Thermomechanical Reactive Blending of Silicone Rubber and LLDPE: Effects of Processing Parameters

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ABSTRACT: To prepare thermoplastic elastomers based on linear low density polyethylene (LLDPE) and silicone rubber (SR) the reactive blending of the two polymers was carried out at different processing conditions. Effects of mixing parameters such as temperature, shear rate, mixing time, and sequence of feeding the ingredients, upon the yield and rate of interfacial reaction, have been evaluated by following the variation of mixing torque and also by determination of the reacted fraction of silicone rubber. The yield and rate of the reaction increased by increasing the temperature of mixing, shear mixing rate, and the time of mixing. Changing the sequence of feeding the ingredients also changed the yield of the reaction. First feeding of polyethylene increased the yield of reaction. According to the obtained results, interfacial reaction between two phases is limited by chemical kinetics of the reaction and by rate of mass transfer during melt mixing. The order of interfacial reaction between these two polymers under thermomechanical conditions was found to be about 1.1. Rheological studies on the blends performed by using rheomechanical spectroscopy showed a distinct rheological behavior with a non-Newtonian characteristic and higher dynamic viscosity at low frequencies for the blends prepared at high temperature and shear rate. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 155–161, 2005

Key words: reactive blending; thermoplastic elastomer; polyethylene; silicone rubber; processing

INTRODUCTION

Polymer blends composed of incompatible polymers form a two-phase system with poor physical and mechanical properties due to the weak interfacial adhesion at their interface. To improve interfacial interaction, and therefore compatibility, *in situ* reactive mixing of the two polymeric phases has been shown to be one of the most effective ways of compatiblization.[1–4] The interaction between the component phases may however be brought by the addition of an agent that interacts with both phases and renders them mutually compatible[1,5–7] or by specific reactions between the two phases.[5,8–13] Occurrence of the reaction between the two polymeric components at their interface is expected to lead to the reduction in interfacial tension. Several factors directly influence the extent of the reaction that happens, including intensity and time of mixing, functionality level, and kinetics of reactive groups, and stability of the covalent bonds to the processing condition.[1,2,14,15]

Blends of polyethylene and silicone rubber can be used for various purposes because of the unique properties of its components. Silicone rubber offers long service life at moderate operating temperature. There is no better flexible electrical insulation than silicone rubber. Silicone rubber has extreme resistance to ozone and corona and its biocompatibility is excellent.[16–19] The use of polyethylene is important because of its easy processing and nontoxicity.

In previous work[20] we showed that linear low density polyethylene (LLDPE) has a large number of C–H bonds weak enough to be broken through the thermomechanical reactive mixing process, so LLDPE has potential for the generation of active free radical sites on the backbone of its chains for being reacted with vinyl groups of the silicone rubber, resulting in grafting as well as crosslinking of the silicone rubber chains during melt mixing of the two polymers. In this work we carried out the melt mixing of silicone rubber and LLDPE at different processing conditions and investigated the effectiveness of the processing parameters such as temperature, speed of rotor, the sequence of feeding the ingredients into the mixer, and time of mixing on the interfacial reaction between the two polymers and determined the order of the reaction. We studied the microstructure of the prepared blends by scanning electron microscopy (SEM). The melt processing behavior of the blends has also been investigated through measuring of torque variation during melt mixing and by rheomechanical spectroscopy (RMS).

TABLE I
Blends Composition and Processing Conditions of Thermomechanical Reaction Between Silicone Rubber (SR) and
Linear Low Density Polyethylene (LLDPE)

