

Carbon Black-Reinforced Dynamically Cured EPDM/PP Thermoplastic Elastomers. I. Morphology, Rheology, and Dynamic Mechanical Properties

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ABSTRACT: The structure development, rheological behavior, and viscoelastic properties of carbon black-filled dynamically vulcanized thermoplastic elastomers based on the ethylene-propylene-diene terpolymer (EPDM) and polypropylene (PP) with the ratio range of 50/50 to 80/20 were studied and compared with similar but unfilled samples. Two-phase morphology was observed at all ratios for the dynamically cured samples in which rubber particles are dispersed in the thermoplastic matrix. Carbon black distribution in each phase and damping behavior was found to be dependent upon the mixing condition and route of carbon black feeding. However, carbon black tends to stay mainly in the rubber phase, which leads to increase in the viscosity difference and, therefore, increase in the rubber particle size. Tensile strength and rupture energy increased with carbon black loading. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1127–1137, 2000

Key words: thermoplastic elastomer; dynamic vulcanization; carbon black; morphology; rheology; mechanical properties

INTRODUCTION

Thermoplastic elastomers (TPEs) are materials with the processing behavior of thermoplastics but having the mechanical properties and elastic recovery similar to the ordinary thermosets or vulcanized rubbers.^{1,2} Among different sorts of TPEs, those prepared by physical melt mixing of a polyolefin and an elastomer has gained significant attention due to the ease of tailoring the required properties and also the simple preparation method.³ Addition of a small quantity of a crosslinking system during melt mixing leads to the *in situ* vulcanization of the dispersed rubber particles that is called dynamic vulcanization. This process provides a number of advantages

over similar but the unvulcanized counterpart, first described by Fisher^{4,5} and then developed by Coran and Patel.^{6–8}

The technical importance of thermoplastic vulcanizates is attributed mainly to the specific microstructure of these materials that consists of a continuous thermoplastic matrix with very tiny dispersed cured rubber particles that enable the blend to be melt-processed similar to the ordinary thermoplastic materials even though the rubber particles are crosslinked. Different types of dynamically cured TPEs have so far been prepared and the effects of the characteristics of the components, ratio, and type of curing system upon the structure development and final end properties have been studied.^{9,10} TPE vulcanizates based on polypropylene (PP) and the ethylene-propylene terpolymer (EPDM) have gained considerable attention due to the structural compatibility of

Table I Characteristics of the Materials Used

| Materials | Characteristics | |
|-----------|--|-------------------------|
| PP | MFI | 6.48 g/10 min |
| | Crystallinity | 48.5% |
| | T_m | 166°C |
| | Density | 0.912 g/cm ³ |
| EPDM | Mooney viscosity ML(1 + 4) 125°C | 40 |
| | PP content | 27% |
| | Density | 0.895 g/cm ³ |
| | Curing rate | Medium |
| | Carbon black HAF (N330) | Medium structure |

these two polymers and many works have been published which deal with the mechanical properties and morphology of this type of TPEs.^{11–15} However, no literature has been published on the effect of reinforcing agents such as carbon black on the rheology, morphology, and mechanical properties of this blend system. The objective of the present work was to study the effect of carbon black on the rheology and viscoelastic properties of dynamically crosslinked EPDM/PP blends along with the accompanying characteristics in the morphology.

EXPERIMENTAL

Materials

The basic characteristics of the polymers used in this study are listed in Table I. The PP was a

Table II Compositions of the Blends

| Blends | EPDM/PP | | | |
|--------|---------|-------|-------|-------|
| | 50/50 | 60/40 | 70/30 | 80/20 |
| U | 1U | 2U | 3U | 4U |
| V | 1V | 2V | 3V | 4V |
| C | 1VC10 | 2VC10 | 3VC10 | 4VC10 |
| | — | 2VC20 | — | — |
| | — | 2VC40 | — | — |
| | — | 2VC60 | — | — |
| | — | 2VC80 | — | — |

^a Vulcanizing system on the basis of 100 phr EPDM: ZnO 5 phr, stearic acid 1.0 phr, MBT 0.4 phr, TMTD 0.65 phr, and sulfur 1.5 phr.

