

Preparation of Thermoplastic Elastomers Based on Silicone Rubber and Polyethylene by Thermomechanical Reactive Blending: Effects of Polyethylene Structural Parameters

A. Jalali-Arani, A. A. Katbab, H. Nazockdast

Polymer Engineering Department, Amirkabir University, Tehran, Iran

Received 5 February 2003; accepted 24 March 2003

ABSTRACT: Attempts have been made to prepare thermoplastic elastomers based on polyethylene and silicone rubber by thermomechanical reactive mixing of the two polymers. Occurrence of both grafting and vulcanization of the silicone rubber chains was evidenced by increase in the mixing torque, solvent extraction data, as well as FTIR and DSC analysis. Among different types of polyethylene, linear low-density polyethylene (LLDPE) showed higher potential to promote reactions between the two phases. The blend

based on LLDPE prepared at high temperature and shear rate exhibited distinct rheological behavior with a non-Newtonian characteristic and higher dynamic viscosity measured by rheomechanical spectroscopy (RMS) than the two individual components at low frequencies. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3402–3408, 2003

Key words: reactive blending; grafting; thermoplastic elastomer; thermomechanical polyethylene; silicone rubber

INTRODUCTION

Blending of immiscible polymers offers attractive opportunities to tailor new materials having useful engineering properties. However, most blends remain immiscible after blending attempts and therefore exhibit poor mechanical properties on a macroscopic scale.^{1–5}

Different methods can be employed for the compatibilization of the blend polymeric phases. Functionalization of the blend components before blending, addition of a copolymer during mixing process,^{5–8} and also compatibilization through *in situ* reactive melt mixing^{9–14} promotes in most cases the compatibilization of the phases in the mix. Blends of polyethylene and silicone rubber (PDMS) would be of particular interest because of low glass transition temperature ($\approx -120^\circ\text{C}$), low surface energy, high permeability to gases, good thermal UV and flame resistance, and also good biocompatibility of silicone rubber.^{15–18} On the other hand, polyethylene is a polyolefin widely employed in many cases because of its easy melt processing together with good chemical and mechanical properties. However due to the inherent incompatibility of these two polymers, their interfacial adhesion needs to be modified. For this purpose, *in situ* reactive compatibilization during melt mixing through free-radical mechanism has been attempted in the present

work. Different routes exist for the initiation of a free-radical reaction.^{19,20} Peroxides are the major sources to generate free radicals necessary for initiating a melt free-radical grafting process.^{21,22} However, our approach has been to use heat and mechanical shear to induce the formation of free radicals on the backbone of polyethylene chains for being reacted with vinyl groups of the silicone rubber.²³ As silicone rubber contains methylvinylsiloxane groups in its structure, crosslink formation between its chains is also a competing reaction which should be considered. This is expected to lead to the formation of a dynamically cured thermoplastic elastomer based on polyethylene and silicone rubber.

Blending has been carried out by the melt mixing of polyethylene and silicone rubber at different processing conditions. The microstructure of the prepared blends and also the effects of polyethylene structural factors have been studied by the use of FTIR, scanning calorimeter, and scanning electron microscope. The melt processing behavior of the blends has also been investigated by rheomechanical spectroscopy (RMS).

EXPERIMENTAL

Materials

High-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE) were obtained from Iranian Petrochemical Industry and used as received.

The type of silicone rubber employed was SR110-3, supplied by Chinese Chenguang Co. The characteris-

Correspondence to: A. A. Katbab (katbab@aut.ac.ir).

TABLE I
Basic Characteristics of the Materials Used in this Study

Polyethylene	Density (g cm ⁻³)	Melt flow index(MFI)
HDPE	0.953	1.44 @ 190°C, 5 Kg
LDPE	0.917	1.62 @ 190°C, 2.16 Kg
LLDPE	0.900	0.86 @ 190°C, 2.16 Kg
Silicone rubber SR110-3	M _w (g/mol) 8 × 10 ⁵	Mol% of methylvinylsiloxane 0.16

tics of the polymers used are listed in Table I. The analytical grades of toluene and ethyl acetate were used as solvents.

