

Optimized Processing Conditions for the Preparation of Dynamically Vulcanized EPDM/PP Thermoplastic Elastomers Containing PP Resins of Various Melt Indexes

Jen-Taut Yeh,^{1,2} Shui-Chuan Lin³

¹Graduate School of Polymer Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

²Faculty of Chemistry and Material Science, Hubei University, Wuhan, China

³Department of Polymer Materials, Vanung University, Taoyuan, Taiwan

Received 27 August 2008; accepted 3 May 2009

DOI 10.1002/app.30865

Published online 16 July 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: We have investigated the mechanical and morphological properties of un-vulcanized and dynamically vulcanized ethylene propylene diene terpolymer/polypropylene (EPDM/PP) thermoplastic elastomers prepared under various processing conditions and possessing various compositions. After melt-blending EPDM and PP resins twice in a twin-screw extruder, the values of tensile strength (σ_f) of the un-vulcanized EPDM/PP samples were at most equal to that of the pure EPDM specimen, but were much lower than those of the pure PP specimens. The elongations at break (ϵ_f) of the un-vulcanized EPDM/PP samples were, however, dramatically higher than those of their respective virgin PP resins, and they improved significantly upon increasing the shear viscosity (η_s) of the PP resins. The tensile properties of the dynamically vulcanized EPDM/PP samples were significantly better than those of the corresponding un-vulcanized EPDM/PP specimens. Similar to the behavior of the un-vulcanized EPDM/PP specimens, the tensile properties of the dynamically vulcanized EPDM/PP specimens were optimized when prepared at a screw rate of 115 rpm. Morphological analysis revealed that the un-vulcanized and dynamically

vulcanized EPDM/PP specimens both featured many EPDM domains finely dispersed in continuous PP matrices. Such domains were present on the surfaces of the dynamically vulcanized EPDM/PP specimens; the relative sizes of the vulcanized EPDM domains were minimized when the vulcanized EPDM/PP specimens were prepared at the optimal screw rate (115 rpm). In fact, under these conditions, the average sizes of the vulcanized EPDM domains decreased upon increasing the values of η_s of the PP resins used to prepare the vulcanized EPDM/PP specimens. To understand these interesting tensile and morphological properties of the un-vulcanized and dynamically vulcanized EPDM/PP specimens, we measured the rheological properties of the base polymers and performed energy-dispersive x-ray (EDX) analyzes of the compositions of the un-vulcanized and dynamically vulcanized EPDM/PP specimens. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2806–2815, 2009

Key words: ethylene propylene diene terpolymer (EPDM); dynamic vulcanization; morphology; viscosity ratio

INTRODUCTION

Dynamic vulcanization is the process of vulcanizing an elastomer during its melt-mixing with a molten thermoplastic resin, wherein the vulcanized elastomers are present as finely dispersed particles in continuously thermoplastic matrices. This processing technology was first described by Gessler¹ in 1962 and then developed by Fisher² and Coran and Patel.^{3,4} Dynamically vulcanized elastomers display the characteristics of both elastomers and thermoplastics; therefore, they can be molded, shaped, and/or reprocessed at temperatures above the melting or softening temperatures of the thermoplastic resins. Because of their excellent elastomeric proper-

ties and ease of processing—without the time-consuming curing step that is required for conventional vulcanizates⁵—dynamically vulcanized elastomers are used widely in automobile parts (e.g., bumper covers, sealing strip, gaskets, interior automotive components), tubing, hosing, and cable sheaths.

Several reports describe the preparation and morphological and mechanical properties of blends of dynamically vulcanized ethylene propylene diene terpolymer (EPDM)/polypropylene (PP),^{6–21} EPDM/polyethylene (PE),^{22–24} nitrile rubber (NBR)/nylon,²⁵ natural rubber (NR)/polyethylene-co-vinyl acetate (EVA),²⁶ epoxidized natural rubber (ENR)/polyvinylchloride (PVC),²⁷ EPDM/polyamide (PA),^{28–30} and chlorinated polyethylene rubber/nylon.³¹ Possible mechanisms have been proposed to explain the significantly improved mechanical properties of these vulcanized elastomeric blends.^{6–31} It is generally recognized^{25–31} that the fine particles of

Correspondence to: S.-C. Lin (scl@mail.vnu.edu.tw).