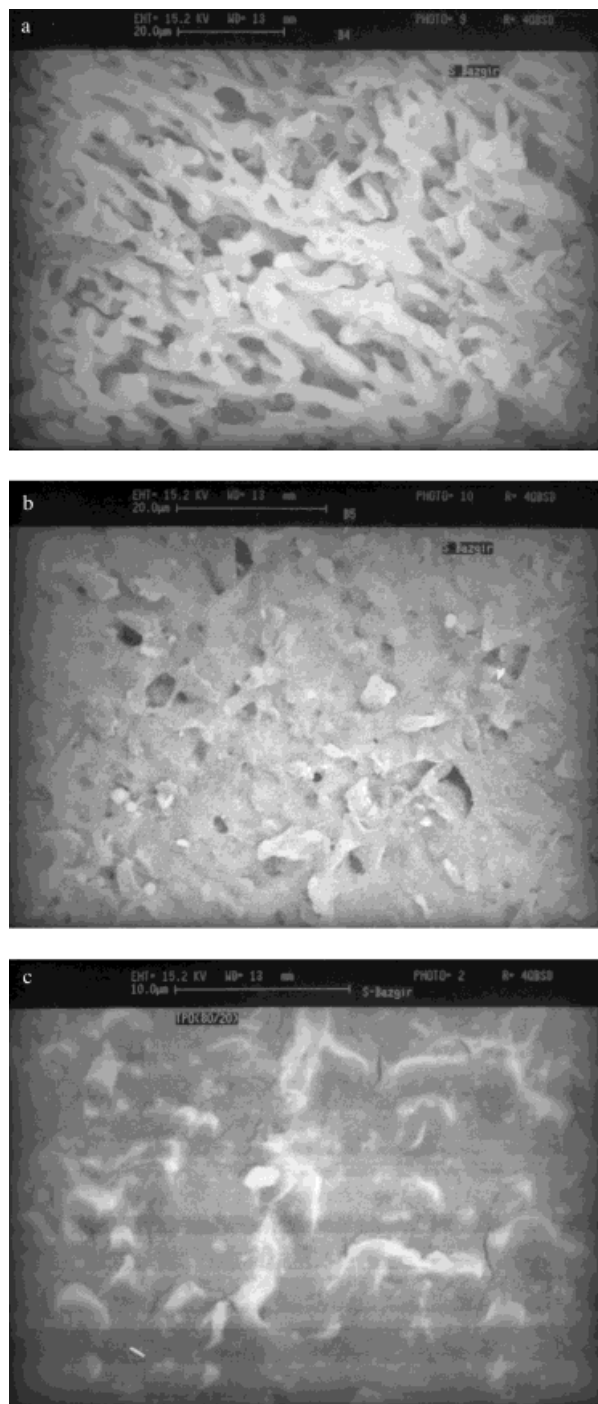


Figure 1 SEM micrographs of unvulcanized, unloaded EPDM/PP blends. EPDM phase was stained by OsO₄ solution. (A) 2U; (B) 3U; (C) 4U.

commercial injection grade from the Iran Petrochemical Co. (Bandar ImamKhomayni, Iran) and the EPDM based on ENB was supplied by the Dutral Co. (Italy) and used as commercially avail-

