

Thermoplastic Elastomers Based on High-Density Polyethylene, Ethylene-Propylene-Diene Terpolymer, and Ground Tire Rubber Dynamically Vulcanized with Dicumyl Peroxide

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ABSTRACT: Thermoplastic vulcanizates (TPVs) based on high-density polyethylene (HDPE), ethylene-propylene-diene terpolymer (EPDM), and ground tire rubber (GTR) were dynamically vulcanized with dicumyl peroxide (DCP). The polymer blend was composed of 40% HDPE, 30% EPDM, and 30% GTR, and the concentration of DCP was varied from 0.3 to 3.6 parts per hundred rubber (phr). The properties of the TPVs were determined by evaluation of the gel fraction content and the mechanical properties. In addition, IR spectroscopy and differential scanning calorimetry analysis were performed as a function of the DCP content. Decreases in the Young's modulus of the blends and the crystallinity of HDPE were observed when the content of DCP was greater than 1.8 phr. The results regarding the gel content indicate that the presence of DCP promoted the crosslinking of the thermoplastic matrix, and optimal properties were obtained with 1.5% DCP. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2013**, *000*, 39901.

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INTRODUCTION

Thermoplastic elastomers (TPEs) were developed in the 1950s. Because of their wide variety of applications, TPEs represent a special area of study in the field of polymers. TPEs are materials composed of a hard phase, which provides mechanical stability, and a soft phase, which imparts flexibility. Typically, high-density polyethylene (HDPE), low-density polyethylene, or polypropylene are used as the hard phase, whereas an elastomer, such as ethylene-propylene-diene terpolymer (EPDM) or ethylene-propylene rubber, is used as the soft phase. TPEs combine the behavior of elastomers with the processing behavior of thermoplastic materials. Moreover, because of their nature, TPEs can be easily reprocessed. Thermoplastic vulcanizates (TPVs) are a class of TPEs in which the rubber phase is crosslinked by dynamic vulcanization and is dispersed in the presence of a molten thermoplastic phase.¹⁻³

In recent years, because of the increasing price of EPDM, other elastomers, such as ethylene-octene, ethylene-butene, and

ground tire rubber (GTR), have been used as substitutes. The use of GTR is an excellent option for reducing the cost of TPVs, and GTR is an environmentally friendly alternative because of its upcycling applications. Specifically, approximately 1.4 billion tires⁴ are sold every year, and these tires often become environmental contaminants.

Several authors have carried out feasibility studies to produce TPVs with GTR, and the final properties of the TPVs have been shown to depend on the elastomer/thermoplastic ratio, the mixing conditions, and the type of curing agent used to crosslink the elastomeric phase.⁵ For example, a 60/40 rubber plastic blend was shown to behave as a TPE, and 50% of the EPDM could be replaced by GTR without adverse effects on the processability and physical properties of the blend.⁶ Similarly, recent work has demonstrated that a composite containing a ratio of 40/30/30 of HDPE, EPDM, and GTR, respectively showed a good balance of mechanical properties, crosslinking, and adhesion between phases.⁵ The presence of fresh rubber in TPVs

with GTR is important because the presence of rubber can produce encapsulations of GTR particles, which creates a cocontinuous phase and improves the compatibility with the matrix and GTR.^{5,7}

The crosslinking of fresh rubber in TPVs is a key factor in the production of blends with good performance. Peroxides, sulfur, and others curing agents have been used to crosslink fresh rubber in TPVs.^{6,8–10} However, a high peroxide content [$>2\%$ parts per hundred rubber (phr)] has a negative impact on the mechanical properties, possibly because of the thermooxidative degradation of the thermoplastic matrix.⁵ Nevertheless, to the best of current knowledge, a systematic study of the effect of the content of dicumyl peroxide (DCP) on the physicochemical properties of TPVs and thermoplastic polymers has not been conducted. Thus, the aim of this study was to prepare TPVs containing 30% GTR and to evaluate the effect of the DCP content on the vulcanization, rheological behavior, mechanical properties, crosslinking degree, morphology of the blend, and crystallinity of the thermoplastic phase.

