Silica-Reinforced Dynamically Vulcanized Ethylene–Propylene–Diene Monomer/Polypropylene Thermoplastic Elastomers: Morphology, Rheology, and Dynamic Mechanical Properties

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ABSTRACT: Attempts were made to prepare dynamically crosslinked ethylene–propylene–diene monomer/polypropylene (EPDM/PP, 60/40 w/w) blends loaded with various amounts of silica as a particulate reinforcing agent. The dispersion of silica between the two phases under mixing conditions, and also extent of interaction, as the two main factors that influence the blend morphology were studied by scanning electron microscopy. Increasing the silica concentration led to the formation of large-size EPDM aggregates shelled by a layer of PP. Dynamic mechanical thermal analysis performed on the dynamically cured silica-loaded blend samples showed reduction in damping behavior with increasing silica content. Higher rubbery-like characteristics under tensile load were exhibited by the silica-filled EPDM/PP-cured blends. However, increasing the silica level to 50 phr led to the enhancement of interface, evidenced by increases in the tensile modulus and extensibility of the blend compared with those of the unloaded sample. Addition of a silane coupling agent (Si69) into the mix improved the mechanical properties of the blend, attributed to the strengthening of interfacial adhesion between the PP matrix and silica-filled EPDM phase. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2000–2007, 2004

Key words: thermoplastics; dynamic vulcanization; silicas; morphology; rheology

INTRODUCTION

Dynamically vulcanized thermoplastic elastomers (TPVs) based on polypropylene (PP) and ethylene–propylene–diene monomer (EPDM) have gained considerable attention because of the structural compatibility of these two polymers and a number of reports have been published dealing with the dynamic mechanical properties, morphology, and rheological behavior of these types of polymeric materials.[1–10]

Because the type of morphology plays a very significant role in controlling all the characteristics of TPVs, research has been focused during the last few years on the mechanism that microstructure is developed from the early stage of blending until the end of the mixing process, especially during the vulcanization stage, as well as the parameters affecting the interface between the two phases. In their recent work, Katbab et al.[8] discussed the formation of matrix dispersed type of morphology in dynamically vulcanized EPDM/PP thermoplastic elastomers and showed that the rubber phase is dispersed throughout the PP matrix in the form of aggregates covered by a layer of PP.

They also correlated the degree of rubber particle networking to the viscoelastic and mechanical properties of the blend. However, little has been reported in the literature dealing with the reinforcement of dynamically crosslinked thermoplastic elastomers. In our previously published work, the effects of the addition of carbon black as reinforcing agent on the morphology of a dynamically crosslinked EPDM/PP blend system were discussed. Nevertheless, sufficient information is still needed to be able to interpret the obtained results.[3] The distribution state of the filler particles between the two phases, extent of interaction of the filler surface with either of the polymeric phases, and thus the final phase morphology are believed to be the most important factors affecting the overall properties of the final blends. However, there are many factors that control the filler distribution. These include the affinity of filler toward the polymeric phases, viscosity ratio of the polymers, and feeding routes.[11]

In the present work, dynamically cured EPDM/PP (60/40) blends loaded with various amounts of silica (SiO_2) as surface active particulate filler were prepared. Distribution of the silica between the two polymeric phases under melt-mixing conditions and its effect on the interface and dynamically vulcanized blend morphology were followed by means of scanning electron microscopy (SEM) and mixing torque time graphs as well as studying the tensile properties

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TABLE I
Characteristics of the Used Materials

Material	Characteristics		Source
PP	MFI (2.160/230):	6 g/10 min	Iran Petrochemical Co.
	Crystallinity:	38%	Bandar Imam Khomaini
	Melting point	163°C	
EPDM	Mooney viscosity ML(1+4)125:	25	DSM
	Ethylene content:	55%	
	ENB content:	8%	
Silica	Ultrasil VN3		Degussa Huls Corp.
Coupling agent	TESPT (Si69)		Degussa Huls Corp.
Curing agents	Sulfur, TMTD, MBTS, ZnO, stearic acid		

and viscoelastic behavior of the final dumped blend samples.

EXPERIMENTAL

Materials

Table I lists the main characteristics of the polymers and other materials used in this work. An injection-grade PP and a low Mooney long chain branch (LCB) EPDM were used in this study. The silica was a precipitated-type ultrasil VN3 prepared by Degussa Huls Corp. (Frankfurt, Germany). Specifications of the other materials are also given in this table.

