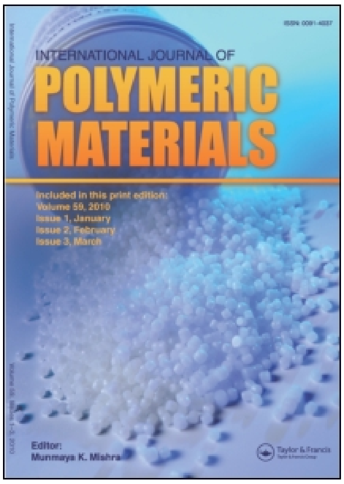

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Ahmad Mousa[a]
[a] Faculty of Engineering, Department of Materials and Metallurgical Engineering, Al-Balqa Applied University, Salt, Jordan

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The Effect of Dynamic Vulcanization on the Mechanical Properties of EPDM/PP Thermoplastic Elastomers

Ahmad Mousa
Faculty of Engineering, Department of Materials and Metallurgical Engineering, Al-Balqa Applied University, Salt, Jordan

EPDM/PP blends were prepared by melt mixing using Brabender Plasticorder at 200°C and 100 rpm. The curative concentration was progressively increased from 1 to 3.5 phr EPDM in order to study the influence of dynamic vulcanization on the mechanical properties of the blend. The effectiveness of dynamic vulcanization was ascertained by Brabender torque Rheometry, the increase in crosslink density, and the reduction in swelling index as well. The mechanical properties were found to increase with sulfur up to 1.4 phr after which reversion occurred. Scanning electron micrographs were inspected to differentiate between the cured EPDM/PP TPEs and the uncured counterpart. The micrographs showed that the blended system contains two incompatible phases. This is evident in both the case of the dynamically cured sample where the EPDM phase remains as dispersed particles in the PP matrix, and in the case of the uncured blend where the EPDM and PP formed two continuous phases.

Keywords: tensile strength, dynamic vulcanization, melt flow index, torque

INTRODUCTION

Research and development that involves blending of polymers for property enhancement has become very popular in the last decade. The ability to yield materials that possess intermediate properties or in some cases better than those exhibited by either of the blend components is believed to be one of the main driving forces for this trend [1]. In recent years elastomeric–plastic blends have become technologically interesting for use as thermoplastic elastomers (TPEs). These materials exhibit some of the physical properties of elastomers at

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Address correspondence to A. Mousa, Faculty of Engineering, Department of Materials and metallurgical Engineering, Al-Balqa Applied University, Salt 19117, Jordan. E-mail: mousa@rocketmail.com

low temperatures and are processable at elevated temperatures [2]. Because of its poor impact strength, PP is often modified by elastomers [3]. Among the various elastomers used as impact modifiers, ethylene-propylene-diene (EPDM) terpolymers have proved to be the most effective ones. Thus considerable work has been reported on the EPDM/PP blends due to their commercial interest [4–5]. Recently it has been found that fully cured EPDM compositions that are fabricable as thermoplastics can be prepared via dynamic or in situ vulcanization [6]. Dynamic vulcanization plays a significant role in the thermoplastic technology, producing thermoplastic vulcanizates via in situ crosslinking of the rubber during mixing with the thermoplastic. Dynamic vulcanization confers increased tensile properties, improved impact resistance and a considerable reduction in swelling by oils [6–7]. Thus, the objective of this work is to investigate the effect of dynamic vulcanization on the mechanical properties of some EPDM/PP thermoplastic elastomers.

EXPERIMENTAL

Materials

Semicrystalline polypropylene (PP) produced by Sabic Saudia Arabia, with MFI of 15.25 g/10 min and density of 0.92 g/ml: Ethylene propylene diene terpolymer (EPDM) supplied by Buna AP with 5% by weight ethylidene norbrene (ENB) as a terpolymer and 25.7% by weight PP were all commercially available grades. Sulfur, tetramethylthiuramdisulfide (TMTD), 2,2-dithiobisbenzothiazole (MBTS), zinc oxide and stearic acid were obtained from the Jordanian local industry.

Formulation

The formulations shown in Table 1 were used in this study. All EPDM compounds were cured by semi-efficient curing systems (semi-EV).