EXPERIMENTAL

Materials

HDPE with a density of 0.96 g/cm^3 and melt flow index of 0.5 g/min was supplied by Mexican Petroleum (PEMEX). GTR was provided by Genbrugger S. A. de C. V (México) and was produced by ambient grinding. The average particle size was between 75 and $150 \mu\text{m}$. EPDM rubber (Nordel IP 4770) containing 70 wt % ethylene, 25 wt % propylene, and 5 wt % ethylene norbornene (ENB) was supplied by DuPont, Mexico. DCP with a purity of 98% was acquired from AkzoNobel.

Formulation of the TPVs and Blend Preparation

All of the composites were formulated with HDPE (40%), EPDM (30%), and GTR (30%). The concentrations of DCP were 0.0, 0.3, 0.6, 0.9, 1.2, 1.5, 1.8, and 3.6 phr.

The composites were prepared in a Brabender plasticorder mixing chamber with a CAM-type rotor, and the blends were prepared at 60 rpm and 180°C for 15 min. First, HDPE was placed in the chamber. After 2 min, EPDM and GTR were added and mixed for 4 min. DCP was then added and allowed to mix for 9 min to promote the curing of the blends. Torque–time curves were recorded during the preparation of the blends.

Specimen Preparation

For the mechanical tests, samples with a thickness of 2 mm were prepared by compression molding at 180°C and 0.245 MPa for 5 min; they were cooled under the same pressure with water circulating through the platens at 30°C/min for 6 min.

Tensile tests were carried out according to ASTM D 412-98 in a United 3M-10 tensile tester at a strain rate of 500 mm/min at 25°C . All of the samples were previously conditioned at $23 \pm 2^\circ\text{C}$ for 40 h, and the relative humidity was $50 \pm 5\%$.

IR spectra were acquired with a PerkinElmer 65 Fourier transform infrared spectrometer coupled to an ATR unit, and we

performed the analyses by conducting 20 scans. The samples were placed in the ATR crystal.

Differential scanning calorimetry of the composites was carried out in an MDSC-2920 instrument (TA Instruments) at temperatures ranging from -50 to 200°C . A heating rate of 10°C/min was applied in a nitrogen atmosphere at a flow rate of 50 mL/min . The degree of crystallinity of the composites was determined with the following equation:

$$X_c = \frac{\Delta H_f^*}{\Delta H_f(1-\phi)} \times 100$$

where ΔH_f^* is the enthalpy of fusion and was determined in each composite by differential scanning calorimetry; ΔH_f is the enthalpy of HDPE with a crystallinity of 100%, the value of which is reported to be 293 J/g ;¹¹ and ϕ is the weight fraction of the dispersed phase in the composites.

The morphology of the TPVs was determined with a JEOL JSM7401F1F field emission scanning electron microscope. The samples were cryogenically fractured, and the cross section was analyzed. The dispersion of GTR in the compounds was observed with an Olympus optical microscope.

The gel content was determined by the extraction of the materials with xylene to estimate the crosslinking degree according to ASTM D 2765. The gel content was calculated as indicated in the following equation:

$$\text{Gel content} = \frac{W_{\text{gel}}}{W_{\text{initial}}} \times 100$$

where W_{gel} is the gel weight and W_{initial} is the weight of the pristine sample.

RESULTS AND DISCUSSION

Mixing Torque

The torque–time curves of the composites and materials are shown in Figure 1, where two characteristic zones can be identified. The first zone corresponded to the torque during the melting, softening, and mixing of the components of the blends. In this zone, between 0 and 2 min, the torque suddenly increased because the coalescence of the particles increased the viscosity of the material; a maximum torque of 34 Nm was reached for HDPE. After 2 min, the intermolecular forces and physical entanglement between the adjacent molecules decreased, and an equilibrium torque of 4.4 Nm was achieved after 8 min. EPDM rubber showed different behavior: the maximum torque was 29.2 Nm at 1.5 min, and it decreased by 20% because of the high molecular weight of the rubber and its nonlinear structure; this was attributed to the diene and pendant groups of propylene, which produced a greater entanglement density of the EPDM rubber molecules. For the HDPE/EPDM/GTR blends, the maximum torque was 25 Nm, whereas the equilibrium torque was 13 Nm. The torque of the blends was located between the torque of HDPE and that of EPDM and was nearly constant throughout the mixing time. This behavior was due to the combination ratio of 40/30/30 of HDPE/EPDM/GTR. In the case of pure GTR, the torque was equal to zero because the macromolecules did not coalesce because of their crosslinked structure.