Blend preparation

Preparation of the simple and vulcanized EPDM/PP (60/40, w/w) blends composed of various amounts of silica was carried out in a 60-cm^3 Brabender plasticorder (PL 2200) with a Banbury-type rotor at an initial temperature of 175°C and rotor speed of 80 rpm. For this purpose, the premasticated EPDM rubber and silica were fed into the running mixer and after 4 min the PP was added and the mixing was continued for 3 min. To study the morphology of the

blend in the molten state, a small sample was removed from the hot running mix by the method described by Coran et al.[5,6] The removed samples were quenched immediately in cooled water ($\sim$ 0°C). To prepare dynamically vulcanized blends, a sulfur curing system was added into the mix 4–6 min after the addition of PP and then the blend was discharged 2–3 min after attaining maximum torque. The recipes and nomenclature of the blends are given in Table II.

Blend characterization

Morphological studies

To study the developed morphology of the uncured and dynamically crosslinked blends, scanning electron microscopy (SEM) examination was performed on the cryofractured gold-coated surfaces by the use of an Oxford scanning electron microscope. In the case of simple uncured blend samples the fractured surfaces were etched by n-heptane at room temperature for 24 h to remove the EPDM phase, whereas the fractured surfaces of the dynamically vulcanized blends were etched by boiling xylene vapor for 30 s to remove the PP.

TABLE II
Recipes of the Blends[a]

Sample	EPDM	PP	ZnO	Stearic acid	Silica	DEG	TMTD	MBTS	Sulfur
EP0	100	—	5	1	—	—	1	0.5	2
EP1	100	—	5	1	20	—	1	0.5	2
EP2	100	—	5	1	20	1	1	0.5	2
EP3	100	—	5	1	20	2	1	0.5	2
EP4	100	—	5	1	40	4	1	0.5	2
CF0	100	66.7	5	1	—	—	1	0.5	2
CF1	100	66.7	5	1	10	1	1	0.5	2
CF2	100	66.7	5	1	20	2	1	0.5	2
CF3	100	66.7	5	1	30	3	1	0.5	2
CF4	100	66.7	5	1	40	4	1	0.5	2
CF5	100	66.7	5	1	50	5	1	0.5	2

[a] C and F: cured blends (C), filled blends (F), respectively.

Rheological studies

Disks of 25 mm diameter were cut from compression-molded sheets for rheological measurements. A gap of at least 1 mm was used in all measurements. Rheological behavior of the molten blends was measured by rheometer spectroscopy (RMS) at 220°C and frequency range of 0.1–1000 Hz. All the experimental data reported here were obtained at 1% strain.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA, model PL; Surrey, UK) was used to study the viscoelastic behavior of the blends with the bending mode and strain amplitude of 0.002 cm and at 1-Hz frequency. The samples were scanned within the temperature range of −100 to 100°C at a heating rate of 5°C/min.

Differential scanning calorimetry

Thermal characterization and melting points of the blends were studied by differential scanning calorimetry (DSC; model 2010, TA Instruments, New Castle, DE). For this purpose 8–9 mg of each sample was thermally scanned within the temperature range of 0–250°C at a heating rate of 10°C/min.

The percentage of crystallinity X (%) was evaluated using the following expression:

$$X(\%) = \frac{\Delta H_f}{\omega \Delta H^*} \times 100$$

where ΔH_f and ΔH^* represent the heat of fusion of the blend sample obtained from the DSC diagram and 100% crystalline PP (209 J/g),[12] respectively; and ω is the weight fraction of polypropylene in the blend sample.

Mechanical properties

To measure the tensile properties of the prepared blends, dumbbell-shape specimens with dimensions according to ASTM D412 and thickness of 2 mm were cut from the compression-molded sheet of each blend, and tested at room temperature and a crosshead speed of 50 mm/min.