Preparation of the blends and test specimens

The composition of the blends and processing conditions employed for their preparation are illustrated in Table II. Blending was carried out in a Brabender W50 (Germany) internal mixer with a fill factor of 0.85. Polyethylene was first fed in to the mixer and allowed to melt, followed by the addition of silicone rubber, and mixing was continued up to 13 min. Then the discharged mix was quenched in cold water to prevent further thermal oxidation.

Characterization of the blends

Solvent extraction

To remove unreacted silicone rubber, specimens of each blend were solvent extracted in cold toluene for 48 h followed by refluxing with ethyl acetate for 10 h. The amount of the reacted silicone rubber was determined using the following relationship:

$$\% \text{ Grafted SR} = (W_1/W_0) \times 100 - \% \text{ PE}$$

where W₀ and W₁ denote the initial and final weight of the specimen, respectively. Then the residual portion of the specimen was immersed in hot toluene to measure the gel fraction of the specimen (%Gel) according to the standard test method ASTM D 2765-95:

$$\% \text{ Gel} = (W_2/W_0) \times 100$$

where W₃ is the weight of the insoluble portion of the specimen in the hot toluene.

Infrared spectroscopy

Fourier transform spectrometer (Bomem, Canada) equipped with attenuated total reflection (FTIR-ATR) was employed to characterize the samples.

Differential scanning calorimetric analysis (DSC)

Differential scanning calorimetry (DuPont 980) was performed on the samples with a heating rate of 10°C/min to assess thermal behavior of the samples such as melting point and heat of fusion from the obtained thermogram. Percentage of crystallinity of the samples was calculated by the use of the following expression:

$$X = (H_m)/(w_i H_c)$$

where w_i is the weight percentage of polyethylene of the blend system, H_m is the measured heat of fusion of the sample, and H_c is the value for a 100% crystalline polyethylene. We used a value of 66.4 cal/g.¹⁹

Morphological studies

The blends of LLDPE/silicone rubber (SR) were characterized with the help of a scanning electron microscope (Geol GX-A 840, Japan). The samples were fractured in liquid nitrogen and coated with an ultrathin layer of gold.

Rheological studies

Rheometric mechanical spectrometer model UDS 200 (Paar Physica, Austria) was employed to study the shear viscosity and rheological properties of the various blend samples. For these purposes the required amount of the sample was put into the rheometer without initial thermal deformation to prevent change in the sample morphology, and the experiment was carried out by using of a 0.25-mm-diameter parallel plate with 1-mm gap and the strain set at 0.1.

RESULTS AND DISCUSSION

Typical curves showing the variation of the mixing torque versus time during blending process of SR with different types of polyethylene at 220°C and rotor speed of 120 rpm has been presented in Figure 1. It is clearly seen that the mixing torque reaches a much higher level in the case of the LLDPE/SR blend system compared

TABLE II
Blends Composition and Processing Conditions

Composition	Blend code			
	PE-1	PE-2	PE-3	PE-4
HDPE	50			
LDPE		50		
LLDPE			50	50
SR	50	50	50	50
Processing parameters				
Mixing temperature (°C)	220	220	220	135
Speed of rotor (rpm)	120	120	120	90

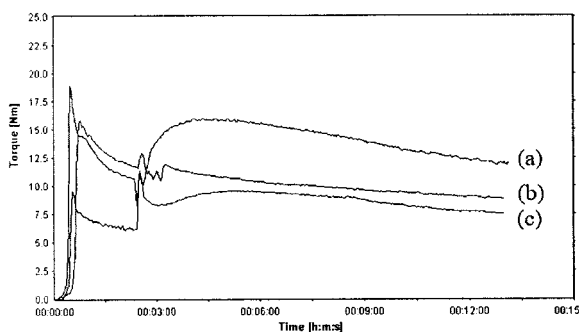


Figure 1 Mixing torque versus time of mixing for (a) LLDPE/SR; (b) HDPE/SR; (c) LDPE/SR blends at 220°C and rotor speed of 120 rpm.