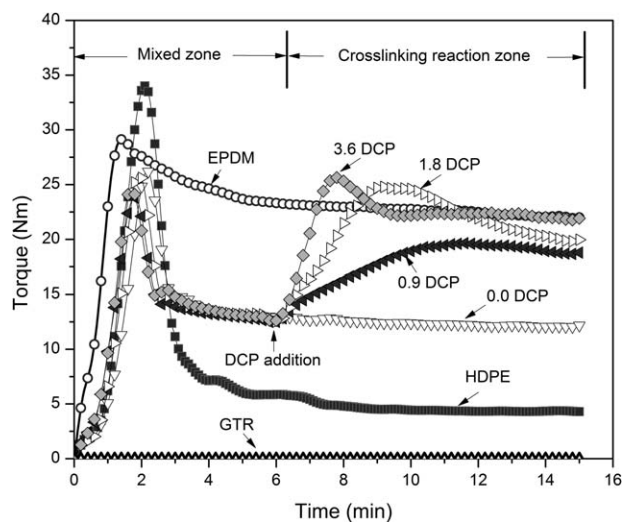


Figure 1. Torque–time curves of the unvulcanized and dynamically vulcanized blends and neat materials. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

During the preparation of the blends, after the addition of DCP at 6 min (crosslinking reaction zone), the torque suddenly increased in the dynamical vulcanized zone because of the crosslinking reaction of EPDM. The observed increase in torque as a function of the DCP content was related to the slope in the crosslinking reaction zone shown in Figure 1. The higher values of the slope indicated that a higher concentration of free radicals promoted an increase in the crosslinking density in the blends and a higher torque during mixing. After the maximum torque in the crosslinking zone of the blends, the torque decreased to a relatively constant value; this indicated that the crosslinking reaction had ended. The observed decrease in the torque after the maximum value in the composites with high contents of DCP (1.8 and 3.6 phr) may have been due to the molecular scission processes experienced by the thermoplastic and rubber phases.

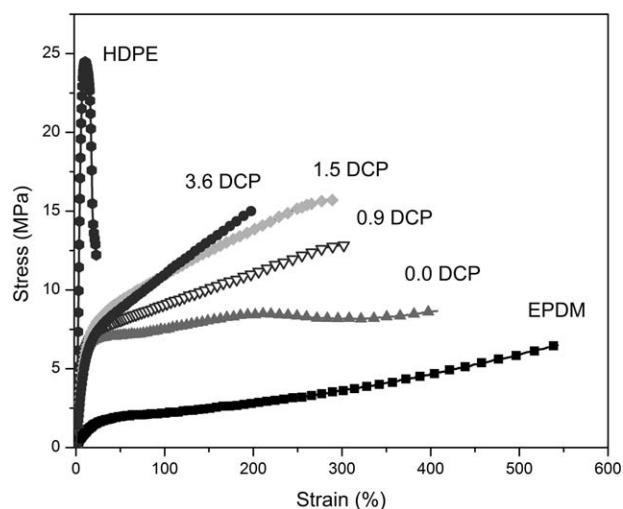


Figure 2. Tensile stress–strain curves of the neat materials and unvulcanized and dynamically vulcanized blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

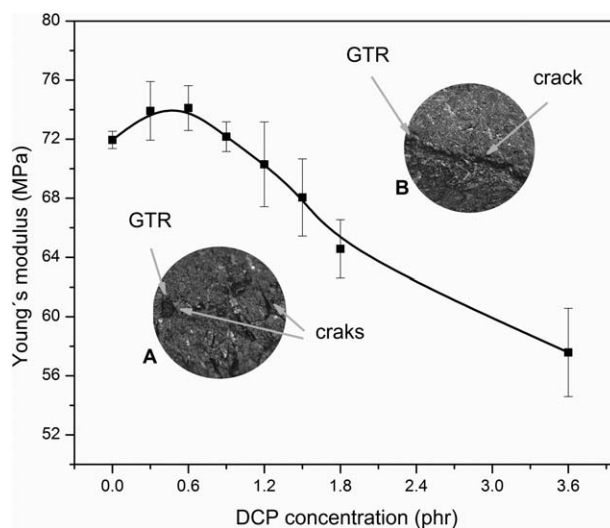


Figure 3. Effect of the DCP content on the Young's modulus of the composites. The inserted pictures were acquired by optical microscopy and represent the (A) unvulcanized blends and (B) dynamically vulcanized blends with 3.6 phr DCP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Mechanical Properties