RESULTS AND DISCUSSION

Figure 1 compares the curing behavior of EPDM compounds consisting of various amounts of silica and diethylene glycol (DEG). It can be seen that in the absence of DEG the cure characteristics of the compounds are influenced by the silica filler, attributed to the absorption of an accelerated sulfur curing system on the active surface of silica, which leads to the
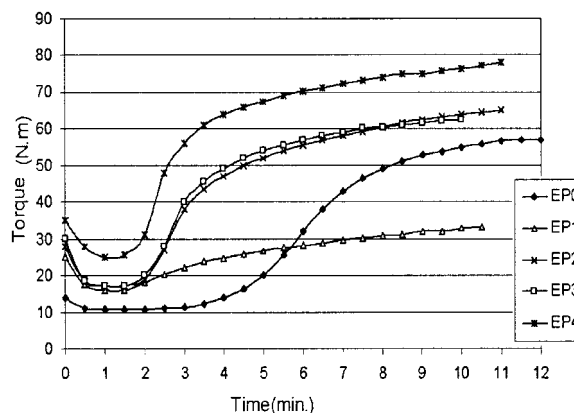

Figure 1 Effects of silica (SiO$_2$) and diethylene glycol (DEG) on the curing characteristics of EPDM.

retardation of crosslinking reaction. As may be observed in Figure 1, the presence of 2 phr DEG in the EPDM compound composed of 20 phr silica increased the curing rate and the delta torque ($T_{\max} - T_{\min}$) of EPDM. Therefore, one can conclude that addition of DEG into the silica-filled EPDM/PP blend system would lead to the enhancement of crosslink density and hence the interface between the two phases. Figures 2 and 3 schematically present the variation of the mixing torque from the early stage of mixing until the end of dynamic vulcanization (stage C) for unfilled and silica-filled blend samples (stage D), respectively. In Figure 3, four distinct mixing intervals can be clearly observed for each curve. In stage C, the silica-loaded blends are uncured and the mixing torque remains constant until the onset of the vulcanization reaction (stage D). Different behavior is exhibited in stage D by the blends filled with various amount of silica, compared with the unfilled sample. Blend samples composed of 10 to 20 phr silica exhibited a lower mixing torque level than that of the unloaded sample (CF0) during dynamic vulcanization. This is explained to be partly attributed to the retardation of the crosslink formation in the dispersed EPDM rubber particles during the vulcanization stage of silica-filled blend samples (CF1, CF2). However, as the concentration of silica increased to 50 phr (CF5) the torque peak maximum achieved a higher level. This is proposed to be attributable to the increase in the stiffness of rubber particles as well as their surface tension by the high concentration of silanol groups, which facilitates their attachment at the early stage of vulcanization leading to the development of strong rubber aggregates attached to the matrix through the adsorbed PP shell. These results are consistent with the observed morphology for the dynamically crosslinked EPDM/PP blends filled with silica as shown in Figure 4. It is clearly seen from the presented micrographs that as the percentage of silica increases, larger-size PP
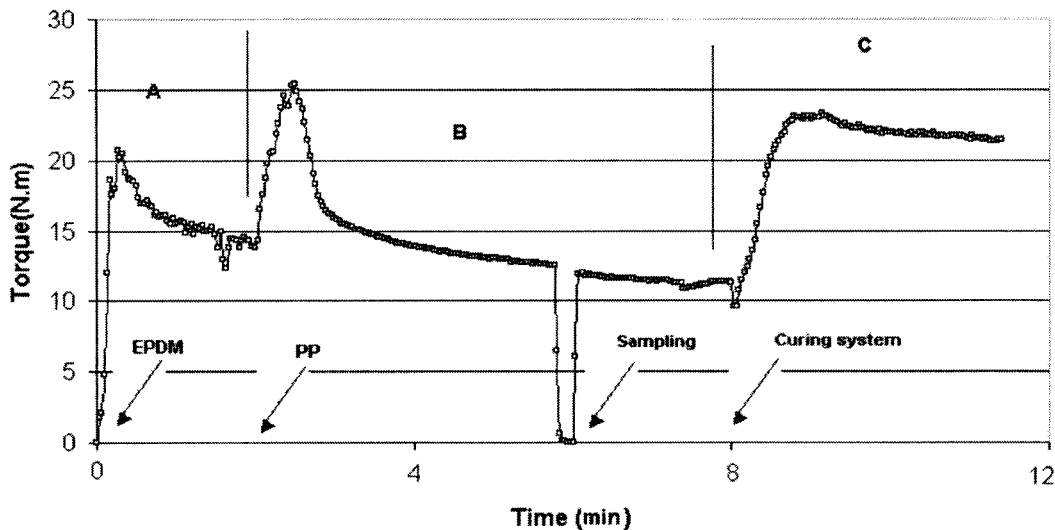
Figure 2 Mixing torque–time graph of the dynamically vulcanized EPDM/PP (60/40) blend.

