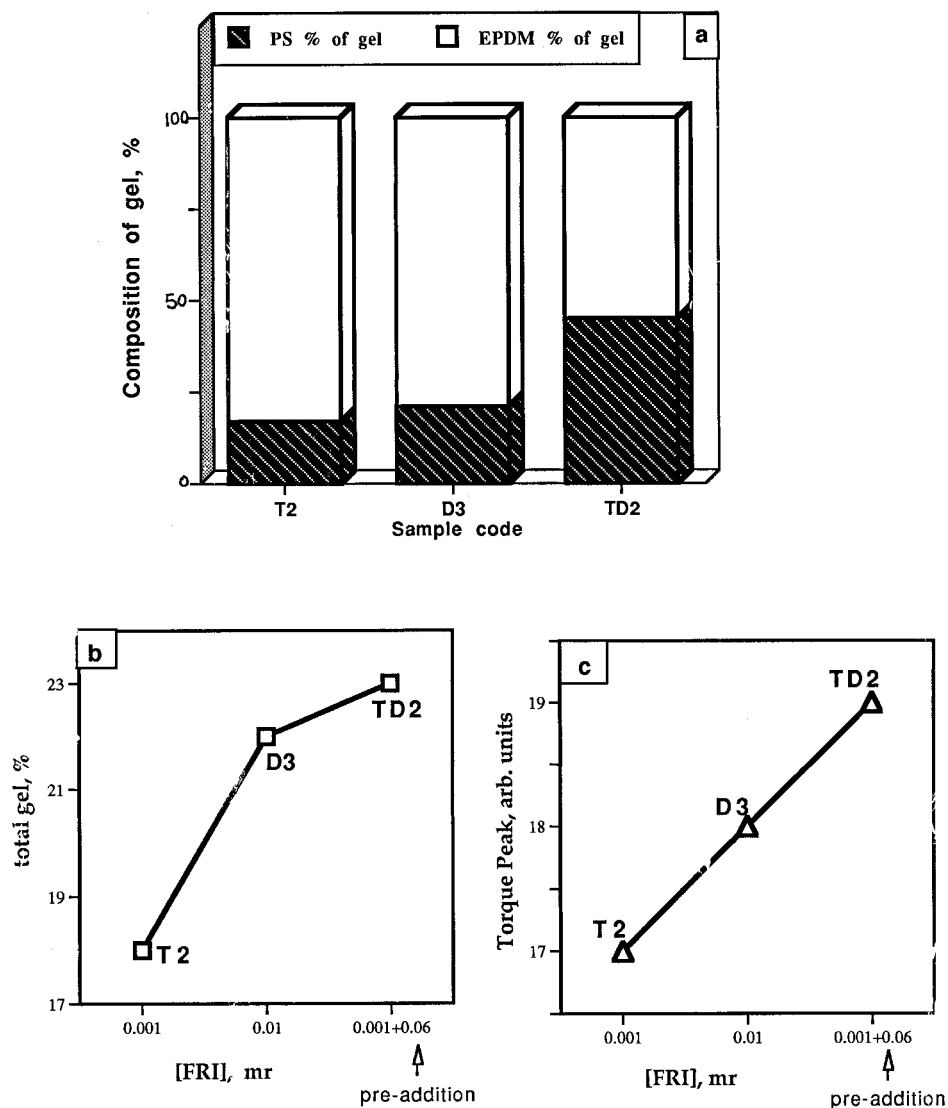
Figure 6   Comparison of (a) gel composition, (b) total gel, and (c) torque peak of a blend sample containing mixed interlinking agents and prepared with PS preinitiation (TD2) with that of two controls each containing only one of the two interlinking agents with optimum initiator concentration.