The tensile stress–strain curves for all of the materials are shown in Figure 2. When a stress of 6.4 MPa was applied, a high strain of up to 550% was observed for EPDM; this is typical behavior for elastomers. Contrary to the expected results, HDPE showed a high stress of 24.6 MPa and a deformation of only 22%. The addition of DCP and the consequent dynamic vulcanization of the HDPE/EPDM/GTR composites changed the shape of the tensile curves, and an increase in the tensile stress and a gradual decrease in the elongation at break was observed. Because peroxides were not selective for unsaturated elastomers, this effect was attributed to the reaction of peroxides with HDPE. In previously reported results, the elongation at break increased as a function of the DCP content; however,^{5,6,10} in this study, the addition of DCP decreased the elongation at break of the composites.

In Figure 3, the curve of the Young's modulus versus the DCP concentration is presented. Composites containing 0.3 and 0.6 phr DCP presented the highest Young's moduli with values of 73.9 and 74.1 MPa, respectively, whereas the Young's modulus of the rest of the composites decreased as a function of the DCP content. This behavior could be explained as follows: at low DCP contents, crosslinking sites interconnected the amorphous chains among lamellae;¹² this was responsible for the slight increase in the Young's modulus (from 72 to 74 MPa). In contrast, at high DCP contents, the observed decrease in the Young's modulus as function of the DCP content may have been associated with certain disturbances in the reorganization and chain-folding processes that occurred during crystallization because of the presence of DCP. This resulted in the formation of imperfect crystallites with smaller sizes. This behavior directly affected the Young's modulus.¹³ According to the aforementioned explanation, the crystallinity of HDPE may have been affected, as previously reported.^{14,15}

Table I. Mechanical Properties of the Composites as a Function of the DCP Content

Blend	DCP (phr)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
EPDM	0	9.890 ± 0.86	6.330 ± 0.12	527.28 ± 10.14
HDPE	0	444.3 ± 1.34	24.48 ± 0.31	24.080 ± 3.060
EPDM/HDPE/GTR	0	71.95 ± 0.58	8.480 ± 0.47	366.60 ± 36.47
EPDM/HDPE/GTR	0.3	73.91 ± 1.99	9.920 ± 0.14	312.67 ± 35.82
EPDM/HDPE/GTR	0.6	74.10 ± 1.52	11.94 ± 0.42	301.42 ± 37.97
EPDM/HDPE/GTR	0.9	72.17 ± 1.00	12.77 ± 0.26	292.56 ± 14.54
EPDM/HDPE/GTR	1.2	70.29 ± 2.87	13.77 ± 0.27	276.06 ± 21.33
EPDM/HDPE/GTR	1.5	68.04 ± 2.61	15.02 ± 0.60	271.61 ± 15.61
EPDM/HDPE/GTR	1.8	64.57 ± 1.98	14.57 ± 0.48	239.98 ± 25.74
EPDM/HDPE/GTR	3.6	57.58 ± 2.99	14.12 ± 1.13	177.09 ± 27.45

Another effect that likely reduced the Young's modulus was related to the poor compatibility of HDPE/EPDM with GTR, as shown in the insets images of Figure 3. In these optical images, cracks zones surround the GTR particles and accumulate stress and decreased the Young's modulus.

The mechanical properties of the composites are shown in Table I. With respect to the tensile strength, the dynamically vulcanized composites possessed a higher tensile strength than the corresponding composites without DCP. The maximum tensile strength was 15.02 MPa, and it corresponded to the composite containing 1.5 phr DCP. The observed improvement in the tensile strength may have been associated with homogeneous crosslinking in the rubber phase. However, composites with high contents of DCP (1.8 and 3.6 phr) may have presented a heterogeneous network because of the existence of densely crosslinked zones (clusters), in which charge transfer between network junctions was slow and stress accumulation was promoted. Cluster formation has been previously reported in crosslinked systems of natural rubber with DCP and was related to a decrease in the elongation at break and the mechanical properties.^{16,17}