TABLE 1 Composition of EPDM/PP Blends (in phr)

Rubber	70	70	70
PP	30	30	30
Stearic acid	3.0	3.0	3.0
Zinc oxide	5.0	5.0	5.0
Sulfur	X		
MBTS	X		
TMTD	1/3X		

X is the sulfur concentration, which was varied from 0–3.5 phr of EPDM phase.

Sample Preparation

Melt mixing was performed using a computerized Brabender Plasticorder PLE 331. Mixing was carried out at 200°C and apparent shear rate of 100 rpm for 10 min. The EPDM was initially charged into the mixing chamber of the Brabender to equilibrate, followed by PP and other related additives. Mixing was allowed to proceed for 8 min after which the curing agent (Sulfur in this case) was added to the compound. Mixing was then continued at a reduced speed of 50 rpm for another 2 min, after which the mixing was terminated once a constant torque was obtained. The compound was removed from the mixer and cut into strips and again subjected to Brabender mixing at 200°C and 100 rpm for 2 min. After which sheets of 2 mm thickness were molded with a Carver Auto Series compression molding machine using a force of 10 Mpa at 200°C for 10 min.

Characterization and Testing

Crosslink Density

EPDM was dynamically vulcanized for 10 min at 200°C and 100 rpm rotor speed in the absence of the PP using a Brabender Plasticorder PLE 330. The cured EPDM was swollen in thin section (2 mm thick), for 24 h in cyclohexane at room temperature. This was necessary because the constraint of rubber imposed by the thermoplastic phase would limit solvent swelling. The effective crosslink density was then estimated by Flory–Rehner equation. At equilibrium, the chemical forces tending to dissolve the rubber in a liquid are balanced by the restraining forces exerted by the rubber network as follows [8]:

$$-\ln(1-V_r) - V_r - \chi V_r^2 = 2V_0 P n_{phys}\left(V_r^{1/3} - Vr/2\right).$$

where

V_r = Volume fraction of the rubber in a swollen material;

χ = EPDM-cyclohexane interaction, for this system it was found to be 0.315 [6];

V_0 = Molar volume of the cyclohexane;

P = Density of the EPDM network;

n_{phys} = physical degree of crosslinking (1/2 M_{cphys}), where M_{cphys} is the number average molecular weight between adjacent physical crosslinks. The volume fraction of the rubber in the swollen network V_r was calculated from the original mass of the test specimen (a_1), the mass of the swollen specimen

(a_2), and the mass of specimen after drying for 6 days at room temperature (a_3), as follows [9]:

$$V_r = \frac{(a_3 - a_1 \cdot S_1/S_2)1/d\gamma}{(a_3 - a_1 \cdot S_1/S_2)1/d\gamma + (a_2 - a_3)1/d_c}$$

where,

S_1 = the sum of the contents of sulfur and zinc oxide (phr);
S_2 = the sum of the contents of all the components in the mix including the rubber (phr);
$d\gamma$ = density of EPDM rubber (1.6 g/ml);
d_c = density of cyclohexane (0.78 g/ml at 20°C).

Swelling Index

Circular discs of EPDM/PP blends of 2 mm thickness and 20 mm diameter were immersed in cyclohexane for 24 h for the determination of swelling index, which is defined as:

$$\text{Swelling Index} = \frac{\text{Swollen Mass}}{\text{Initial Mass}}$$

Tensile Tests

Tensile tests were performed on 2 mm thick dumb-bell at ambient temperatures (25 ± 2°C), on a Monsanto Tensometer T10 at a deformation rate of 500 mm min^{-1} according to ASTM D412. Five specimens were used and the median value was taken in each case.

Impact Test

Izod impact tests were carried out with the Instrumentad Custom Scientific Pendulum Impact Tester, model Ceast, in accordance with ASTM D256.

Melt Flow Index (MFI)

The processibility of EPDM/PP TPEs was determined using a CEAST melt flow indexer according to ASTM D1238-90b. A load with 2.16 Kg at a 200°C was employed in the measurement.

Morphology

Examination of the fracture surface was carried out using a scanning electron microscope (SEM) model Leica Cambridge S-360. The samples with dimensions 64 × 10 × 2 mm were fractured after being in liquid nitrogen for 30 min. All the surfaces were inspected after staining with OsO_4 vapors for 36 h at room temperatures.