functional interlinking agents (individually or mixed, samples T4 and TD2, respectively) in one reactive processing step, which led to an increase in the extent of the coupling reaction between the functionalized PS and EPDM components of the blends, that is, "across-phase" interaction. For example, examination of the morphology of sample TD2—this sample gave rise to the highest amount of interpolymer gel [Fig. 6(b)] with a near equal contribution from both polymer components [Fig. 6(a)] and was characterized by a single T_g (Fig. 7)—illustrates clearly the enhanced compatibility achieved as a result of the "across-phase" reactive modification. This is reflected by the presence of a well-dispersed second phase which has a size of below 1–2 microns (Fig. 10). This reactive processing approach which has led to the optimization of interpolymer formation and *in situ* compatibilization must also be responsible for the maximum improvement in the tensile properties, for example, elongation to break and toughness factor, observed in this sample compared to the control (physical blend) sample and all other reactively processed blend samples examined in this work (Table III). Scheme 3 shows a schematic illus-
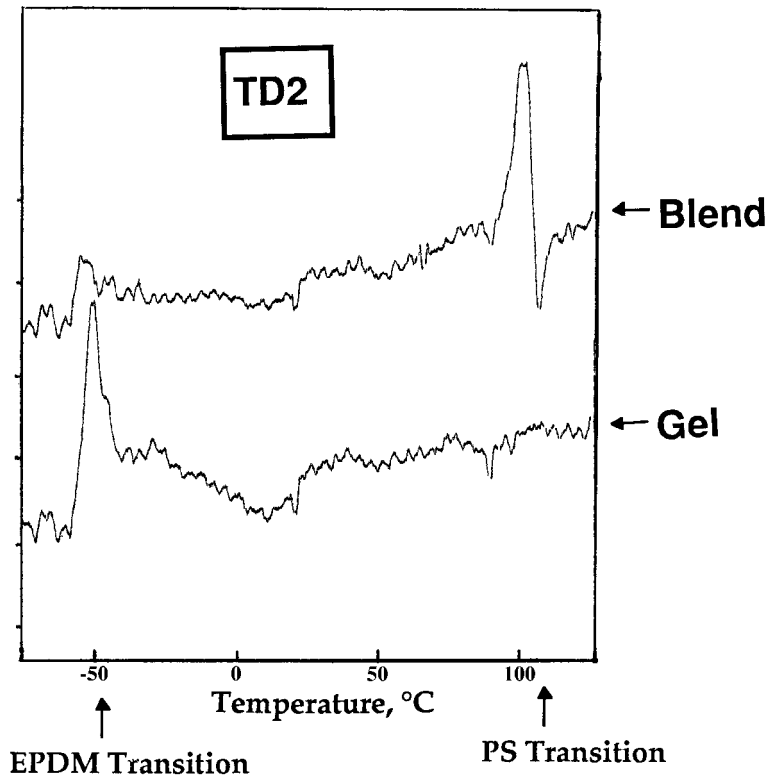
Figure 7 First-derivative DSC scan traces for a sample containing mixed interlinking agents and prepared with PS preinitiation and its insoluble gel fraction.
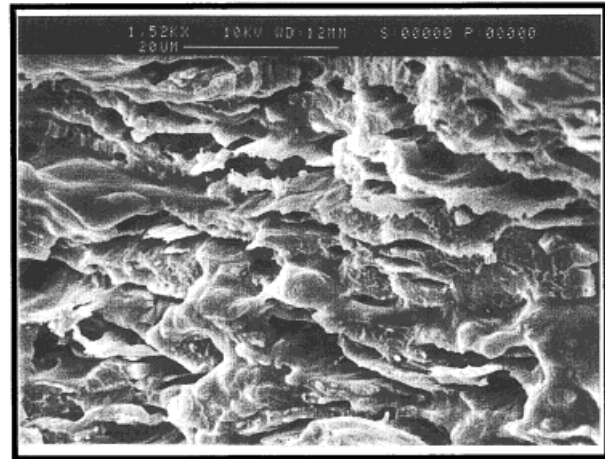

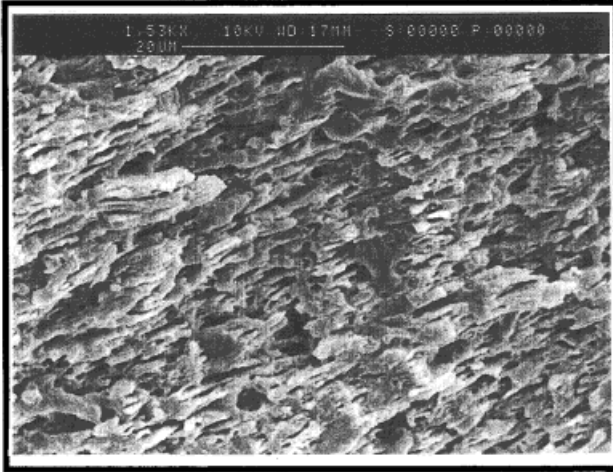**Figure 8** Scanning electron micrograph of a fractured surface (from a tensile test) of (a) the control (physical blend) sample and (b) the blend sample containing 5% TRIS and high FRI : TRIS molar ratio.