In general, the elongation at break tended to decrease (see Table I) with an increase in the DCP content, and this increased the hardness of the blends. Moreover, EPDM rubber formed denser networks, and the chain length of HDPE decreased because of DCP-induced degradation. If the number or length of chains that were available for elongation decreased, the probability of sliding between chains also decreased, and this reduced the strain of the material. However, the elongation at break of the composites (except that of 3.6% DCP) ranged between 200 and 600%, and the tensile strength varied from 2 to 30 MPa; these are typical values for TPVs.¹⁸

Gel Content

The effect of the peroxide content (DCP) on the gel content of the composites is shown in Figure 4. In the unvulcanized blend, the gel content was approximately 30.5%; this corresponded to the GTR content of the composite (30%). In contrast, as shown in Figure 4, a continuous increase in the gel content was observed as the DCP content increased to 1.5 phr.

After this value, the observed tendency gradually leveled off. According to the tensile strength results presented previously, the gel content and tensile strength as a function of the DCP content were in good agreement, and both properties presented similar behavior.

According to the formulation of the 40/30/30 HDPE/EPDM/GTR composites, the maximum gel content was approximately 82.5%, and this corresponded to a DCP content of 1.5 phr. Because all of the EPDM was crosslinked, the gel content of EPDM and GTR would be equivalent to 60%. The difference in the gel content at a DCP content of 1.5 phr was equal to 22.5%; this indicated that a fraction of HDPE was crosslinked. HDPE crosslinking was expected because DCP is not selective for EPDM. A decrease in the gel content at a DCP content of 1.8 phr may have been observed because peroxide promotes the degradation of the thermoplastic and rubber phases.

The mechanism of crosslinking of polyethylene (PE) with DCP was proposed by Campus and Matey¹⁹ and Lazar et al.²⁰ Free radicals generated from the thermal decomposition of peroxides can attack PE chains and crosslink the polymer, as demonstrated in this study. A general scheme for the crosslinking reaction of PE initiated by free radicals is presented in Scheme 1

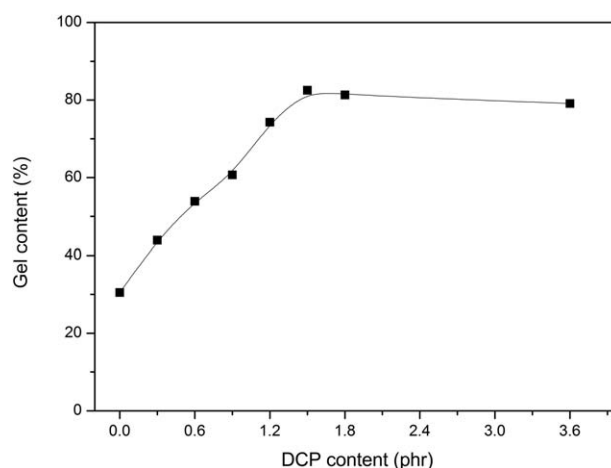
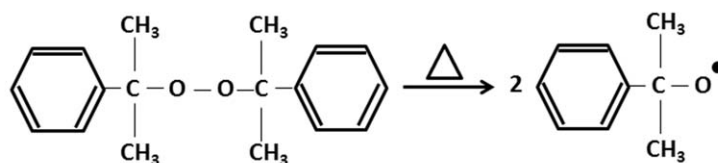
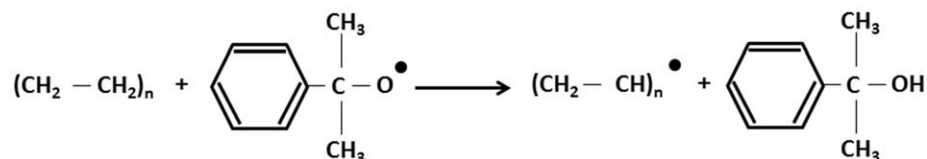


Figure 4. Effect of the DCP content on the gel content of the crosslinked HDPE/EPDM/GTR composites.

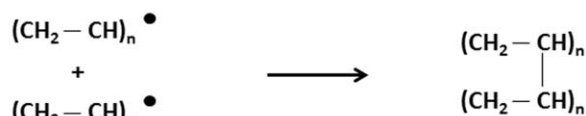
Thermal decomposition of peroxide:



H abstraction



Crosslinking



Scheme 1. Thermal decomposition of peroxide.

and consists of the formation of macroradicals and their subsequent recombination.

These chemical reactions explain the properties of the prepared composites.