No.	Blend code[a]	Composition (LLDPE/SR)	Speed of rotor(rpm)	Temperature (°C)	Mixing time (min)	Order of addition
1	S50501	50/50	60	200	Up to steady condition (ca. 15 min)	LLDPE, SR
2	S50502	50/50	90	200	Up to steady condition (ca. 15 min)	LLDPE, SR
3	S50503	50/50	120	200	Up to steady condition (ca. 15 min)	LLDPE, SR
4	S70301	70/30	40	135	Up to steady condition (ca. 15 min)	LLDPE, SR
5	S70302	70/30	60	135	Up to steady condition (ca. 15 min)	LLDPE, SR
6	S70303	70/30	90	135	Up to steady condition (ca. 15 min)	LLDPE, SR
7	S70304	70/30	120	135	Up to steady condition (ca. 15 min)	LLDPE, SR
8	T50501	50/50	90	135	Up to steady condition (ca. 15 min)	LLDPE, SR
9	T50502	50/50	120	160	Up to steady condition (ca. 15 min)	LLDPE, SR
10	T50503	50/50	120	180	Up to steady condition (ca. 15 min)	LLDPE, SR
11	T50504	50/50	120	200	Up to steady condition (ca. 15 min)	LLDPE, SR
12	T50505	50/50	120	220	Up to steady condition (ca. 15 min)	LLDPE, SR
13	T70301	70/30	60	135	Up to steady condition (ca. 15 min)	LLDPE, SR
14	T70302	70/30	60	160	Up to steady condition (ca. 15 min)	LLDPE, SR
15	T70303	70/30	60	200	Up to steady condition (ca. 15 min)	LLDPE, SR
16	F50501	50/50	120	220	Up to steady condition (ca. 15 min)	SR, LLDPE
17	F50502	50/50	120	220	Up to steady condition (ca. 15 min)	LLDPE, SR
18	M50501	50/50	120	220	3	LLDPE, SR
19	M50502	50/50	120	220	3.7	LLDPE, SR
20	M50503	50/50	120	220	4.5	LLDPE, SR
21	M50504	50/50	120	220	6	LLDPE, SR
22	M50505	50/50	120	220	13	LLDPE, SR

[a] S, speed of rotor; T, time of mixing; F, feeding sequence of ingredients into the mixer; M, mixing time.

EXPERIMENTAL

Materials

LLDPE (melt flow index: 0.86 at 190°C and 2.16 kg; Density: 0.9 g cm^{-3}) was obtained from Iranian Petrochemical Industry. Silicon rubber as SR110–3 (PDMS with 8×10^5 g mol^{-1} M_w and containing 0.16 mol % of methylvinylsiloxane groups) was supplied by Chinese Chenguang Company. 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 the processing conditions employed for their preparation are given in Table I. All blends were mixed in an internal mixer model Brabender W50 made in Germany with a fill factor (0.85). For the preparation of the blends, except blend No.16 (F50501), polyethylene was first fed in to the mixer and allowed to melt, followed by the addition of silicone rubber. To prepare blend No.16 (F50501), silicone rubber was the first ingredient fed into the mixer. Mixing time for most of runs was about 15 min. On completion of mixing the samples were rapidly removed and quenched in cold water to prevent further thermal oxidation. Variation of the torque as a function of time was also followed.

Yield of the reaction

To determine yield of the reaction, 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 expression:

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

where W_0 and W_1 denote the initial and final weight of the specimen, respectively.

Morphological studies

Morphological studies on the various blends were carried out by using 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

A 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
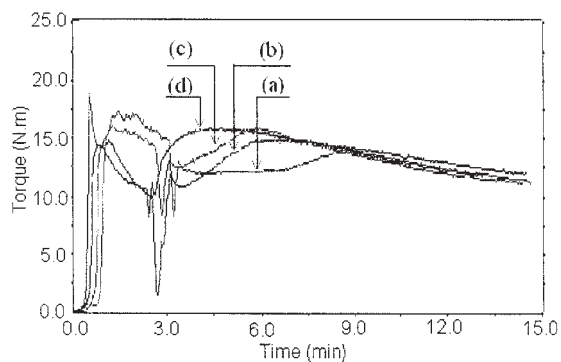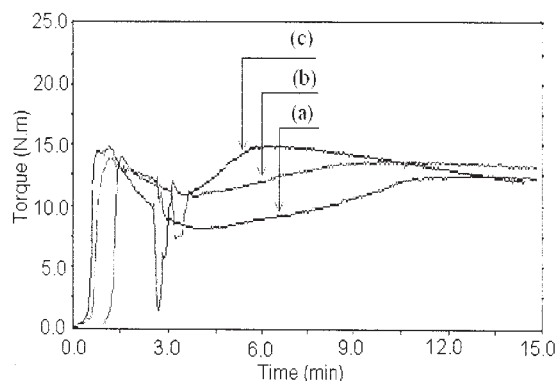
Figure 1 Variation of torque versus mixing time during thermomechanical mixing of LLDPE and SR (50/50, wt : wt) at rotor speed of 120 rpm and mixing temperatures (a)160°C, (b) 180°C, (c) 200°C, (d) 220°C.