with LDPE/SR and HDPE/SR. This confirms the occurrence of the mechanochemical reaction between LLDPE and SR, which is indicative of higher concentration and more stable macroradicals generated by LLDPE. It is also observed that addition of silicone rubber into the HDPE melt would not lead to the increase in the mixing torque, suggesting that this type of polyethylene does not have any potential for the generation of active free-radical sites on its backbone. Different behavior observed for these three blend systems is attributed to the difference in the microstructure of LLDPE, LDPE, and HDPE. Generation of macroradicals during melt mixing of polyethylene is mainly influenced by the degree of branching as well as the chain's molecular weight. Abstraction of tertiary hydrogen from the backbone of polyethylene chains is much easier than secondary and primary ones.²² Therefore the yield of macroradicals formation during thermomechanical mixing is expected to be much higher for the branched types of polyethylene such as LLDPE compared with HDPE. Moreover, the higher graft yield observed for the LLDPE/SR blend system compared with LDPE/SR is explained to be the result of the higher molecular weight of LLDPE than LDPE as presented by their MFI in Table I. As the molecular weight and hence chain entanglement in polyethylene increases, the melt viscosity also increases. This would lead to the more intensive mixing and therefore higher rate of the chain cleavage, which results in the greater concentration of macroradicals and consequently higher rate of tertiary hydrogen abstraction.

As we can see in Figure 2, when the mixing shear rate was increased, the mixing torque increased to a higher level, which is attributed to more C—H cleavage and therefore creation of higher macroradicals of LLDPE. This would result in more grafting as well as higher crosslinking of the silicone rubber chains. This is in accordance with the greater percentage of silicone rubber gels formed during melt mixing of LLDPE and silicone rubber at the shear rate of 120 rpm, as given in Table III. As can be observed in this table, the percentage of insoluble gel formed during mechanical melt

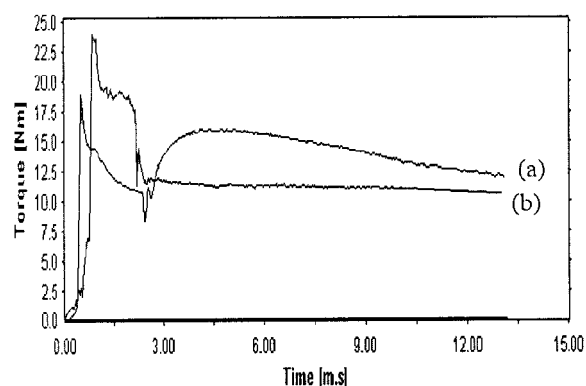


Figure 2 Comparison of torque versus time for LLDPE/SR blend at (a) 220°C and 120 rpm and (b) 135°C and 90 rpm.

mixing of LLDPE and SR at higher temperature and shear rate (PE-3) is higher than the other blend systems. As no radical initiator was added to the blends, we are led to the conclusion that radicals formed on the backbone of the LLDPE chains play as radical initiator for vinyl groups of the SR chains. In the case of LDPE/SR blend, the largest fraction of silicone rubber was found to be soluble in the cold toluene and the blend could dissolve in the boiled toluene. These results indicate insignificant graft yield so a small amount of silicone rubber has been only grafted on LDPE. Insoluble fraction of HDPE/SR blend in the cold toluene corresponds exactly to the amount of introduced HDPE and this blend showed no insoluble fraction when boiled in hot toluene.

Figures 3-5 illustrate the FTIR spectra obtained for the pure SR and different blend samples. The characteristic absorption bands of silicone rubber are located at 800, 1260, and 1000–1110 cm^{-1} assigned to Si—CH₃ and Si—O—Si bands, respectively. Comparison between the spectrum of cold toluene extracted HDPE/SR, LDPE/SR, and LLDPE/SR blend samples presented in Figure 4 clearly shows that the silicone rubber characteristic peaks have only appeared strongly in the spectrum of LLDPE/SR blend sample, suggesting that silicone rubber chains have been able to be grafted onto the polyethylene backbone of LLDPE during the thermomechanical mixing process. This result again leads to the conclusion that LLDPE has much more potential to yield free-radical sites to be