RESULTS AND DISCUSSION

Brabender Torque and Stock Temperature

Mixing parameters that may influence the phase morphology and physical properties of melt mixed formulations are rotor speed, mixing time, and mixing temperature. Such parameters have been kept the same for all compositions of the dynamically vulcanized EPDM/PP blends. Changes in the torque and the stock temperature caused by the mixing process are given in Figure 1. Note that the torque gradually reduces with mixing time and shows steady values form the 7th min of mixing. The progress of the stock temperature of the EPDM/PP blend as a function of mixing time is represented in Figure 1 as well. The initial lowering of the stock temperature from the set temperature (200°C) could be traced to the quick addition of EPDM into the molten PP. However, the vigorous shearing causes the stock temperature to rise steeply above the mixing temperture as early as two and half minutes of mixing. As the blending progresses the stock temperature

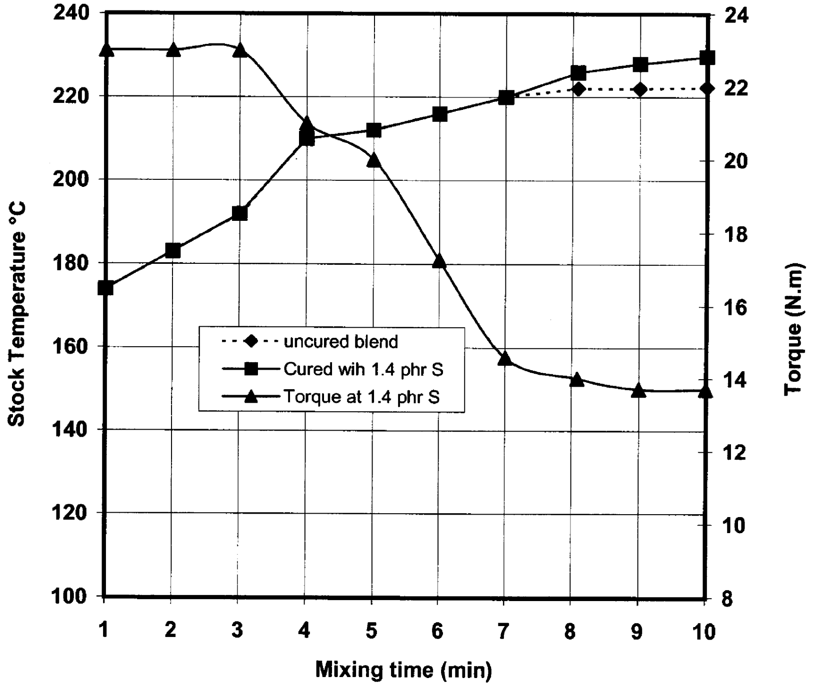

FIGURE 1 The effect of mixing time on torque and stock temperature of EPDM/PP blend.

undergoes a gradual rise until a final steady temperature value is attained. Concomitantly, the torque and viscosity of the blending system decrease. It can be noted that the stock temperature for the cured blend is slightly higher than that of its uncured counterpart. This should be attributed to the exothermic nature of the curing reaction where more heat is expected. Based on the previous observations it can be inferred that the attainment of steady values of stock temperature and torque indicates the completion of the exothermic mixing process. Now, the influence of sulfur loading on the torque behavior at the end of mixing process (i.e., 10th min) of EPDM/PP formulations is presented in Table 2. Note that the torque values have increased steadily with sulfur. Remember that torque is an indirect indication of the degree of curing as mentioned earlier. This scenario can be related to the formation of network structure due to the selective curing of EPDM via dynamic vulcanization. Thus, it may be plausible that the interfacial adhesion between the dispersed EPDM particles and the PP phase has been promoted by the curing agent (sulfur) [10]. The observed trend is consistent with a previous work on dynamically cured PVC/NBR thermoplastic elastomers [11]. Similar trends were reported earlier regarding PVC/ENR blends and PP/EPDM, respectively [6, 12–14]. The influence of sulfur concentration on the processibility of the EPDM/PP TPEs was checked by measuring the melt flow index. The variation of melt flow index with sulfur concentration of the melts is illustrated in Figure 2. It is shown that the melt flow index decreases with increase in sulfur loading. Again, this might be due to the formation of a tighter intermolecular network structure at higher sulfur concentration. These crosslinks will obviously decrease the mobility of the polymer chain and consequently prevent the chains from slipping past one another. Thus, the ability of the samples to resist the flow increased with increase in sulfur content. Recall that the introduction of crosslinks via dynamic curing is expected to increase the viscosity of the EPDM phase leading to the increase of