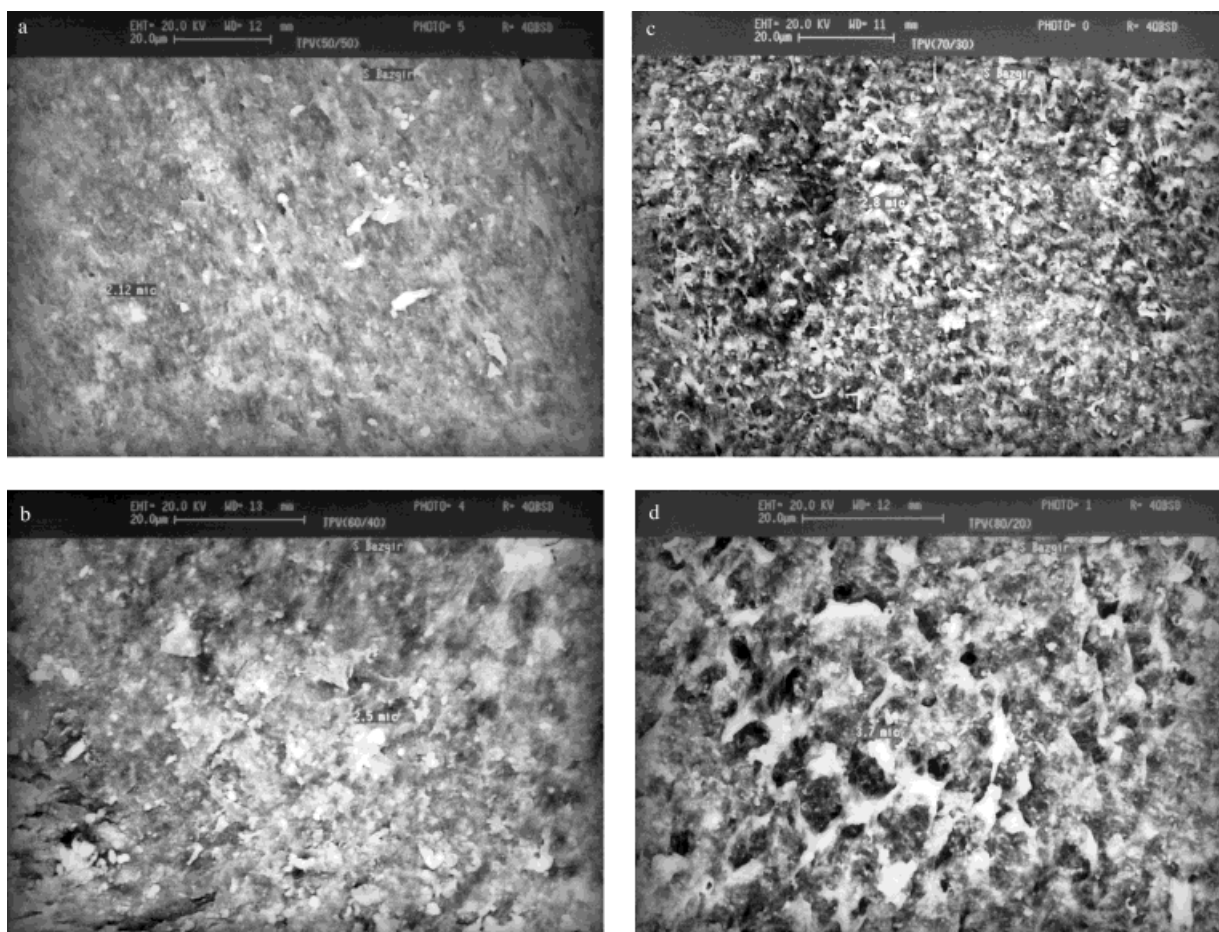


Figure 2 SEM micrographs of dynamically vulcanized EPDM/PP blends with varying composition: (A) 1V; (B) 2V; (C) 3V; (D) 4V.

able. The carbon black used was high abrasion furnace type, N330, supplied by the Ahvaz Carbon Black Co. (Ahvaz, Iran).

Blend Preparation

The compositions of the blends are given in Table II. The blend ratios are denoted by the numbers 1, 2, 3, and 4, and letters U and V denote blends containing no crosslinking agent and those having a vulcanizing system, respectively. The blends that contain carbon black are identified by the letter C followed by a number indicating the carbon black content (phr). Therefore, the blend identified as 2VC40 indicates that the EPDM/PP ratio is 60 : 40 and has been dynamically vulcanized and filled with 40 phr carbon black. Blending was carried out by first feeding the EPDM rubber into the laboratory-size Haake mixer (type

Rheocord 90) at 175°C, and after 2 min, PP was added and blending was continued for 6 min, after which the mixture was taken out and sheeted through a laboratory-size two-rolled mill and then was cut into pieces. In the case of blends of group C, carbon black was added to the EPDM and mixed for 2 min before the addition of PP. For the blends of group V, the curing system including zinc oxide, stearic acid, sulfur, and accelerators was added into the mixer 6 min after the blending of EPDM with PP, and at the end of 8 min, the dynamically cured blend was taken out and sheeted through the two-rolled mill and then cut into pieces.

To prepare test specimens, each sheeted blend was put into the cavity of a specially designed mold and warmed for 4 min at 200°C in an electrically heated press and then pressure (300 kgf/

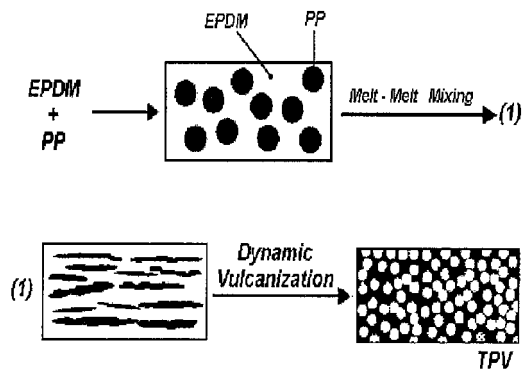


Figure 3 Schematic presentation for the morphology development of EPDM/PP blend under dynamic vulcanization.

cm²) was applied for 2 min, after which the mold was immediately cooled.

Morphology Studies

The morphology and structure of the blends were studied using a scanning electron microscopy Model Cambridge S36. Samples of thickness 2 mm were cryogenically fractured in liquid nitrogen and then stained with osmium tetroxide (OsO₄) to increase the contrast between the rubber and plastic phases. The stained surfaces were sputter-coated with gold and then viewed with SEM.

Measurement of Dynamic and Mechanical Properties

The dynamic mechanical properties of the blends were investigated using a dynamic mechanical analyzer (DMA) Model Dupont 983 at a resonance mode over the temperature range of -80 to $+100^{\circ}\text{C}$ with the heating rate of $5^{\circ}\text{C}/\text{min}$. Samples were vibrated at the amplitude of 0.2 mm. Tensile strength, elongation at break, and 100% modulus were studied using a tensile tester Model DY-26 made by the Adamel Co. (France). These tests were carried out using dumbbell-shaped specimens according to ASTM-D412 at a crosshead speed of 500 mm/min and ambient temperature.

Rheological Properties

The rheological properties of the samples were studied using a capillary rheometer Model In-

stron 3211 with the length and diameter of 2.0 and 0.0407 in., respectively. The L/D of the capillary was 40 and measurements were carried out at 200°C .