TRIS as ILA, Low [FRI], # T2

DVB as ILA, Low [FRI], # D2

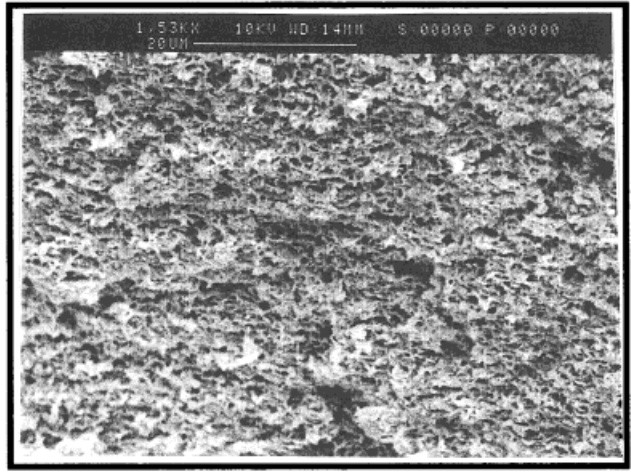**Figure 9** Scanning electron micrograph of a fractured surface (from a tensile test) of the blend sample containing either either of the two interlinking agents and a low FRI : TRIS molar ratio.

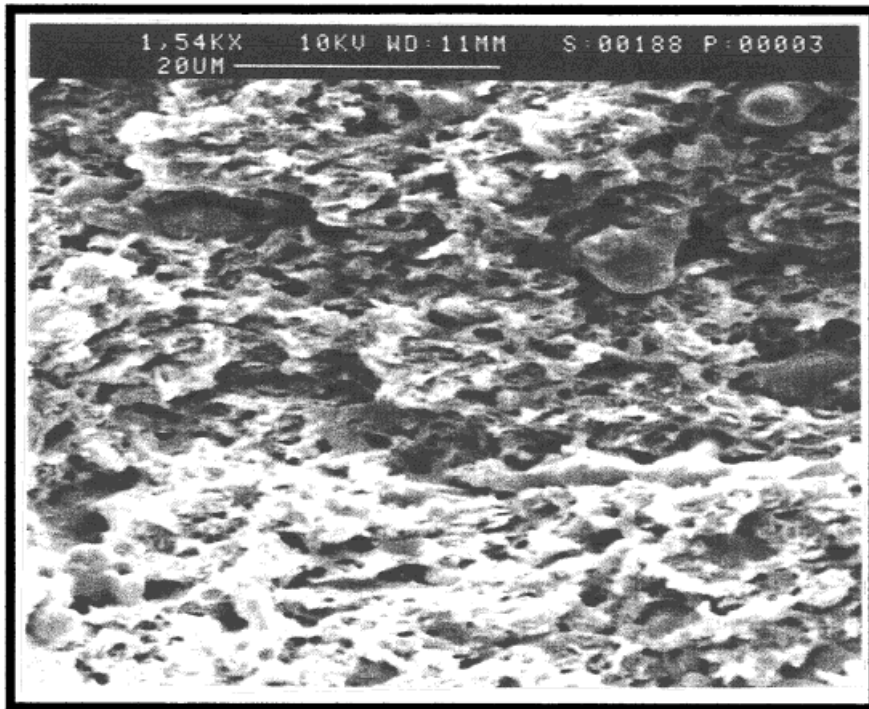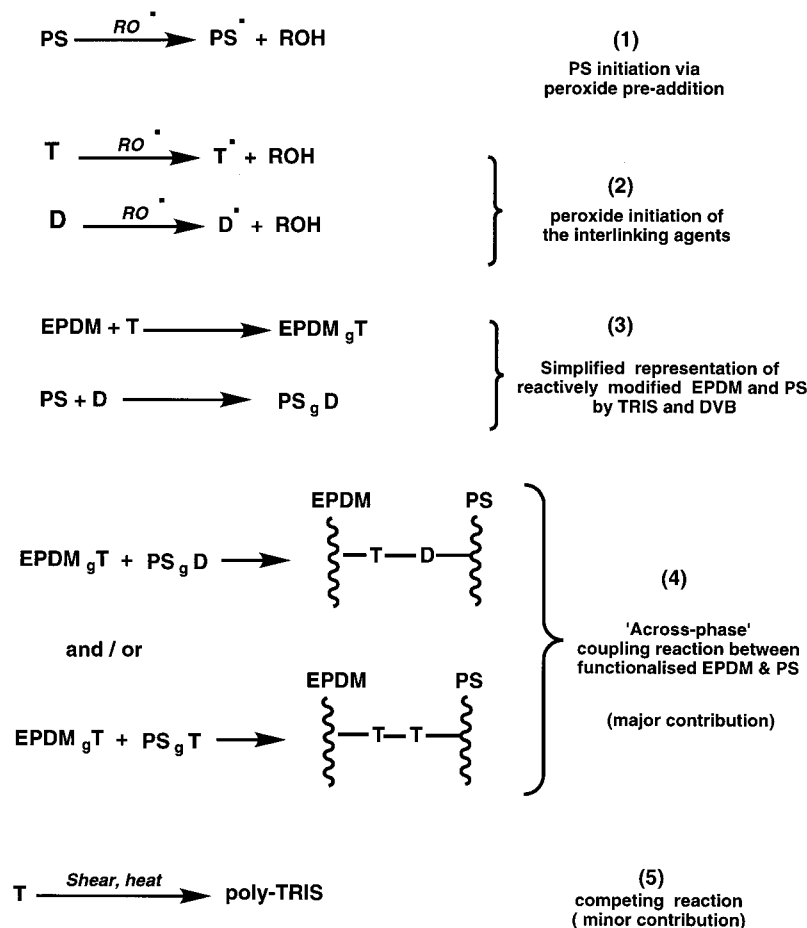**Mixed ILA & PS pre-initn**