TABLE II
The Insoluble Percentage of Silicon Rubber of LLDPE/ SR Blend Samples Prepared by Thermomechanical Mixing Process

No.	Blend code	Insoluble SR (%)	No.	Blend code	Insoluble SR (%)
1	S50501	12	12	T50505	25.5
2	S50502	15	13	T70301	6
3	S50503	25	14	T70302	20
4	S70301	4	15	T70303	23
5	S70302	6	16	F50501	10.8
6	S70303	10.5	17	F50502	25.5
7	S70304	12	18	M50501	0
8	T50501	5	19	M50502	4
9	T50502	16	20	M50503	6.5
10	T50503	23	21	M50504	15
11	T50504	25	22	M50505	25.5

changes in the sample morphology, and the experiment was carried out by use of a 25-mm-diameter parallel plate with 1-mm gap and the strain set at 0.1.

RESULTS AND DISCUSSION

Figures 1 and 2 exhibit the effects of mixing temperature and shear rate upon the mixing torque of LLDPE and SR (50/50, wt : wt), respectively. It can be observed that the torque rises significantly after initial mixing of the two polymers, which indicates the occurrence of the reaction between LLDPE and silicone rubber. In Figure 1 the mixing torque reached a higher level as the initial temperature of mixing increased to 220°C, suggesting the interfacial reaction between these two polymers is activated by the increase of temperature due to the catalytic effect of temperature upon the cleavage of C–H bonds on the LLDPE chains. This would result in the increase of the reaction yield, obtained by measuring the insoluble fraction of silicone rubber from the blend system after being thermomechanically mixed, through solvent extraction in

cold toluene for 48 h followed by refluxing with ethyl acetate for 10 h as exhibited in both Table II (blends 8–12) and Figure 3(a). The increase in the yield of reaction was also observed at the 70/30 (wt : wt) ratio of the two phases, mixed at 60 rpm as given in Figure 3(b) and Table II (blends 13–15). The route of feeding of LLDPE and SR into the mixer was found to influence the graft yield as presented in Table II (blends 16 and 17) and Figure 4. Comparison between the percent insoluble silicone rubbers, measured for the blend samples 16 and 17 with the ratio of 50/50, shows that the yield of the interfacial reaction between the two polymers and therefore the percent of insoluble silicone rubber increases significantly by the first feeding of polyethylene. This is due to the higher generation of radical sites on the backbone of LLDPE. From these results one would conclude that reaction between SR and LLDPE is controlled by the chemical kinetics of the reaction.

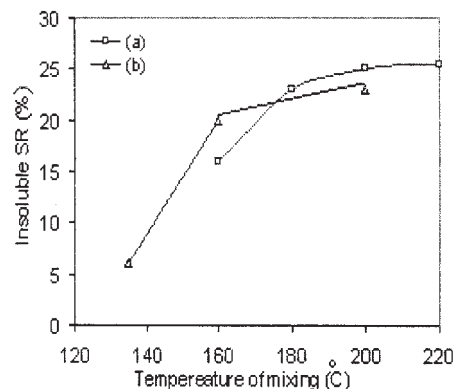It is clearly seen in Figure 2 that, for the samples prepared at 60 and 90 rpm, the mixing torque gradu-

Figure 2 Variation of torque versus mixing time during thermomechanical mixing of LLDPE and SR (50/50, wt : wt) at 200°C and rotor speeds (a) 60 rpm, (b) 90 rpm, (c) 120 rpm.

Figure 3 Effects of the mixing temperature upon the interfacial reaction in LLDPE/SR blends: (a) 50/50 mixed at 120 rpm rotor speed; (b) 70/30 mixed at 60 rpm rotor speed.
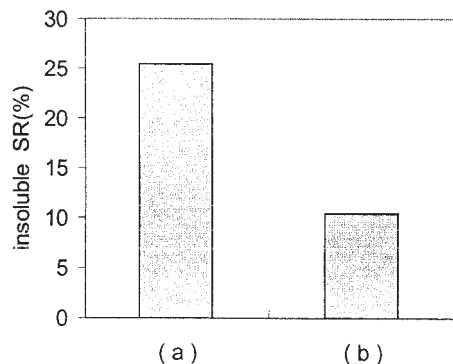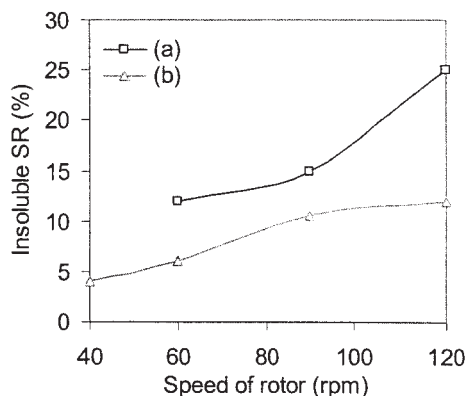
Figure 4 Effects of the feeding sequence of the ingredients into the mixer upon the thermomechanical reaction between LLDPE and SR (50/50) mixed at 220°C and rotor speed of 120 rpm. (a) LLDPE was fed first; (b) SR was fed first.
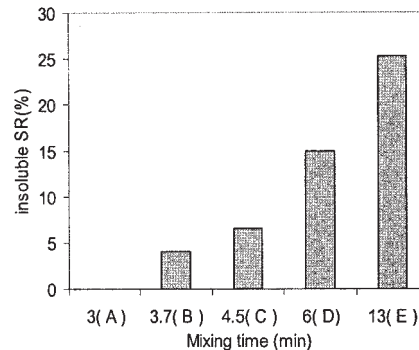