TABLE III
The Percentage of Grafted SR and Gels Formed Within the Blends

Code of blends	% Grafted SR	% Gel
PE-1	0	0
PE-2	3.5	0
PE-3	25.5	25.3
PE-4	6	4

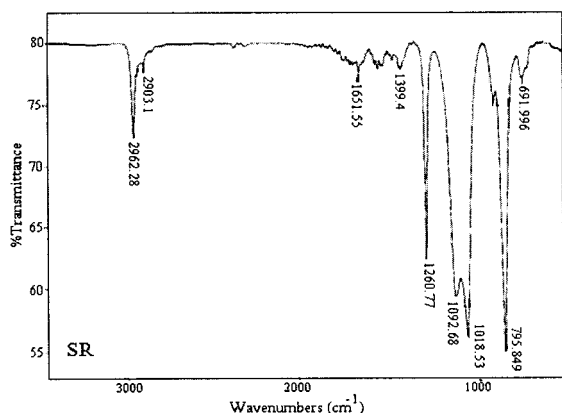


Figure 3 The FTIR-ATR spectra of the silicone rubber.

reacted with the vinyl group of silicone rubber chains and therefore formation of graft structure. It should be emphasized that the FTIR-ATR spectrum obtained from the extractable fraction (extraction by cold toluene and ethyl acetate) of the sample of LLDPE/SR blend was the same as observed for the unblended silicone rubber (Fig. 5). As hot toluene extraction performed on the LLDPE/SR (PE-3) blend confirmed the presence of silicone rubber gels (Fig. 5), we are led to the conclusion that silicone rubber has been simultaneously involved in both grafting and crosslinking reactions to yield a matrix-dispersed type of morphology, as shown in Figure 6(a). However, we can see a cocontinuous type of morphology for LLDPE/SR blend mixed at 135°C and 90 rpm [Fig. 6(b)].

Thermal characterization

The DSC thermograms of the HDPE and its associated blend are typically exhibited in Figure 7. Table IV also presents the thermal analysis data related to the different types of polyethylene and their related blend systems. It is clearly seen that reactive mixing of LLDPE and silicone rubber has led to the reduction in melting heat of fusion and therefore crystallinity of LLDPE compared with the LDPE/SR and HDPE/SR blend systems. This is suggested to be due to the inclusion of the soft and flexible silicone chains within the crystalline regimes and consequently decrease in the degree of crystallinity. On the contrary, the low interfacial reaction between the LDPE or HDPE and silicone rubber has not affected the crystallization behavior of LDPE and HDPE. These results are consistent with the low potential of these two polymers to yield graft structure with silicone rubber under thermomechanical mixing conditions.

Rheological properties

Variation of complex viscosity versus frequency obtained by RMS for the blend samples and their com-

ponents have been presented and compared in Figure 8. Non-Newtonian flow behaviors exhibited both HDPE and LDPE in the molten state at the studied range of frequency, whereas both LLDPE and SR show almost a Newtonian flow characteristic within the frequency range lower than 10 s^{-1} . It is also clearly observed that both HDPE/SR and LDPE/SR blend samples exhibit complex viscosity lower than that of the HDPE and LDPE, respectively, at the studied range of frequency, whereas the LLDPE/SR sample prepared at 220°C and 120 rpm mixing rate (PE-3) shows higher viscosity at low shear rates than that of