TABLE 2 The Influence of Sulfur Loading on the Torque Value of the PP/EPDM Formulations

Sulfur content (phr)	Torque (N.m)
0	11
0.7	13
1.4	14
2.8	16
3.5	19

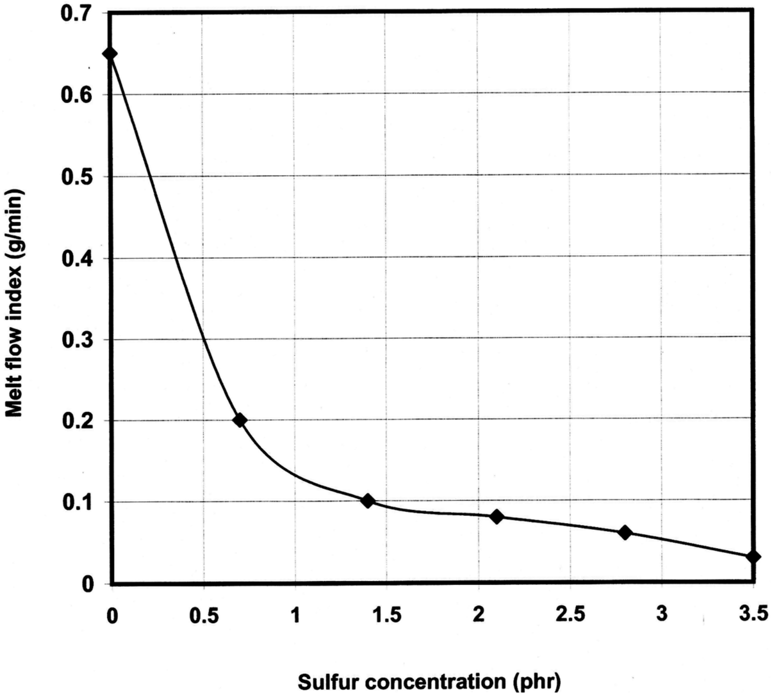

FIGURE 2 The effect of sulfur loading on the melt flow index of EPDM/PP blend.

the viscosity of the whole system. Thus, the melt flow index decrease. To support the claim that lowering the melt flow index was due to the introduction of crosslinks, the crosslink density of the virgin EPDM was calculated, in parallel with the swelling index of the EPDM/PP blends. The crosslink density and swelling index data are shown in Figure 3. As expected, the crosslink density of EPDM and the swelling index of the EPDM/PP display opposite trends. Thus, it can be inferred that changes down to the molecular level have taken place due to the dynamic vulcanization process. This observation agrees quite well with an early work on dynamically cured PVC/ENR blend [12–13]. Furthermore, this is consistent with an early report on SBR reinforced hydrolyzed polyurethane [15].

Dynamic Vulcanization and Mechanical Properties

The effect of sulfur concentration on the tensile strength of the EPDM/PP blend is present in Figure 4. Note that the tensile strength