Figure 6 Effects of time of mixing upon the interfacial reaction in LLDPE/SR (50/50) mixed at 220°C and 120 rpm rotor speed (blends 18–22).

ally increases until a mixing time of 12 min and then reaches a constant level, while at 120 rpm the torque decreases after 6 min. This leads to the conclusion that, at a higher mixing rate, the chemical reaction occurs faster as a result of higher macroradicals generated during mixing.

In accordance with Figure 2, the rate and also the yield of the interfacial reaction between SR and LL-DPE are dependent on the shear mixing rate and both of them have been increased by increasing the mixing rate. These conclusions are supported by Table II (blends 1–3) and curve (a) shown in Figure 5. The same results were obtained for the LLDPE/SR (70/30) blend mixed at 135°C and a different rotor speed as shown in Table II (blends 4–7) and Figure 5(b). Therefore we can conclude that the interfacial reaction between the two polymers is not only controlled by the chemical kinetics but also by mass transfer considerations (mixing speed).

To study the effects of mixing time on the reaction, LLDPE and SR with the ratio of 50/50 (wt : wt)

were mixed at a temperature of 220°C, rotor speed of 120 rpm, and different times (blends 18–22). Figure 6 shows the variation of the insoluble fraction of silicone rubber versus time of mixing for these blends and Figure 7 represents the state of mixing of these blends. As we observe (Fig. 6), the amount of the reacted silicone rubber increases with an increase in mixing time. Comparison of the results shown in Figures 6 and 7 indicates that the reaction continued even after the mixing torque was decreased. The increasing of the mixing torque after stage A is related to the formation of an agglomerate structure due to the crosslinking of silicone rubber proceeding during melt mixing. Above a certain degree of reaction the agglomerate structure breaks down and the mixing torque decreases. In accordance with the obtained results in this work, the decreasing rate of mixing torque depends upon the balance between the rate of reaction and the rate of agglomerate structure breakdown.

The fracture surface observation of the LLDPE/SR (50/50) blend mixed at 135°C [Fig. 8(a)] showed a cocontinuous type of morphology. However, as we
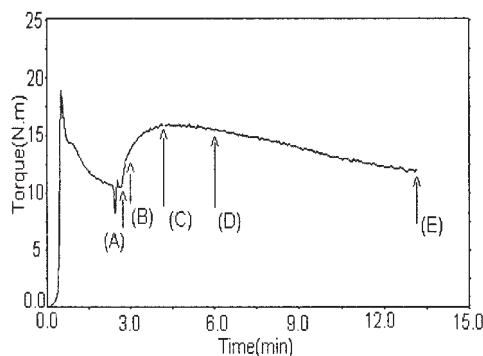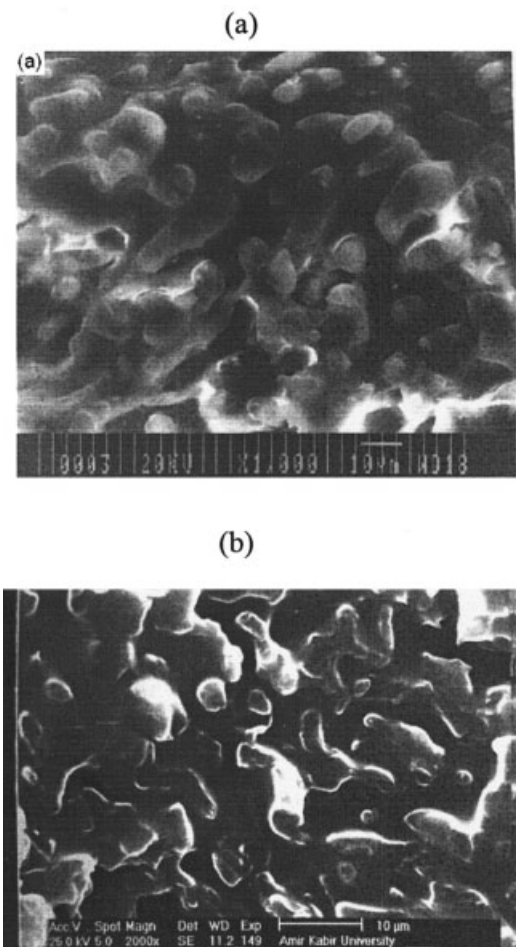