Thermal Properties

The effect of the DCP content on the thermal properties of the composites is shown in Table II. The fusion and crystallization temperatures were not significantly affected by the addition of DCP. However, decreases in ΔH_f° and the degree of crystallinity were observed with an increase in the DCP content. This result could be explained as follows: as the amount of DCP increased, the crosslinking density increased, and the degree of crystallinity of HDPE decreased.

According to literature reports, the formation of crosslinked junctions occurred when the polymer was in its melt state,

which disturbed the reorganization and chain-folding process during crystallization and resulted in the formation of imperfect crystals with smaller sizes.

Infrared Spectroscopy

Figure 5 shows the ATR-IR spectra of the pristine materials and the spectra of the vulcanized and unvulcanized blends. The main characteristic bands of GTR were 2914 and 2849 cm^{-1} and were associated with the asymmetric and symmetric stretching of C—H methylene groups, respectively. The strong peak located at 1540 cm^{-1} was assigned to the stretching of the COO^- group of zinc stearate, which was a product of the reaction between zinc oxide and stearic acid. Zinc oxide and stearic acid are used as additives in the formulation of tires to protect the material from oxidation via air, UV radiation, and ozone.²¹ The band located at 1464 cm^{-1} corresponded to the scissoring vibration of methylene and overlapped with the signal located at 1450 cm^{-1} , which corresponded to the

Table II. Gel Content and Thermal Properties of the Composites as a Function of the DCP Content

Blend	DCP (phr)	Melting temperature T_f ($^\circ\text{C}$)	Crystallization temperature T_c ($^\circ\text{C}$)	ΔH_f (J/g)	Degree of crystallinity X_c of HDPE (%)	Gel content (%)
HDPE			130.4	200	68.2	
EPDM/HDPE/GTR	0	114.1	128.1	87.8	74.9	30.5
EPDM/HDPE/GTR	0.3	114.4	127.6	85.9	73.2	43.9
EPDM/HDPE/GTR	0.6	114.3	127.2	84.4	72.0	53.9
EPDM/HDPE/GTR	0.9	114.8	127.2	81.0	70.5	60.7
EPDM/HDPE/GTR	1.2	115.0	126.8	80.1	68.3	74.3
EPDM/HDPE/GTR	1.5	115.6	126.5	79.4	67.7	82.5
EPDM/HDPE/GTR	1.8	115.9	126.3	74.4	66.5	81.3
EPDM/HDPE/GTR	3.6	116.2	126.5	63.4	59.4	79.1

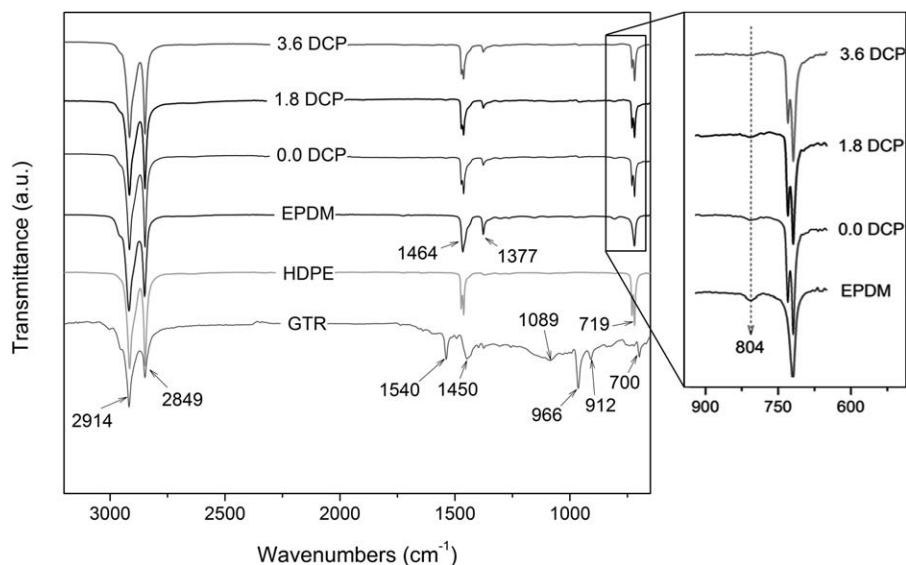


Figure 5. ATR-IR spectra of the pristine materials and vulcanized and unvulcanized composites.

asymmetric flexion of the methyl group. The broad signal at 1089 cm^{-1} was associated with the Si-O stretching mode,²¹ and the intense signals at 966 and 912 cm^{-1} were characteristic of the C-H flexion of the vinyl group of polybutadiene.