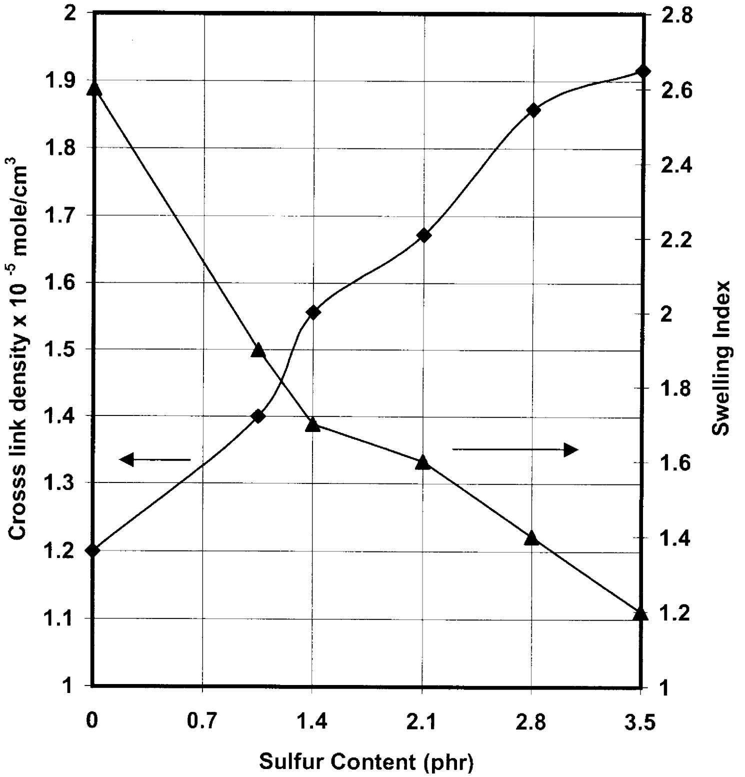

FIGURE 3 The effect of sulfur loading on curing density of EPDM and swelling index of EPDM/PP blend.

of the TPEs passed through a maximum at 1.4 phr sulfur loading. The initial increase in tensile strength could be assigned to the increase in the degree of curing and the extent of dispersion of the dynamically cured EPDM particles in the PP matrix. Recall that the increase in tensile strength was accompanied with reduction in the swelling index of the EPDM/PP TPEs and increase in crosslink density as depicted in Figure 3. The trend observed in Figure 4 is in agreement with a previous work where it has been indicated that it is advantageous to crosslink the rubber phase lighted [5]. Furthermore, it has been stated that the use of curing agent up to a certain limit (1.4 phr sulfur in this investigation) is expected to promote the interfacial adhesion between different phases [5]. Thus, improved tensile strength of the dynamically vulcanized TPEs compositions is expected. It seem that the crosslink density of the thermoplastic vulcanizates presented in Figure 3 is

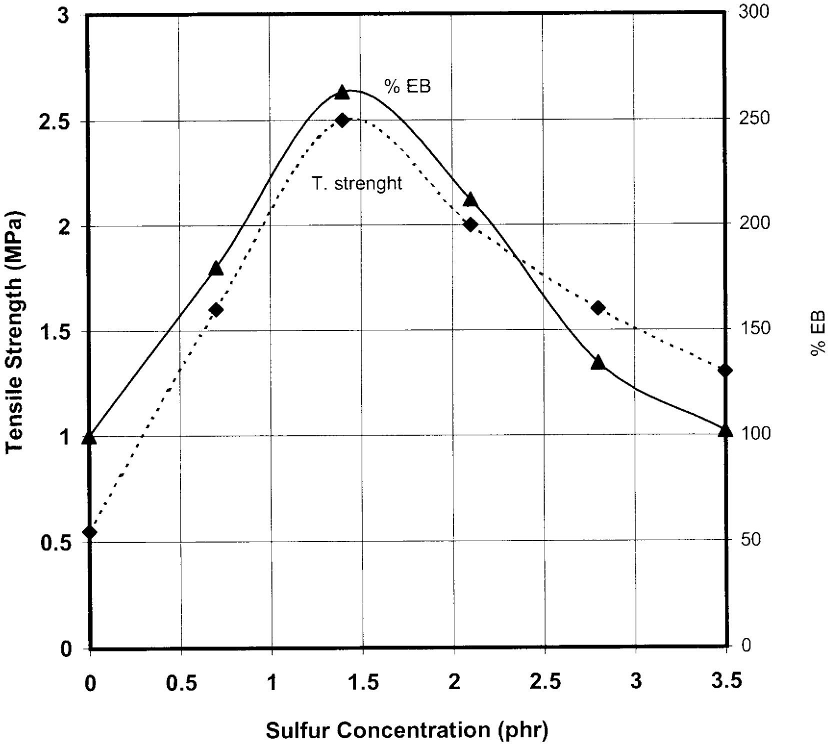

FIGURE 4 The effect of sulfur loading on tensile strength and elongation at break of EPDM/PP blend.