Figure 5 Effects of the mixing speed upon the interfacial reaction between LLDPE and silicone rubber: (a) 50/50 mixed at 200°C (b) 70/30 mixed at 135°C.

Figure 7 Variation of torque versus time for LLDPE/SR (50/50) blends prepared at 220°C and rotor speed of 120 rpm.(a), (b), (c), (d), and (e) represent the state of mixing for the blends of Figure 6.
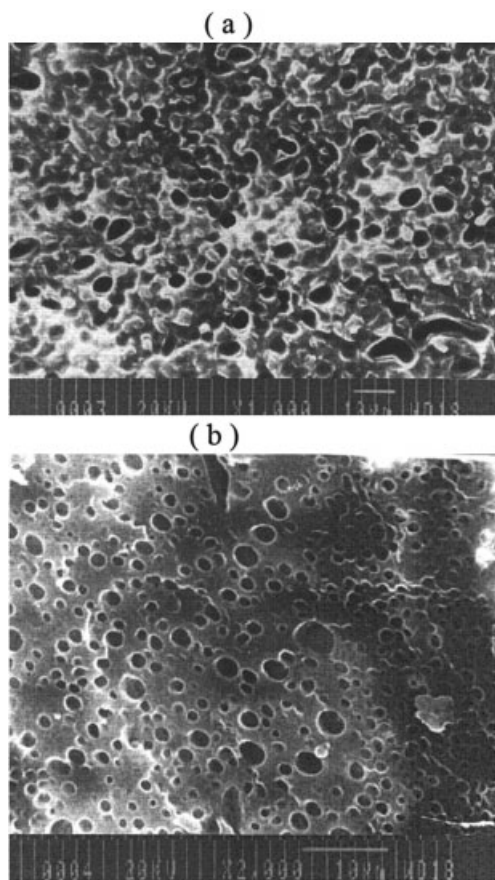
(a)

(b)

Figure 8 Scanning electron micrograph of LLDPE/SR (50/50) blends prepared at (a) 135°C and 90 rpm and (b) 220°C and 120 rpm.


(a)

(b)

Figure 9 Scanning electron micrograph of LLDPE/SR (70/30) blends prepared at 135°C and 60 rpm (a) before etching and (b) after etching the specimen with cold toluene.

can see a matrix-dispersed type of morphology [Fig. 8(b)] for the LLDPE/SR (50/50) blend mixed at 220°C, we are led to the conclusion that silicone rubber has simultaneously involved in both grafting and crosslinking reactions leading to the development of a matrix-dispersed morphology similar to the dynamically cured thermoplastic elastomers. Figures 9 and 10 show the SEM micrographs for LLDPE/SR (70/30, wt : wt) blends mixed at 135 and 160°C, respectively. We can see a matrix-dispersed type of morphology for both of them; however, by increasing the temperature of mixing, more SR particles appeared to be covered with the PE due to increase of the yield of reaction. The covered particles suggest that LLDPE–SR graft copolymers are produced on the interface during the melt mixing.