Four sharp peaks dominated the spectrum of HDPE, including the methylene stretching vibrations located at 2920 and 2850 cm^{-1} and the methylene deformations located at 1464 and 719 cm^{-1} .

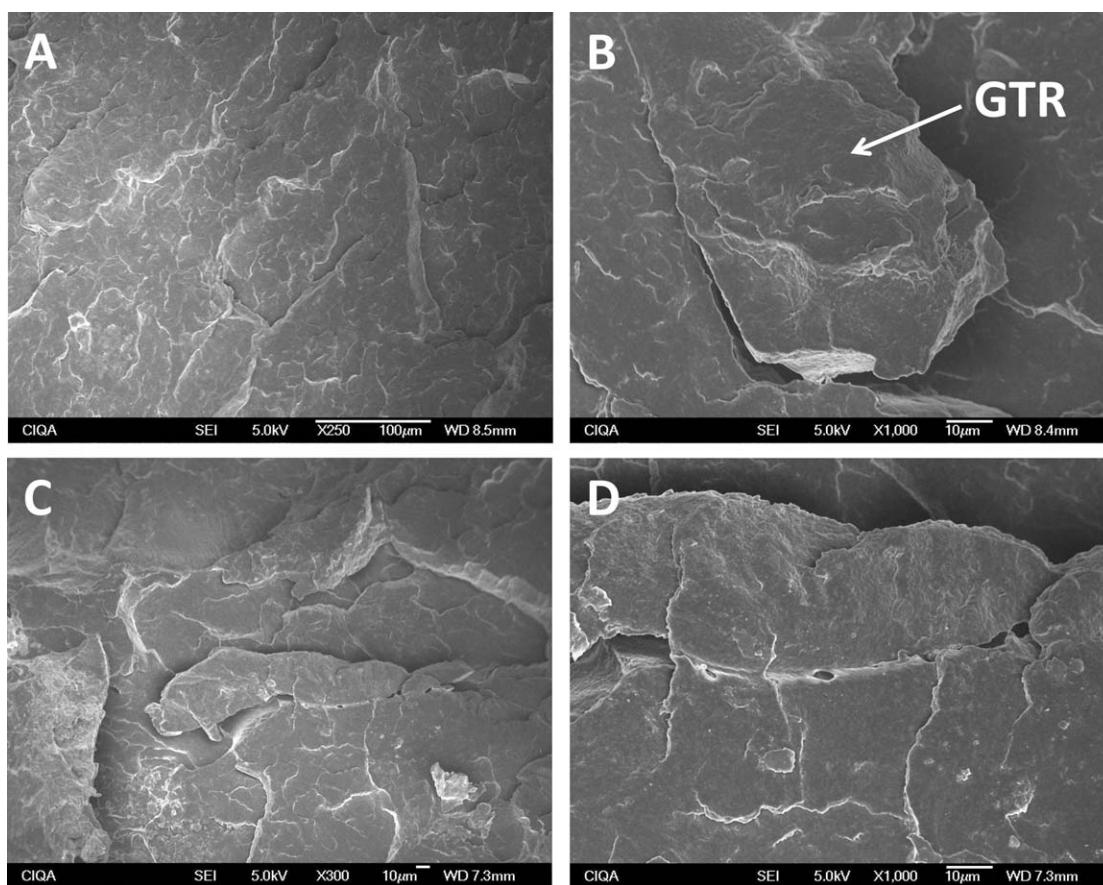


Figure 6. SEM micrographs of the HDPE/EPDM/GTR composites: (A) unvulcanized blend ($250\times$), (B) unvulcanized blend ($1000\times$), (C) dynamically vulcanized blend with 0.9 phr DCP ($300\times$), and (D) dynamically vulcanized blend with 0.9 phr DCP ($1000\times$).