not likely to decrease after 1.4 phr sulfur. Such results are partially contradictory, especially the tensile strength reduction and increased crosslink density are at odds with the finding that the EPDM became more crosslinked. Two factors may be considered to justify the observed trend. First, the overcuring of the rubber phase due to successive crosslinking during the dynamic vulcanization process. Second, one should not forget that the additives might be localized in the PP phase or at the interphase between PP and EPDM domains causing the deterioration of the mechanical properties at sulfur loading beyond 1.4 phr. Thus, it can be concluded that there should be an optimum crosslink density where the enhanced tensile strength is maximum (1.4 phr in this report). This is consistent with previous findings reported by Joseph et al. regarding the cure characteristics and the vulcanizatiate properties of NR/SBR blend [16]. Figure 4 also reflects the influence of sulfur loading on the elongation at break (EB) for EPDM/PP blends. Note that EB passed through maximum at 1.4 phr sulfur then a drop in the EB was recorded. This trend is expected because EB is known to behave in such a manner due to an increase in crosslink density for lightly vulcanized rubber [5]. This behavior indicates that crosslink formation at 1.4 phr sulfur loading in the EPDM phase of the blend has not yet peaked off [5–6], thus asserting that the EPDM in the blend is lightly crosslinked [6–7]. On the other hand, the deterioration in the %EB over 1.4 phr sulfur should be attributed to the excessive degree of curing, which reduces the chain mobility and confers rigidity to the intermolecular network structure. These materials with extra crosslinks are expected to have less flexibility due to the overcure. This should explain the marked reduction in the %EB beyond 1.4 phr sulfur content. Figure 5 illustrates the relationship between sulfur loading and the impact energy of the EPDM/PP vulcanizates. It can be seen that the improvement continues until the notched Izod impact strength is at maximum at

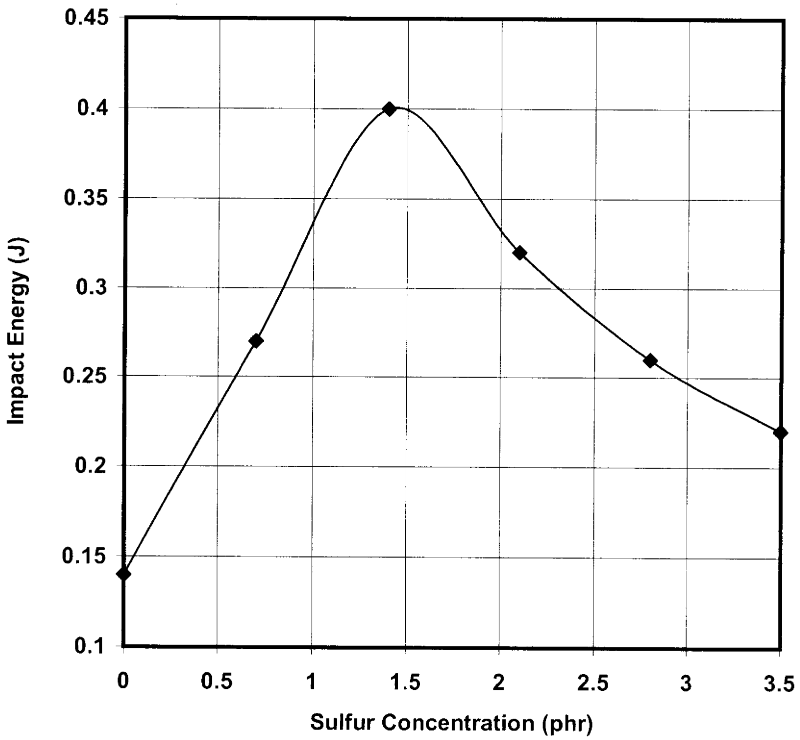

FIGURE 5 The effect of sulfur loading on impact energy of EPDM/PP blend.