Kinetics

There is no easy method for evaluating the kinetics of interfacial reaction between blend components. When the torque in a batch mixer reaches a steady state it may be assumed that the interfacial reaction has been completed.[2] The increase in the torque with mixing time (dT/dt) under a given condition may be expressed as

$$dT/dt = k(T_\infty - T)^n \qquad (1)$$

Equation (1) reduces to eq. (2) on integration
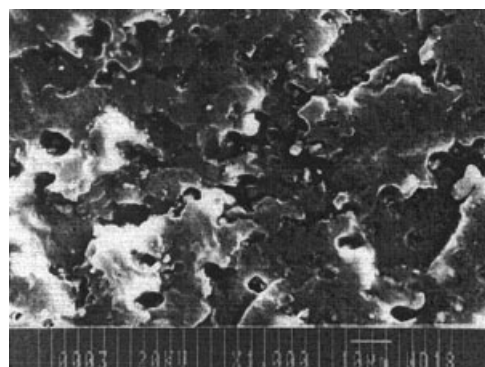
Figure 10 Scanning electron micrograph of LLDPE/SR (70/30) blend prepared at 160°C and 60 rpm.

$$(-n+1)\ln(T_\infty - T) = \ln[(n-1)k] + \ln t \quad (2)$$

where T is the torque at time t; k is the specific rate constant; T_∞ is the torque of mixing when the reaction comes to the end, and n is the order of the reaction.

Plotting of $\ln(T_\infty - T)$ versus $\ln t$ leads to the determination of the specific rate constant through measurement of its slope. The value of the order of reaction between LLDPE and SR (n) determined for the LLDPE/SR (50/50, T50505) blend was 1.1.

Rheological properties

Variation of complex viscosity versus frequency obtained by RMS for some of the sample blends has been presented and compared in Figures 11 and 12. As shown in Figure 11, the LLDPE/SR (50/50) blend sample prepared at 220°C and a mixing rate of 120 rpm presents a non-Newtonian flow behavior with the higher viscosity at lower frequency than that of LLDPE/SR (50/50) blend prepared at 135°C and 90 rpm. It is believed that, under high temperature and shear mixing process, free radicals are formed on the backbone of the LLDPE chains that can undergo free radical interaction with unsaturated vinyl groups attached to the SR chains. This would result in both grafting and crosslinking of silicone rubber during melt mixing, leading to the formation of the agglomerate structure by the dispersed SR particles. Therefore, the blend shows more resistance to flow at low frequencies. However, as the shear rate increases, the agglomerates are broken, resulting in the reduction of the blend viscosity. Figure 12 shows similar result for the LLDPE/SR (70/30) blend sample, however, the generation of macroradicals during melt mixing at 160°C is not sufficient to produce enough agglomerate structure to resist the flow at low frequencies.
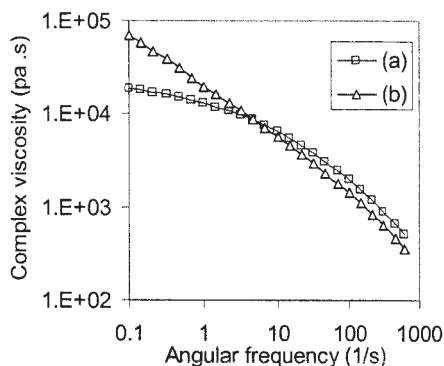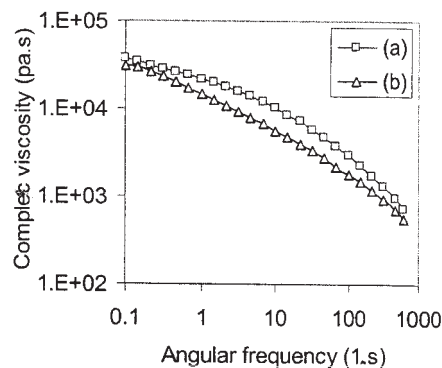
Figure 12 Variation of complex viscosity versus angular frequency of LLDPE/SR (70/30) blend samples mixed at (a) 135°C and 60 rpm and (b) 160°C and 60 rpm.

CONCLUSION

Results obtained lead us to the conclusion that blending of LLDPE and silicone rubber under a thermomechanical mixing process would generate macroradicals on the backbone of polyethylene chains as well as the formation of a matrix-dispersed type of morphology in which the rubber phase is dispersed in the form of agglomerates or aggregates. Above a certain degree of reaction the network structure formed during melt mixing breaks down, which results in the decrease of the mixing torque. The rate of the mixing torque reduction depends upon the balance between the rate of reaction and rate of disagglomeration.

The yield of the reaction between silicone rubber and linear low density polyethylene is dependent on the temperature of mixing, the sequence of feeding the ingredients, and also on the mixing shear rate. Therefore, reaction is limited by chemical kinetics as well as mass transfer with the reaction order of about 1.1 under the mentioned processing conditions.

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Figure 11 Variation of complex viscosity versus angular frequency for LLDPE/SR (50/50) blend samples mixed at (a) 135°C and 90 rpm and (b) 220°C and 120 rpm.

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