shelled rubber aggregates are developed with a greater tendency to form agglomerates or network structure by joint shell mechanism.[13]

SEM photomicrographs of the filled blends removed from the hot running mixer in stage C before the onset of vulcanization are also given in Figure 5. As may be observed in this figure, the size of the dispersed rubber phase, appearing as black spots, increases with increasing the amount of silica in the blend composition. This is explained to be attributed to the increase of the EPDM/PP viscosity ratio and weak interfacial interaction between the PP and

EPDM, which results in the formation of large-size rubber droplets.[14,15] To verify these results, DMTA was performed on the dynamically crosslinked silica-loaded samples, as illustrated in Figure 6. It is evident from this figure that damping characteristics of the dynamically crosslinked EPDM/PP blend sample within the glass-transition temperature of both rubber and PP decreases with increasing the silica content. Reduction in the damping behavior within the rubber-transition temperature (−40 to −20°C) exhibited by the CF3 and CF5 blends is explained to be attributed to the higher filler–polymer interaction through surface
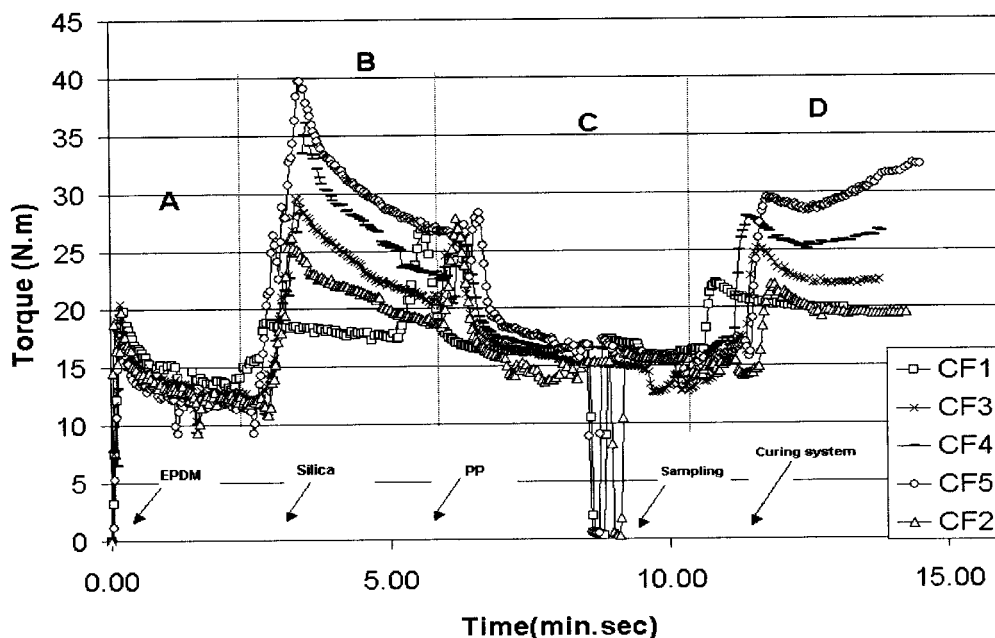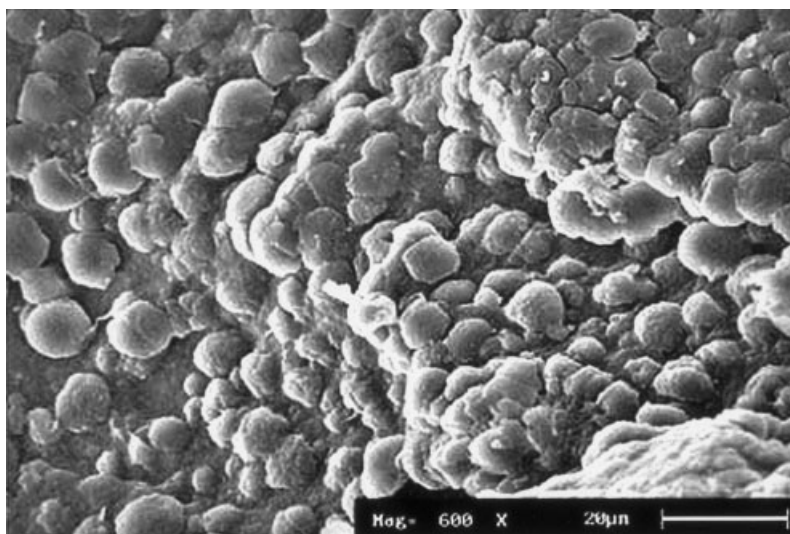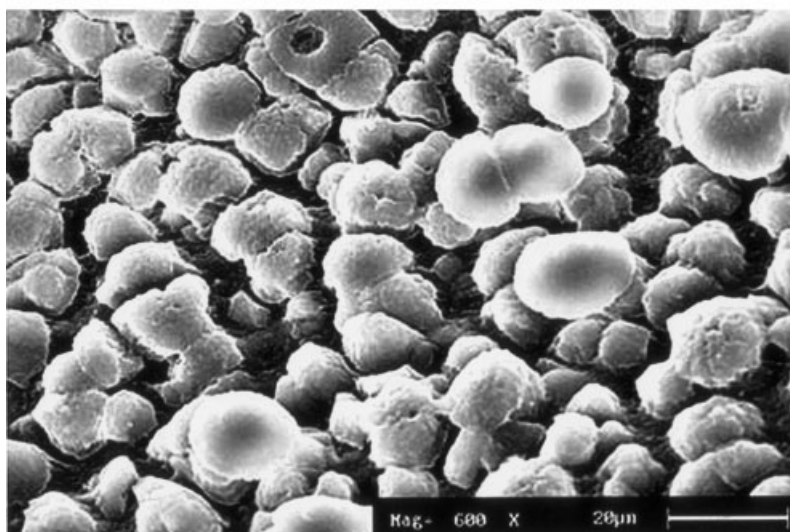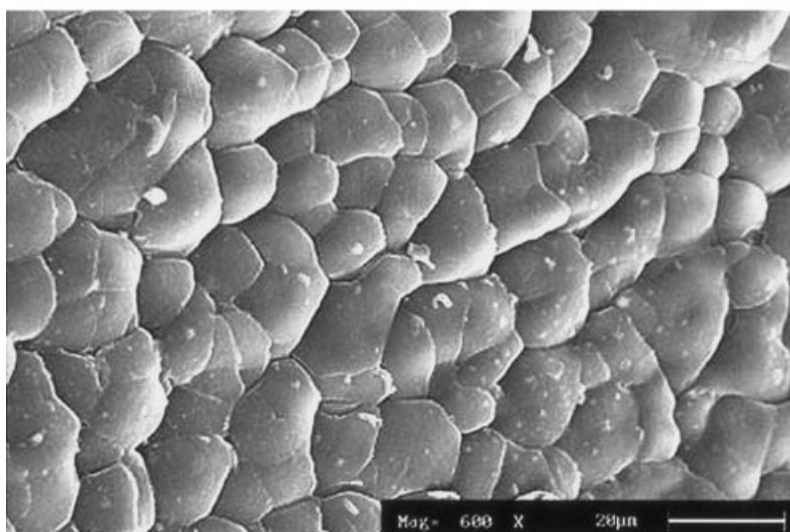