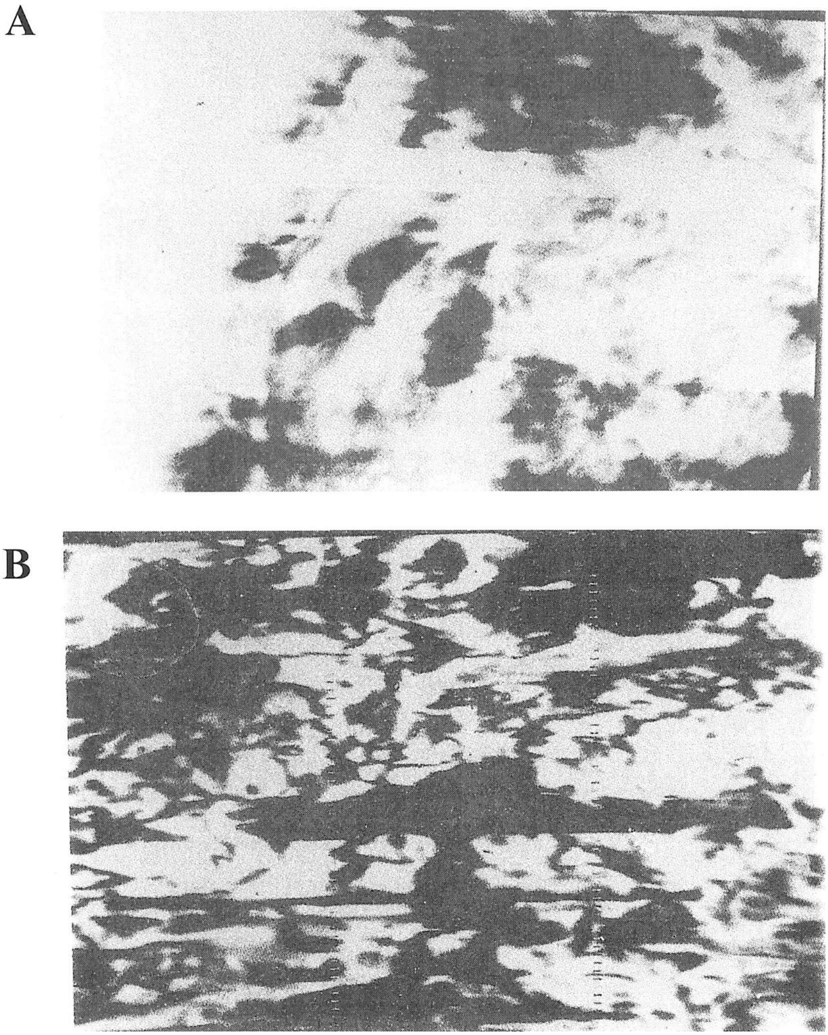

FIGURE 6 SEM micrographs for the dynamically cured and uncured PP/EPDM blends.

1.4 phr sulfur. Beyond this point subsequent sulfur addition yields reduced impact strength. The observed trend is more or less similar to that obtained in the case of the tensile properties presented in Figure 4. The improvement in the impact strength could be due to the action of dynamic vulcanization, which is expected to improve the elastic properties and the molecular retractability of the network structure on deformation of the thermoplastic vulcanizates [6–7]. Thus, it can be assumed that the cured and dispersed EPDM particles, which act as regions of energy absorption, have been stiffened due to dynamic vulcanization [17]. On the other hand the reduced impact strength beyond 1.4 phr sulfur might be traced to the overcuring.

MORPHOLOGY

Figure 6a and b shows scanning electron micrographs of the fracture surfaces of EPDM/PP TPEs with and without sulfur. These SEM pictures reveal that the morphology of the control recipe differs from the dynamically cured formulation. The fracture surface of the cured sample presented in Figure 6a indicated that the rubber particles (indicated by the black areas) were dispersed in PP matrix. This could be due to the fact that shear stress during the extensive mixing is able to produce particles by fracturing the crosslinked rubber phase. Thus fine rubber particles are expected due to the fact that the cured blend has higher torque (energy uptake) than the uncured sample [18]. By contrast, the SEM picture presented in Figure 6b reveals that both PP and EPDM formed continuous phases, unlike the cured sample that shows that the rubber particles are dispersed in the PP matrix. Comparing the two SEM micrographs, one can see that both the cured and uncured EPDM/PP compositions are incompatible systems with two phases.

CONCLUSIONS

First, dynamic vulcanization has introduced crosslinks to the EPDM that resulted in improved mechanical properties up to 1.4 phr sulfur, the mechanical properties are further enhanced, as can be seen by the decrease in swelling index, increase in curing density, and torque values coupled with decrease in MFI, which are all direct functions of curatives concentration.

Second, the changes in tensile properties of the dynamically vulcanized TPEs are indicative of effective dynamic vulcanization, which can be used to account for the observed synergism in mechanical properties, that is, the mechanical properties of the TPEs are better after dynamic vulcanization. Recall that there was an optimum sulfur concentration, particularly 1.4 phr sulfur, beyond which the properties deteriorated. Scanning electron microscope photographs revealed the EPDM/PP belends are incompatible systems with two phases.

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