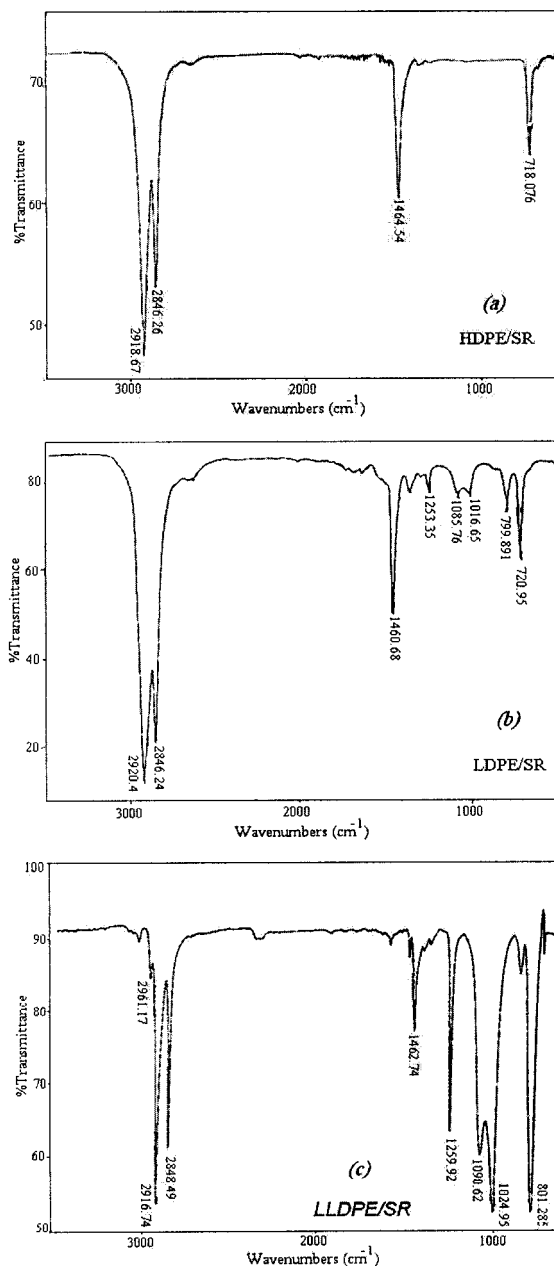


Figure 4 The FTIR-ATR spectra of solvent (cold toluene and refluxed ethyl acetate) extracted (a) HDPE/SR; (b) LDPE/SR; and (c) LLDPE/SR (PE-3) blend samples.

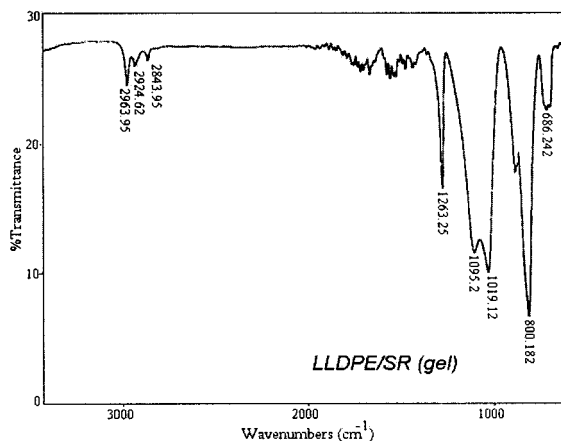


Figure 5 The FTIR-ATR spectra of the residual remained from the hot toluene extracted of LLDPE/SR (PE-3) blend sample.

unprocessed LLDPE. This is believed to be due to the formation of the agglomerate²⁴ structure by the dispersed SR particles that lead to more resistance of the blend to flow at low frequencies. However, as the shear rate increases, the agglomerates are broken, resulting in the reduction of the blend viscosity [Fig. 8(c)]. Moreover,

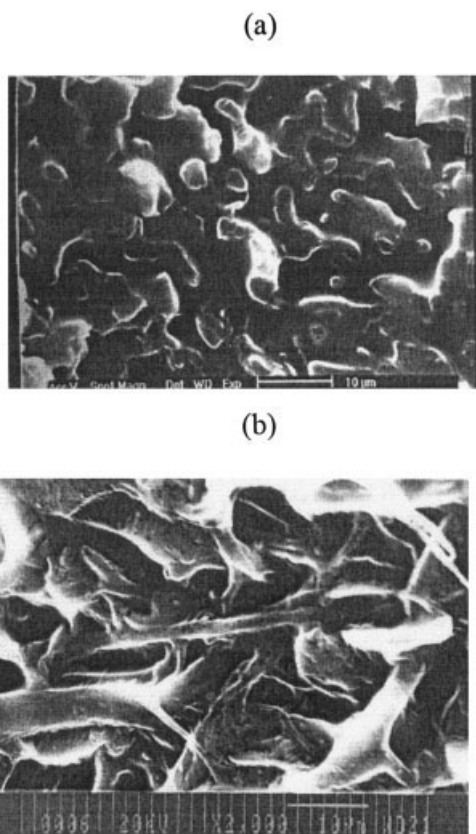


Figure 6 Scanning electron micrograph of LLDPE/SR blends prepared at (a) 220°C and 120 rpm; (b) 135°C and 90 rpm.