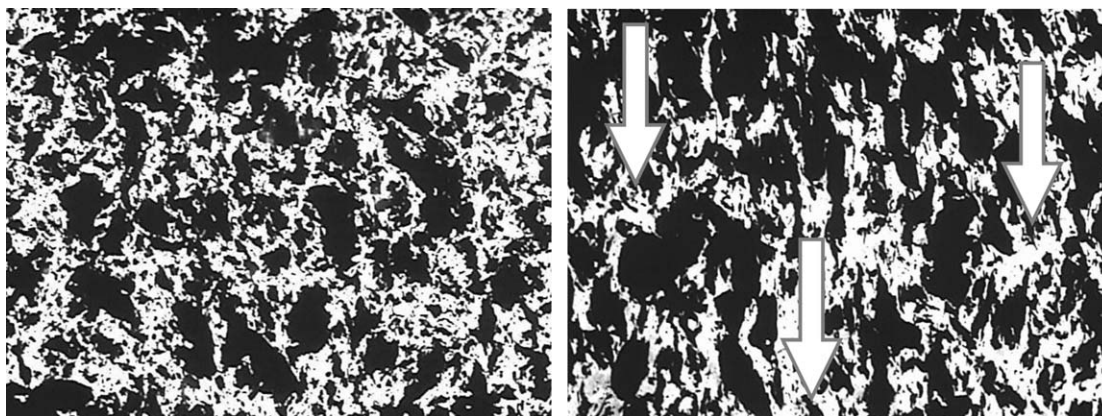


Figure 7. Optical microscopy images at 50 \times in reflected light: (left) unvulcanized blend and (right) vulcanized blend with 3.6 phr DCP.

The IR spectrum of EPDM was dominated by the methylene peaks located at 2925, 2854, 1464, and 721 cm^{-1} .²² The methyl peak located at 1377 cm^{-1} was also significant; however, from an analytical standpoint, the most interesting peak was the signal located at 804 cm^{-1} . This signal was attributed to the vibration outside of the plane of the CH double bonds linked to the C=C of diene groups.²³

By comparing the normalized spectra of the blends, we observed a progressive decrease in the intensity of the band located at 804 cm^{-1} , which was attributed to the loss of the double bond. Specifically, crosslinking reactions preferentially occurred with this functional group.

Scanning Electronic Microscopy

Figure 6 presents the SEM micrographs of vulcanized and unvulcanized blends fractured under cryogenic conditions. Figure 6(A) shows the micrograph obtained at 250 \times , which displayed a fragile crack and GTR particles. In these three-phase compounds, two types of structures were observed. In one structure, the elastomer and filler particles were dispersed separately on the polymeric matrix,^{24,25} whereas the elastomeric phase encapsulated these particles in the second structure.²⁶ In previous studies based on HDPE/EPDM/GTR systems, EPDM tended to encapsulate GTR.^{5,6} In this study, the same behavior likely occurred, although there was not sufficient evidence to corroborate this hypothesis. Figure 6(B) shows the micrograph obtained at 1000 \times , which focused on a GTR particle that was not completely attached to the matrix; this indicated that the interfacial interaction between the phases was poor. In contrast, the vulcanized blend [Figure 6(c,d)] presented some areas in which the GTR particles were joined to the thermoplastic matrix. The compatibility zones of the vulcanized blend containing 0.9 phr DCP likely promoted the crosslinking reaction between EPDM and the external molecules of GTR. The observed improvement in the tensile strength was attributed to the addition of DCP, which promoted the interfacial adhesion between HDPE/EPDM and GTR.

Optical Microscopy

Figure 7 shows images that reveal several characteristics of the vulcanized and unvulcanized blends. In Figure 7(a), a good dispersion of GTR particles (represented by the dark phase in the image) and HDPE/EPDM (as represented by the white phase in

the image) is shown. GTR particles did not have a preferential orientation in the polymeric matrix. Figure 7(b) presents the GTR particles in the vulcanized composite with 3.6 phr DCP. In this particular case, the GTR particles showed a preferential orientation in the flow direction, which is represented by gray arrows. The orientation of the particles was related to the observed increase in the viscosity of the material and was attributed to the reactions between DCP, EPDM, and HDPE. An increase in the viscosity was also corroborated by the torque-time curves presented in Figure 1.

CONCLUSIONS

The properties of the HDPE/EPDM/GTR composites were significantly affected by the DCP content. Decreases in the Young's modulus and elongation at break were observed, but the tensile strength improved as a function of the DCP content. The addition of DCP decreased the degree of crystallinity of HDPE. The optimal content of DCP was 1.5 phr, and the composites still behaved as TPVs.

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