 # TD2

Figure 10 Scanning electron micrograph of a fractured surface (from a tensile test) of the blend sample containing mixed interlinking agents and prepared with PS preinitiation.

$$PS \xrightarrow{RO^{\bullet}} PS^{\bullet} + ROH \qquad (1)$$

PS initiation via peroxide pre-addition

$$T \xrightarrow{RO^{\bullet}} T^{\bullet} + ROH$$

$$D \xrightarrow{RO^{\bullet}} D^{\bullet} + ROH \qquad (2)$$

peroxide initiation of the interlinking agents

$$EPDM + T \longrightarrow EPDM_gT$$

$$PS + D \longrightarrow PS_gD \qquad (3)$$

Simplified representation of reactively modified EPDM and PS by TRIS and DVB

$$EPDM_gT + PS_gD \longrightarrow \quad EPDM{-}T{-}D{-}PS \qquad (4)$$

and / or

$$EPDM_gT + PS_gT \longrightarrow \quad EPDM{-}T{-}T{-}PS$$

'Across-phase' coupling reaction between functionalised EPDM & PS

(major contribution)

$$T \xrightarrow{Shear, heat} poly\text{-}TRIS \qquad (5)$$

competing reaction (minor contribution)

Scheme 3 Simplified schematic representation of free radical-initiated reactions occurring during melt-reactive processing of PS : EPDM (70 : 30 w/w) blends containing [e.g., TRIS (**T**)] or mixed (TRIS and DVB, **D**) interlinking agents using preaddition of peroxide to PS, for example, sample **T4** and **TD2**.