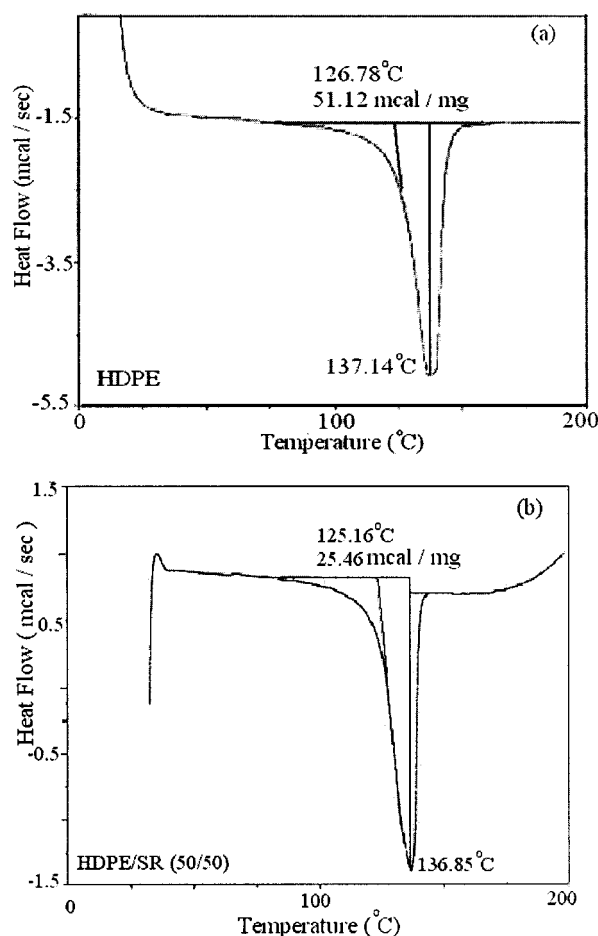


Figure 7 DSC thermogram of (a) HDPE and (b) HDPE/SR blend samples.

higher complex viscosity observed for the PE-4 blend sample at higher angular frequencies compared with the PE-3 sample [Fig. 8(c)] is suggested to be attributed to the occurrence of more scission by the LLDPE chains processed at higher temperature and mixing speed.

However, at angular frequencies lower than 10 s^{-1} , the PE-3 sample illustrates higher melt viscosity that is consistent with the networking of the grafted and dispersed silicone rubber particles. From these rheological results it can be concluded that only blending of LLDPE

TABLE IV
Heat of Fusion and Percentage of Crystallinity of Blend Samples and Their Components

Material	Heat of fusion (mcal/mg)	Crystallinity (%)
HDPE	51.2	77
HDPE/SR(PE-1)	25.46	76.6
LDPE	28.67	43
LDPE/SR(PE-2)	14.18	42.8
LLDPE	31.84	48
LLDPE/SR(PE-3)	13.32	40