RESULTS AND DISCUSSION

Morphology

The phase morphology of uncrosslinked and unloaded EPDM/PP blends of varying components are illustrated in Figure 1. It is apparent from the micrographs shown that for the EPDM/PP ratios of 80/20 and 70/30 EPDM forms the continuous matrix (white background), and PP, the dispersed phase (black specks). However, at the ratio of 60/40, phase inversion occurs where the two phases coexist as a continuous phase. The formation of a two-cocontinuous phase morphology has also been reported for the simple blends of NR/LDPE between the ratios of 60/40 to 40/60 by Qin and coworkers.¹⁶ As the rubber phase is dynamically crosslinked during mixing, the viscosity of the rubber phase becomes higher than that of PP, which plays an important role in driving the morphology of the blend toward the formation of rubber particles dispersed throughout the continuous PP matrix. The formation of a dispersed morphology by the most viscous phase in the EPDM/BR blend system has also been reported¹⁷ and explained to be due to the tendency of the less viscous phase to encapsulate the most viscous phase to minimize the mixing energy. The SEM micrographs shown in Figure 2, for dynamically vulcanized EPDM/PP blends of varying compositions, indicate that dynamic curing can cause phase inversion even for blends of high EPDM/PP ratios, yielding a morphology with the rubber particles dispersed in the continuous phase of PP. This could be attributed to the immobilization of the rubber particles by crosslinking and therefore breaking down to small sizes under the applied shear field.

The structure development for the dynamically crosslinked EPDM/PP thermoplastic elastomers can be modeled as shown in Figure 3. The presence of carbon black as the third phase and the route of its feeding is found to have a profound effect upon the morphology of the EPDM/PP thermoplastic elastomers. The phase morphology of dynamically vulcanized 60/40 EPDM/PP blends loaded with a premixed EPDM/carbon black mas-

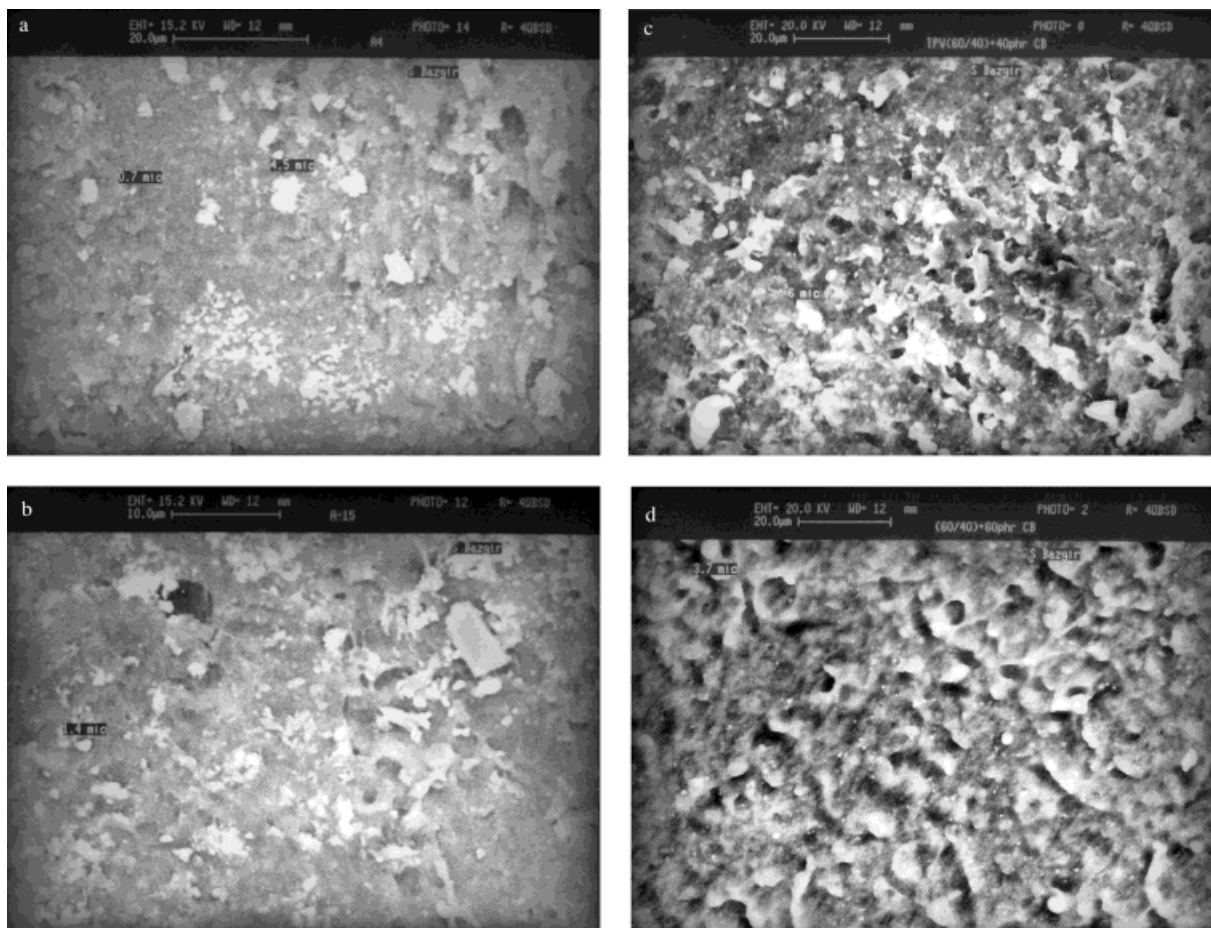


Figure 4 SEM micrographs of dynamically vulcanized 60/40 EPDM/PP blends loaded with carbon black as premixed EPDM/carbon black masterbatch: (A) 2VC10; (B) 2VC20; (C) 2VC40; (D) 2VC60.