tration of the reactions leading to the desired "across-phase" interpolymer formation between the functionalized components of reactively processed PS : EPDM blends.
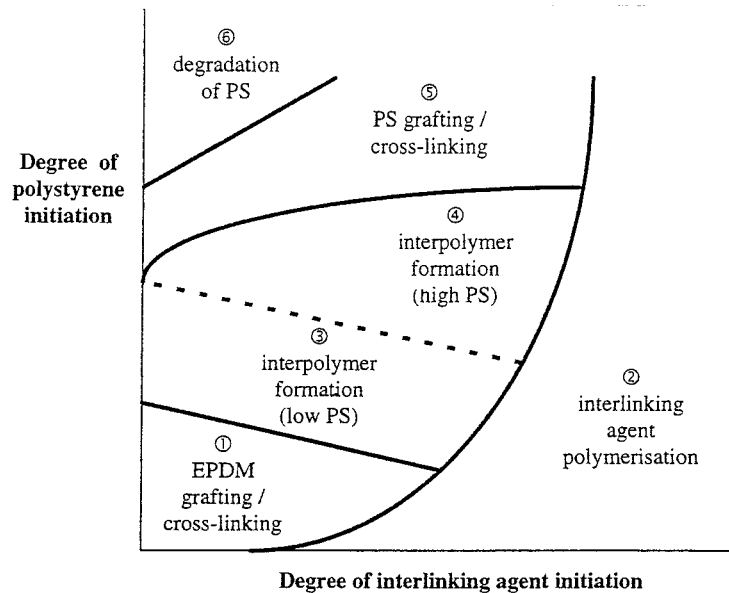
CONCLUSIONS

Three principal factors were shown to be involved in the reactive processing of PS/EPDM immiscible blends with interlinking agents: the reactivity of the constituent polymers (hence, the importance of the blend composition), the level of the addition, the physicochemical nature of the interlinking agent, and the method of application and concentration of the FRI. The primary mode of action of these factors in combination was to influence the balance between different reaction routes possible within and between components,

affecting the conditions under which a sufficient and suitable interpolymer would result.

In line with the above factors, the important features of the addition of interlinking agents, TRIS and DVB, to PS/EPDM blends that are believed to have major effects on the outcome of reactive processing are

1. The reluctance of PS to enter into the reaction and its incorporation into the interpolymer, unless sufficient polystyryl radicals could be initiated, at an appropriate time, in the process to overcome otherwise favored competitive reactions.
2. The extremely facile reaction of EPDM to addition by radicals to pendant unsaturation in the diene units.
3. The ease of "within-phase" polymer modifi-

(Diagram axes: "Degree of polystyrene initiation" (vertical), "Degree of interlinking agent initiation" (horizontal), with regions: ⑥ degradation of PS, ⑤ PS grafting / cross-linking, ④ interpolymer formation (high PS), ③ interpolymer formation (low PS), ② interlinking agent polymerisation, ① EPDM grafting / cross-linking)

Test of Key Regions vs Actual Outcomes.

Region	Predicted Outcome	Sample No & Reference
① low IA + PS initiation	EPDM grafting / cross-linking	T1 TD1 [11]
② very high IA initiation	IA polymerisation	T3
③ high IA + low PS initiation	Interpolymer formation (low PS content)	T2 D3
④ low to high IA + high PS initiation	Interpolymer formation (high PS content)	T4 TD2 [15]
⑤ high PS initiation	PS grafting / cross-linking	D2
⑥ very high PS initiation	PS degradation	[11]

Figure 11 Overall perspective of the predominant reaction outcomes from reactive processing of PS/EPDM blends with interlinking agents.

cation by grafting TRIS at low levels of acrylate radical generation.

4. The extent of highly crosslinked gel formation by triacrylate polymerization at high levels of initiation.
5. The affinity of the structurally similar DVB for modification of the PS component will predominate, unless a high enough degree of initiation is affected to allow the reaction of EPDM to occur before partitioning into the PS phase.

6. The dependence of the reaction rate and extent of both modifier and PS on the FRI concentration and its method of application.

Based on the mapping of the predominant outcomes of the above effects according to the different conditions and approaches attempted, an overall perspective of the reactive processing of the PS and EPDM blends with interlinking agents is illustrated in Figure 11. This is consistent with the mechanisms proposed to operate

within the blends both in this study and from the literature[11,15] (Fig. 11, regions 1, 4, and 6). These general principles may, therefore, have universal application in the selection of appropriate polymer blends and suitable interlinking agents to harness the full potential of the *in situ* chemical modification of blends by reactive melt processing.

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