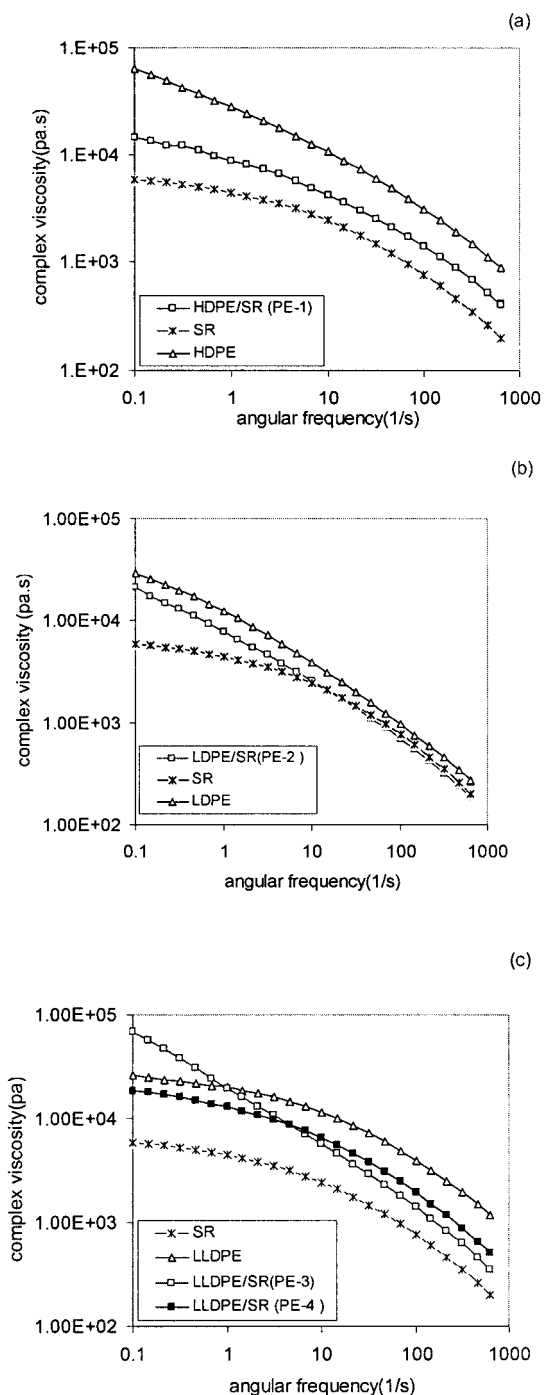


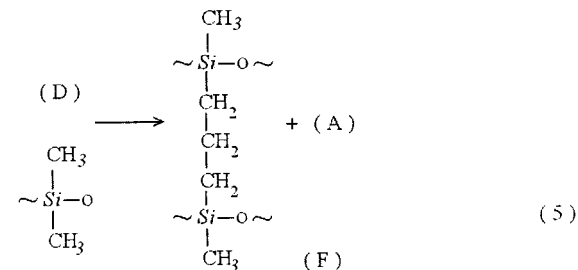
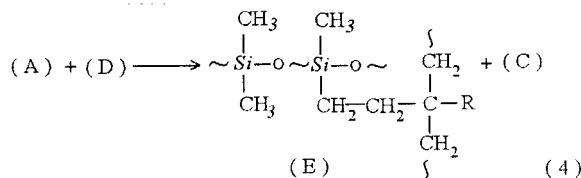
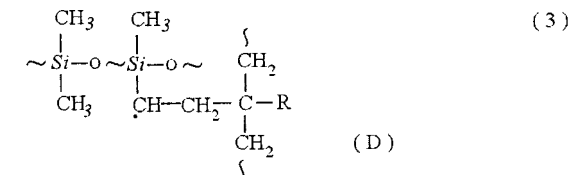
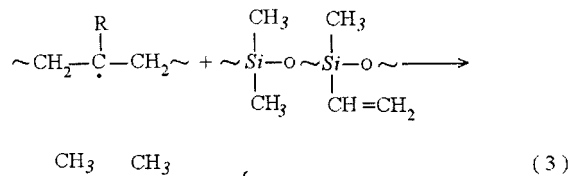
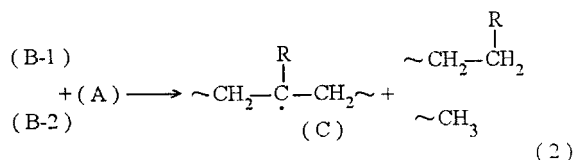
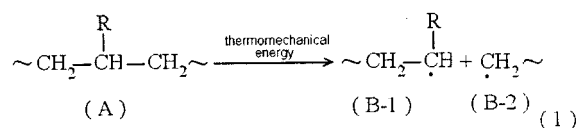
Figure 8 Variation of the complex viscosity versus angular frequency for different blend samples (a) HDPE/SR; (b) LDPE/SR; and(c) LLDPE/SR.

and silicone rubber at high temperature and high mixing speed would generate enough macroradicals to initiate both grafting and vulcanization of SR chains. This is in agreement with the results presented in Table III.

Probable mechanism for the interfacial reaction between LLDPE and silicone rubber

Based on the obtained results, the following mechanism is suggested by the authors for the thermomechanical

reactive mixing between LLDPE and silicone rubber. Under high shear mixing process, macroradicals are formed as a result of mechanical cleavage of the polyethylene chains. These macroradicals then react with the tertiary hydrogen present on the backbone of the adjacent chains, which yields to the formation of carbon radicals; these radicals can then undergo free-radical interaction with the unsaturated vinyl group attached to the SR chains. This would result in the formation of graft microstructure by the two polymers, as shown in eqs. (4) and (7) in Scheme 1. Grafting is also accompanied by crosslinking of the silicone rubber as shown in eqs. (5) and (6) in Scheme 1, leading to the development of a



Scheme 1