terbatch is illustrated by Figure 4. The presence of light specks within the dispersed rubber particles is apparent, which implies that carbon black particles prefer to remain within the more viscous EPDM rubber phases.¹⁸ This can be attributed to the greater carbon black affinity toward EPDM than to PP and also to stronger interactions between the active groups on the surface of carbon black and unsaturated rubber segments than the less reactive PP, which would result in the formation of a rubber–filler network as well as enhancement of the carbon black solubility in the EPDM phase.^{19–21} Under otherwise comparable conditions, the dispersed cured EPDM particles seemed to be larger in size for the blends loaded with carbon black. This could be observed by comparing the SEM micrographs presented in Figure



Figure 5 SEM micrograph of dynamically vulcanized 50/50 EPDM/PP blend loaded with 10 phr carbon black. Carbon black was added to the mix as an ingredient.

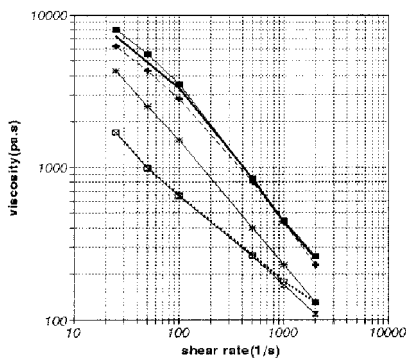


Figure 6 Flow behavior of EPDM and PP at various processing temperatures compared with a 50/50 dynamically vulcanized blend of the two polymers: (□) PP (190°C); (X) PP (180°C); (*) 1V (190°C); (+) EPDM (190°C); (–) EPDM (180°C); (■) EPDM (170°C).

2(B) and those given in Figure 4. This might be attributed to the higher difference between the melt viscosity of the PP matrix and the loaded EPDM phases, which leads to the formation of larger-size rubber particles.²² When carbon black was fed to the mixer as an ingredient while EPDM and PP were being mixed, the uniformity in size and dispersion of the cured rubber particles was disturbed (Fig. 5). It is clearly seen in this micrograph that carbon black clusters (large specks) have preferentially diffused into the more viscous rubber phases (white areas) and partly appeared within the interface of the two phases.

Rheological Properties

The variation of shear viscosity over a wide range of shear rate and temperature for uncompounded EPDM and PP is presented in Figure 6

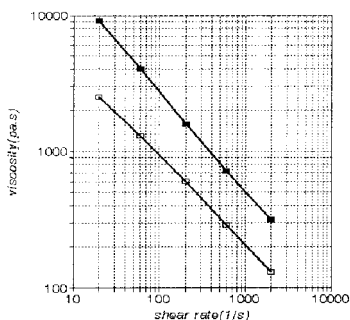


Figure 7 Viscosity versus shear rate for 70/30 EPDM/PP blend at 200°C: (□) 3U; (■) 3V.

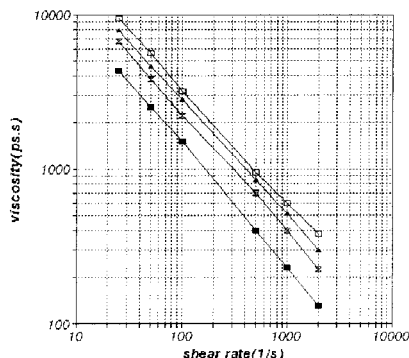


Figure 8 Variation of viscosity with shear rate for dynamically vulcanized EPDM/PP blends: (■) 1V; (X) 2V; (▲) 3V; (□) 4V, at 200°C.

and compared with a sample of a 50/50 simple blend of EPDM and PP in which the rubber phase is not crosslinked. It can be seen that the viscosity of both EPDM and PP is highly shear-sensitive with significant drops at a high shear rate, but not affected by temperature. At high shear rates, the viscosity difference between EPDM and PP is reduced, which is desired to decrease the size of the dispersed rubber particles in the blends of the two polymers.²² In Figure 7, the shear viscosity versus shear rate of a dynamically cured 70/30 EPDM/PP blend sample is shown and compared with that of a similar but uncrosslinked one. It is obvious that not only does the thermoplastic elastomer vulcanizate (TPV) show higher viscosity but also that its flow behavior follows the power law model over the entire range of the studied shear rates. These are attributed to the formation of crosslinks between the rubber chains within the rubber particles, which increases their stability toward shear breakdown during mixing and, therefore, less reduction in the shear viscosity of the TPVs. Effects of the blend ratio upon the rheological behavior of the TPVs are demonstrated in Figures 8 and 9. As the concentration of the cured tiny rubber particles increases, not only the shear viscosity of the TPVs increases but also the blend viscosity shows much higher values at low shear stresses.