Figure 3 Mixing torque–time graphs of the dynamically vulcanized EPDM/PP (60/40) blends filled with various amounts of silica: CF1: 10 phr; CF2: 20 phr; CF3: 30 phr; CF4: 40 phr; CF5: 50 phr silica. Silica was first premixed with EPDM.
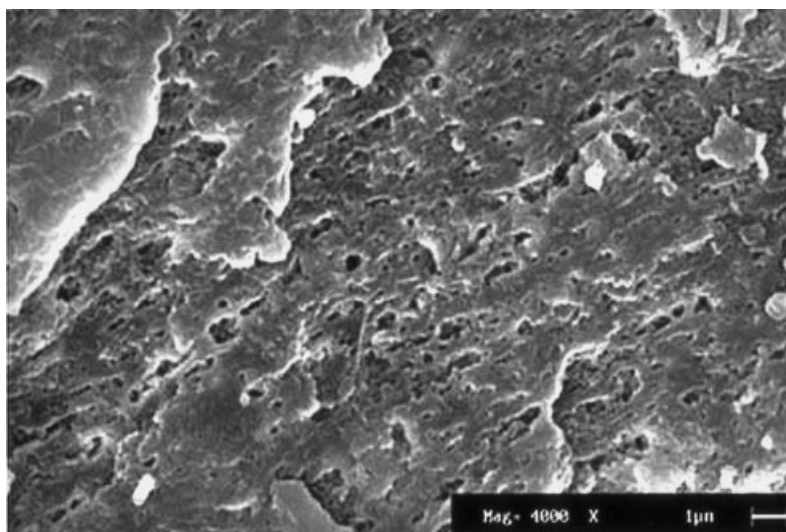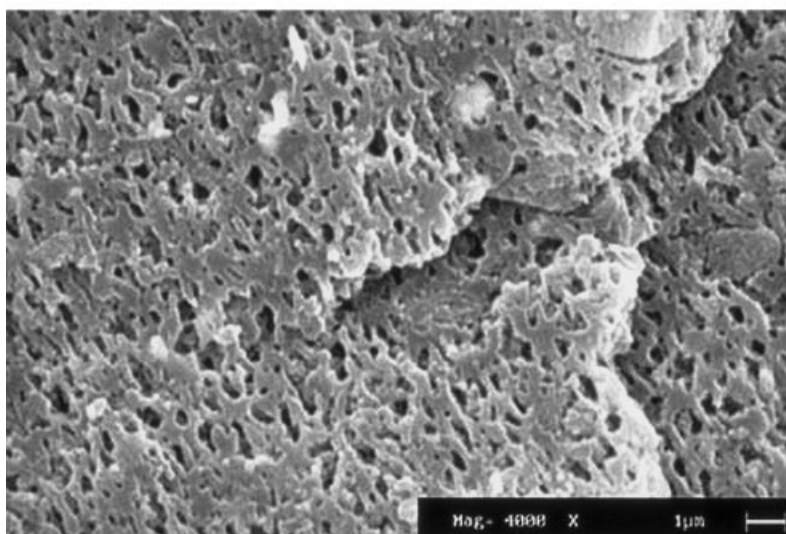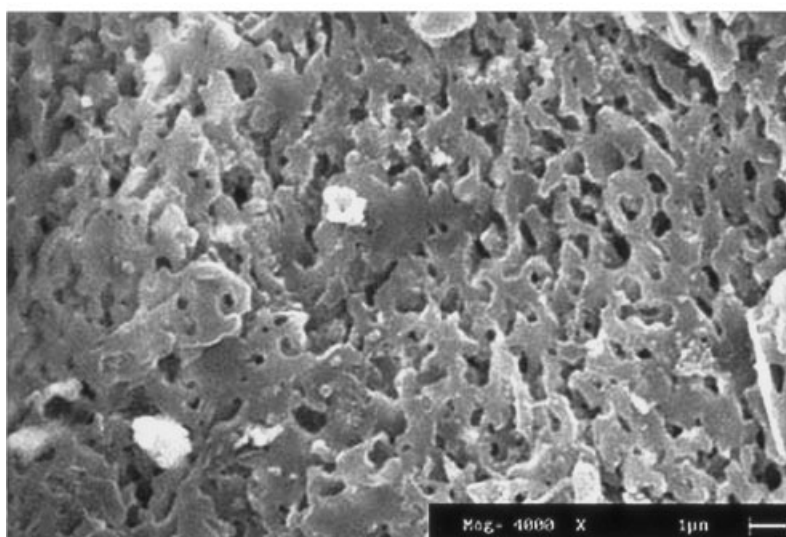
(A)