TPVs with a high concentration of rubber have been shown to behave like highly filled molten thermoplastics,^{23,24} so that the interface between the less mobile dispersed rubber particle and the thermoplastic phase increases, which leads to the

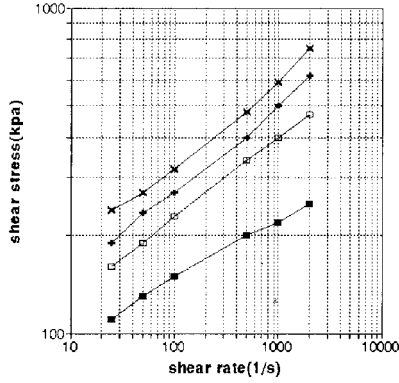


Figure 9 Effects of EPDM concentration upon the capillary flow behavior of dynamically vulcanized EPDM/PP blend: (■) 1V; (□) 2V; (+) 3V; (X) 4V.

increase in shear viscosity. Also, the blend shows a tendency for the formation of a physical structure by the association of the particles at low shear stresses (Fig. 10).

The rheological properties of the 60/40 EPDM/PP thermoplastic vulcanizates filled with various amounts of carbon black are presented in Figures 11 and 12. It can be seen that all the TPVs filled with different amounts of carbon black show almost the same melt viscosity and rheological behavior and exhibit flow characteristics similar to the unfilled corresponding TPEs (2V). This could be attributed to the combined effects of the greater affinity of carbon black toward EPDM than toward PP during melt mixing, which enhances the carbon black incorporation (wetting) into the dispersed rubber phases. This would result in increase of

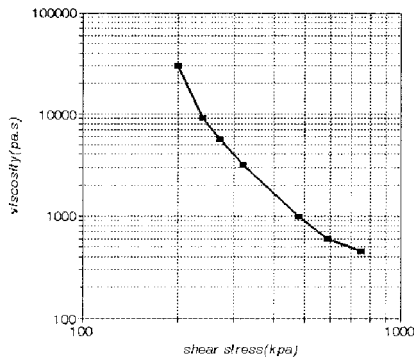


Figure 10 Variation of viscosity with shear stress for unfilled dynamically vulcanized 80/20 EPDM/PP blend.

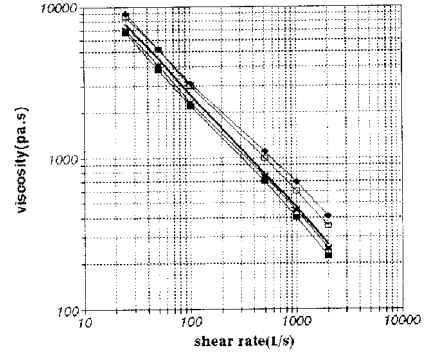


Figure 11 Melt viscosity as a function of shear rate for dynamically vulcanized EPDM/PP/carbon black composite at constant blend ratio (60/40) and varying carbon black concentration (wt %): (■) 2V; (X) 2VC10; (–) 2VC20; (□) 2VC40; (+) 2VC60.

the mix shear viscosity, on the one hand, and the acceleration of the mechanochemically activated chain scission of the mobile continuous PP matrix,^{23,24} leading to decrease of its viscosity, on the other hand. However, as illustrated in Figure 11, all the filled samples show pseudoplastic flow behavior over the studied range of shear rates.

Mechanical Properties

The stress–strain curves of the unfilled EPDM/PP thermoplastic vulcanizates at various blend compositions are shown in Figure 13 and variation of the ultimate tensile strength

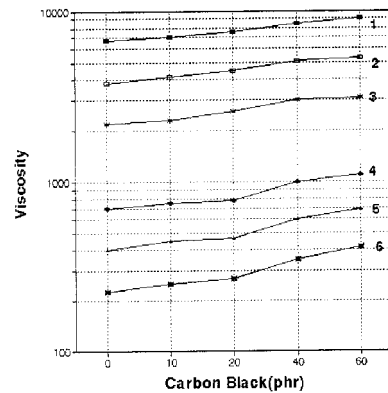


Figure 12 Influence of the carbon black concentration on the shear viscosity at various shear rates for 60/40 EPDM/PP thermoplastic vulcanizate: (1): 25 s⁻¹; (2) 50 s⁻¹; (3) 100 s⁻¹; (4) 500 s⁻¹; (5) 1000 s⁻¹; (6) 2000 s⁻¹.

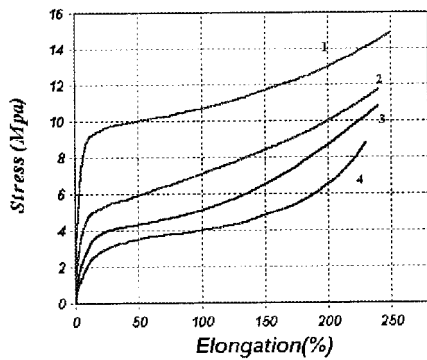


Figure 13 Tensile stress–strain curves of dynamically vulcanized EPDM/PP blend at various compositions: (1) 1V; (2) 2V; (3) 3V; (4) 4V.

with composition is also shown in Figure 14. It is apparent that stress increases with strain sharply and then gradually after passing through the yield point of the PP. The yielding process undergoes changes with increase in the EPDM content of the dynamically vulcanized blends such that the yield peak disappears at the composition ratio of 80/20 (EPDM/PP) and the tensile behavior of the TPEs shifts toward that of the vulcanized EPDM. However, the dynamically cured samples show improved tensile strength at all examined EPDM/PP ratios compared with similar but unvulcanized blends. Tensile strength shows an inverse relation with EPDM content (Fig. 14), which is explained to

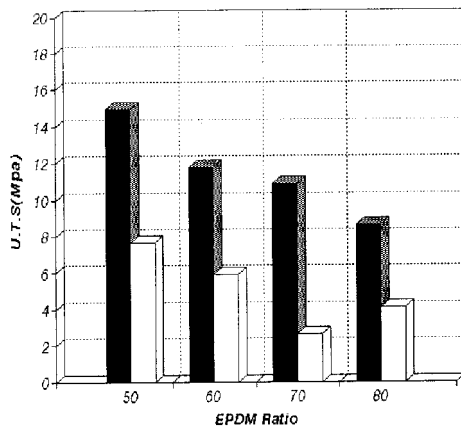


Figure 14 Effect of EPDM concentration upon the ultimate tensile strength of EPDM/PP TPV and compared with corresponding simple blend: (■) dynamic vulcanized; (□) simple blend.

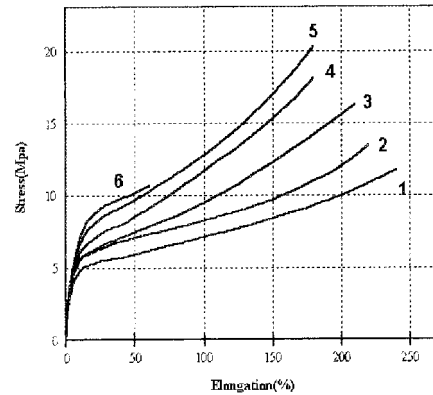


Figure 15 Stress–strain curves of dynamically vulcanized EPDM/PP (60/40) blends filled with various amounts of carbon black: (1) 2V; (2) 2VC10; (3) 2VC20; (4) 2VC40; (5) 2VC60; (6) 2VC80.

be due to the decrease in the concentration of semicrystalline PP as the continuous phase and increase in the size of the dispersed rubber particles.⁶

The stress–strain curves of dynamically vulcanized 60/40 EPDM/PP blends filled with carbon black are presented in Figure 15. Also, in Figures 16 and 17 are given the variation of the ultimate tensile strength and the elongation at break with carbon black loading, respectively. All the filled samples showed increase in stress at break up to the concentration of 60 phr carbon black. Above this level, the mechanical strength declines,

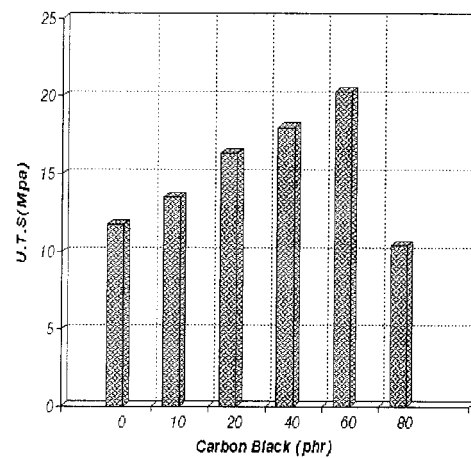


Figure 16 Effect of carbon black loading on the ultimate tensile strength of dynamically cured EPDM/PP (60/40) TPE.

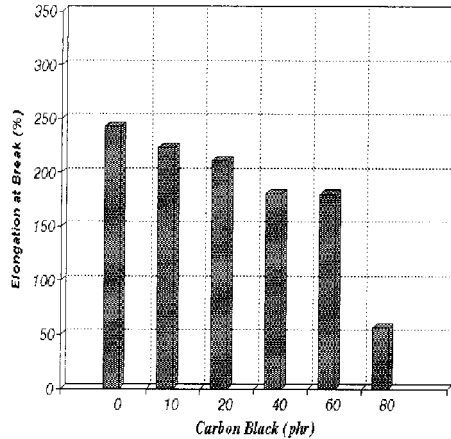


Figure 17 Elongation at break versus carbon black loading for dynamically cured EPDM/PP (60/40) TPE.

which is due to less wetting of the black particles by the rubber chains.

Dynamic Mechanical Properties

The variation of the elastic or storage modulus (E'), loss factor ($\tan \delta$) and loss modulus (E'') with temperature are presented in Figures 18–20. Above the rubber glass transition (T_g), both the storage modulus (E') and the loss modulus are found to decrease with increase in the EPDM content of the dynamically cured EPDM/PP blends. However, the decrease in loss

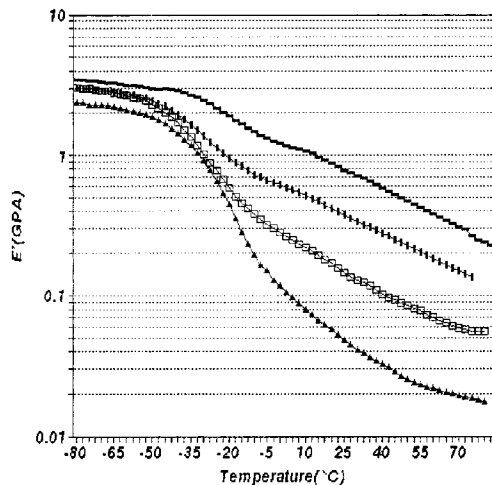


Figure 18 Effect of EPDM concentration upon the storage modulus (E'): (◻) 1V; (●) 2V; (◻) 3V; (▲) 4V.