(B)

(C)

Figure 4 SEM photomicrographs of the cryofractured surface of dynamically vulcanized EPDM/PP (60/40) blend samples loaded with different amounts of silica: (A) 0.0 phr (CF0); (B) 20 phr (CF2); (C) 50 phr (CF5). Silica was first premixed with EPDM.

(A)

(B)

(C)

Figure 5 SEM photomicrographs of the cryofractured surface of unvulcanized EPDM/PP (60/40) blends loaded with various levels of silica: (A) 0.0 phr (UF0); (B) 20 phr (UF2); (C) 50 phr (UF5).
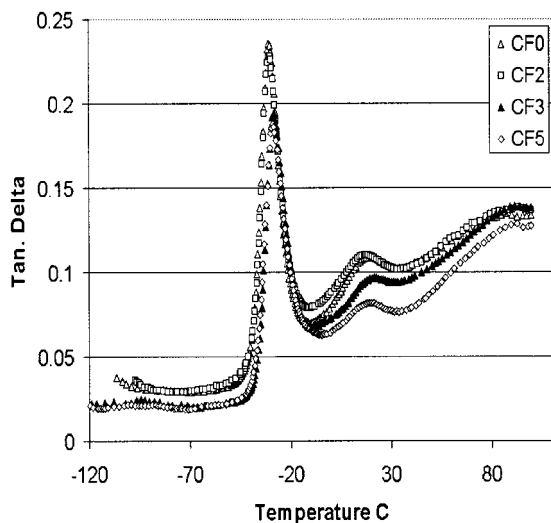
Figure 6 Effects of silica concentration on damping properties of dynamically cured EPDM/PP (60/40, w/w) blend systems.
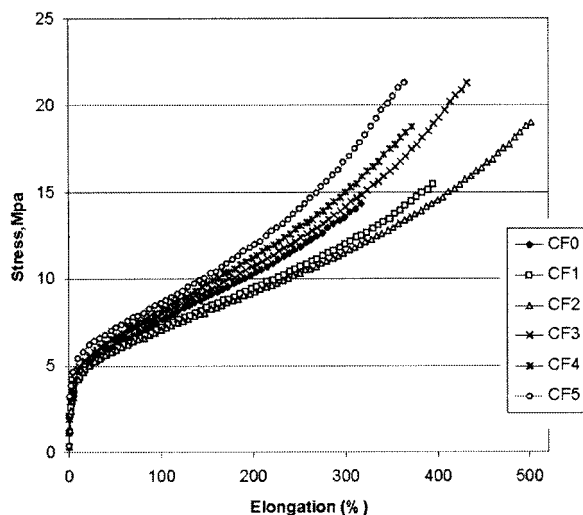

Figure 7 Effects of silica loading level on the tensile properties of dynamically cured EPDM/PP (60/40) blend systems.

adsorption inside the rubber particles, which reduces the degree of slippage between the rubber segments, and also to reduction in the fraction of rubber segments contributing to the viscoelastic response as a result of more entrapped rubber inside the silica network. Higher polymer–filler interaction is evident by the shift of the EPDM tan δ peak maximum toward higher temperature in CF3 and CF5 blend samples. The decrease in mechanical damping shown by the blends, which contain high concentrations of silica, can also be attributed to the promotion of PP crystallization caused by the surface-active silica aggregates that are diffused from EPDM into the PP matrix as shown in Table III.

The most interesting feature of the silica-filled dynamically crosslinked EPDM/PP (60/40, w/w) blends is the rubbery-like behavior shown under tensile load as presented in Figure 7. Through comparison of the tensile curves given in this figure, it is seen that increasing the silica content to 20 phr (CF2) would increase the extensibility of the crosslinked EPDM/PP blend sample together with more rubbery characteristics. This is suggested to be attributed to the retard-

ing effect of silica on sulfur vulcanization, which decreases the density of the crosslinks formed in the rubber particles. This would result in the formation of low-modulus rubber particles or aggregates attached to the PP matrix by means of an interlocking mechanism, which increases the deformability of the EPDM/PP blend system. However, above 20 phr silica content the modulus of the blends increases mainly at high tensile elongation.

This is attributed not only to the increase in silica–rubber interaction inside the rubber particles but also to the strong interface between the two phases together with the greater crystallinity of the PP matrix.

These are in agreement with the higher torque peak maximum shown by the CF3 to CF5 blend samples during vulcanization stage as shown in Figure 3. The higher rubbery-like behavior as well as enhanced tensile modulus exhibited by the silica-filled EPDM/PP dynamically cured thermoplastic elastomers (TPEs) can be considered as the main important consequences of feeding silica into this class of materials.

In Figure 8 the effects of an organosilane coupling agent on the tensile properties of the dynamically cured silica-filled EPDM/PP blend sample are presented and compared with the sample that does not contain organosilane. It is clearly observed that the blend sample loaded with 20 phr silica and 2 phr exhibits not only high extensibility but also higher tensile modulus. These results lead to the conclusion that the inclusion of Si69 coupling agent not only increases the interaction between EPDM network and silica, but also reduces the retarding effect of silica on the vulcanization reaction leading to the formation of stiffer rubber particles and also intensification of interface between the two phases. This would allow the

TABLE III
Effects of Silica Level on the Crystallinity of Dynamically Crosslinked EPDM/PP (60/40) Blend Systems

Sample	PP (%)	Crystallinity	T_m (°C)
PP	100	38	163
CF0	37.82	42	164
CF1	34.8	47	165
CF2	33.67	48.5	165
CF5	28.8	51	166

samples to be extended to 400–500% of its initial length. Moreover, Si69 has sulfur linkages, which are involved in the sulfur vulcanization of the rubber particles, leading to the increase in the modulus of rubber particles. Comparison of the curves given in Figures 7 and 8 shows interesting and distinct results, which are high rubbery behavior together with high tensile strength for the silica-filled dynamically cured EPDM/PP blend having Si69 in its recipes.