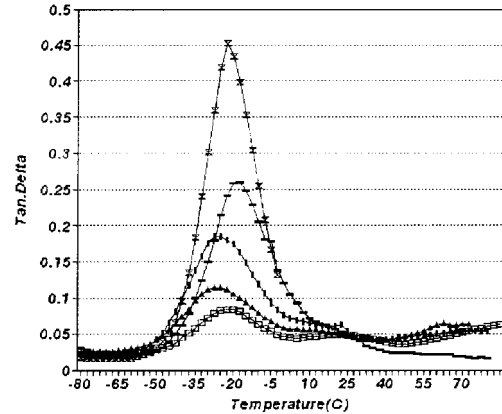


Figure 19 Effect of EPDM concentration upon $\tan \delta$: (◻) 1V; (▲) 2V; (●) 3V; (◻) 4V; (X) pure EPDM.

modulus (E'') with the increase in the rubber content is more prominent within the T_g range of PP ($\approx 10^\circ\text{C}$) than of EPDM. This is attributed to the two-phase morphology of the blends in which the thermoplastic PP forms the continuous matrix, having rubber particles as the dispersed phase. The loss tangent beyond the T_g of EPDM increases with increasing the concentration of the cured rubber particles, which is explained to be due to decrease in the content of semicrystalline domains that are mainly involved in the elastic behavior of the blends. Figure 21 demonstrates the effect of reinforcing carbon black upon the loss tangent of the 60EPDM/40PP dynamically vulcanized blends in which the carbon black was incorporated into the mix in the form of a masterbatch with

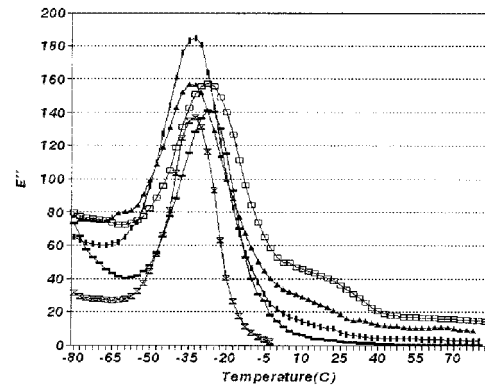


Figure 20 Effect of EPDM concentration on loss modulus (E''): (◻) 1V; (▲) 2V; (●) 3V; (◻) 4V; (X) pure EPDM.

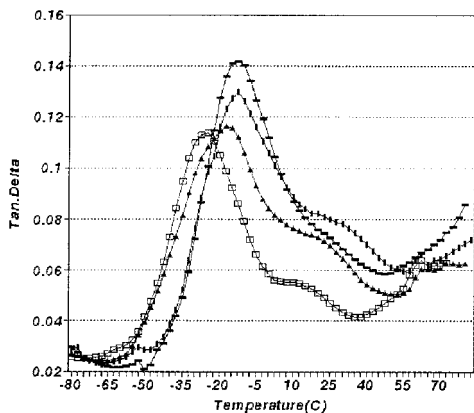


Figure 21 Effect of carbon black concentration on $\tan \delta$: (□) 2V; (▲) 2VC20; (○) 2VC40; (■) 2VC60.

EPDM as described in the Experimental section. It can be seen that all the carbon black-filled samples exhibit a higher $\tan \delta$ than that of the similar but unfilled one. Moreover, the area under the $\tan \delta$ peak does also increase with carbon black loading within the temperature range of the EPDM glass transition.

These results are indicative of high interaction between the rubber chains and functional groups on the surface of carbon black particles that retards the motion of the rubber segments and, therefore, lengthening the rubber response time toward dynamic stress fields. Similar results have been reported for NR/HDPE and NR/PP blend systems.^{9,25}

CONCLUSIONS

Comparative studies of the microstructure, rheological behavior, and mechanical properties were carried out between the unfilled and carbon black-loaded dynamically cured EPDM/PP blends. Results exhibited two-phase morphology with the rubber particles dispersed in a continuous matrix of the PP. The size of the dispersed rubber particles were shown to be larger for the carbon black-filled thermoplastic vulcanizates and carbon black particles preferentially diffuse into the more viscose rubber phases.

However, the microstructure of the black-reinforced EPDM/PP vulcanizates was affected by the route of the black feeding into the mix.

Although the addition of carbon black leads to a slight increase in shear viscosity of the EPDM/PP dynamically vulcanized blends, all the filled TPEs showed rheological characteristics similar to the unloaded samples. Under equal conditions, all the carbon black-filled EPDM/PP thermoplastic vulcanizates showed enhancement in yield stress and stress at break compared with similar but unreinforced samples. Above the EPDM glass transition temperature, both the storage and loss moduli decreased with increasing EPDM content of the dynamically crosslinked EPDM/PP blends.

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