Figure 9 presents the variation of the melt complex viscosity versus angular frequency or shear rates for the dynamically crosslinked EPDM/PP blends composed of different amounts of silica. It is seen from this figure that as the silica content increases, the melt viscosity of the cured blend also increases. This is again proposed to be attributed to the increase in the silica–rubber interaction inside the rubber particles and also enhancement of the interface between the two phases, as was explained earlier. Higher melt viscosity shown by the blend samples filled with higher silica concentration is in accordance with the morphology and dynamic mechanical characteristics of the blends as discussed. Moreover, all the silica-filled blend samples show pseudoplastic behavior with shear rate in the molten state, which should mainly be the result of the breakdown of the EPDM rubber network structure at high shear stresses.

CONCLUSIONS

Our investigations on dynamically crosslinked EPDM/PP (60/40) blends filled by silica as an active

Figure 9 Complex viscosity of silica-filled dynamically cured EPDM/PP (60/40) blends: CF0: 0 phr; CF1: 10 phr; CF2: 20 phr; CF3: 30 phr; CF4: 40 phr silica.

filler showed that silica tends to remain encapsulated by EPDM rubber when it is mixed with EPDM before the feeding of PP. The highly filled blend samples showed higher mixing torque during dynamic vulcanization with high final melt viscosity when dumped after the torque peak maximum. Incorporation of silica increased the rubbery-like behavior as well as the extensibility of the blend. Addition of silane coupling agents (Si69) into the formulation of the silica-filled dynamically crosslinked EPDM/PP (60/40) in which silica is premixed with EPDM during the mixing process led to the increase of the tensile modulus and extensibility of the blend. This confirms the increase in the EPDM affinity to accept silica, which leads to the increase of the interfacial interaction between EPDM and silica particles.
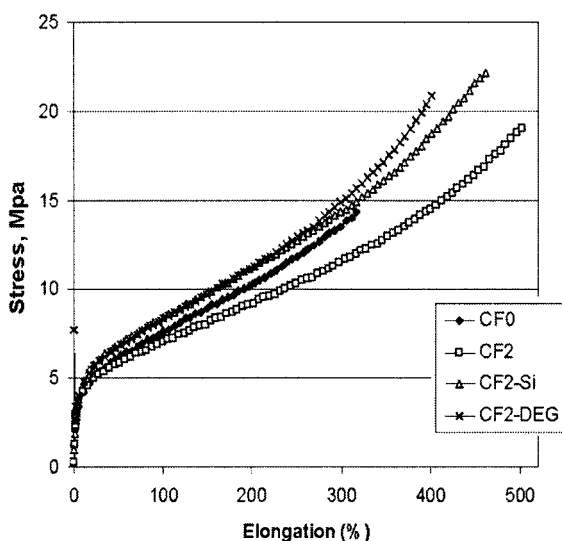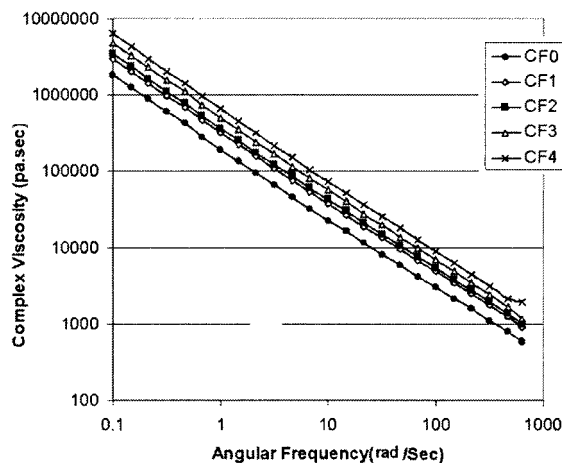
Figure 8 Effects of silane coupling agent (Si69) and functionalized PP on the tensile properties of silica-filled dynamically cured EPDM/PP filled with silica: CF0: 0 phr; CF2: 20 phr; CF2–Si: 20 phr silica + 2 phr Si69; CF2–DEG: 20 phr silica + 4 phr DEG.

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