TABLE I
Characteristics of the PP and EPDM Resins and Additives Used to Prepare the Dynamically Vulcanized EPDM/PP Thermoplastic Elastomers

Material	Trade name	Comments
PP ^a	PT181	MFI (g/10 min) = 0.4 Specific gravity (g/cm ³) = 0.902
PP ^b	PT100	MFI (g/10 min) = 1.6 Specific gravity (g/cm ³) = 0.903
PP ^c	6331F	MFI (g/10 min) = 14 Specific gravity (g/cm ³) = 0.904
EPDM	3745	E/P weight ratio = 69/30.5 ENB (ethylidene 2-norbornene) = 0.5 wt % Mooney viscosity (ML1 + 4,125 °C) = 45 Specific gravity (g/cm ³) = 0.87
Dimethylol phenolic resin	SP 1405	Melting point = 63°C Specific gravity (g/cm ³) = 1.05 Molecular weight, 500; contents of hydroxylic and phenolic groups, 19.0 wt %; CH ₂ OH groups, 11.0 wt %; nitrogen, 2.4 wt %
SnCl ₂	8176	Analytical reagent Molecular weight, 225.63
Naphthenic oil	SUN 450	Molecular weight, 500; Specific gravity (g/cm ³) = 0.9291 Viscosity (at 40°C) = 96.82 cps Flash point = 196°C

vulcanizates dispersed in continuously thermoplastic matrices—the fundamental morphological characteristics of dynamically vulcanized elastomers—account for their improved impact, mechanical, and elastomeric properties. The phase structures formed by the thermoplastic elastomers are closely related to the viscosity ratios of the corresponding vulcanized rubbers and thermoplastic resins,^{19–31} the blend compositions,^{6–31} the mixing conditions, and the types of mixing devices employed.^{21,32–35} For example, Kuriakose and De³⁴ reported that the shear stress is a more important factor in controlling the sizes of vulcanized NR particles in NR/PP thermoplastic elastomers than is the shear rate-dependent viscosity ratio. Oderkerk and Groeninckx³⁰ observed, however, a significant difference in the morphology of EPDM/nylon-6 blends prepared using nylon-6 samples having various melt shear viscosities. They observed significantly coarser vulcanized EPDM particles in the continuous nylon-6 matrices upon decreasing the melt shear viscosity of the nylon-6 sample. In contrast, Xiao and coauthors²¹ studied the effect of the mixing devices employed on the morphological properties of EPDM/PP blends. They found that EPDM/PP blends prepared in a single-screw extruder displayed superior mechanical properties, dispersion, and fineness of the EPDM vulcanizates than did those prepared using an open mill.

Because the rheological properties of elastomer-modified polymer blends are of prime importance for their applications, a better understanding of these properties would aid in optimizing the com-

mercial production of such blends.^{36–39} To determine the optimal melt-blending conditions and to further enhance the mechanical properties of dynamically vulcanized EPDM/PP blends, we prepared a series of dynamically vulcanized EPDM/PP resins through pre-blending of the EPDM resins twice using PP resins of various melt indexes and varying screw speeds before further vulcanization of the dispersed EPDM particles. In this article, we report a systematic study of the influences of (i) the viscosity ratio of the EPDM/PP resins and (ii) the screw rate on the rheological behavior, structural development, and mechanical properties of dynamically vulcanized EPDM/PP thermoplastic elastomers.

EXPERIMENTAL

Materials

The basic polymers used to prepare the EPDM/PP thermoplastic elastomers were PP and EPDM with ethylidene 2-norbornene (ENB) resins. EPDM and PP resins of various MFI values were obtained from Dupont and the Taiwan PP Corporation, respectively. Dimethylol phenolic resin (SP 1405) and SnCl₂ were obtained from Schenectady International and Mallinckrodt Baker, respectively; they were used as a curing agent and as an accelerator to vulcanize the EPDM in the reactive extrusion processes, respectively. Table I lists the key characteristics of the commercially available polymers and curing agents employed in this study.

TABLE II
Compositions and Sample Designations of the Un-Vulcanized and Dynamically Vulcanized EPDM/PP Specimens

Compositions and screw rates/sample	EPDM (parts)	PP (parts)	Phenolic resin (parts)	SnCl ₂ (parts)	Naphthenic oil (parts)	Screw rate (rpm)
EP ^a ₋₈₀	60	40 (PP ^a)	0	0	10	80
EP ^a ₋₉₅	60	40 (PP ^a)	0	0	10	95
EP ^a ₋₁₁₅	60	40 (PP ^a)	0	0	10	115
EP ^a ₋₁₂₅	60	40 (PP ^a)	0	0	10	125
EP ^a _{v10-80}	60	40 (PP ^a)	10	2	10	80
EP ^a _{v10-95}	60	40 (PP ^a)	10	2	10	95
EP ^a _{v10-115}	60	40 (PP ^a)	10	2	10	115
EP ^a _{v10-125}	60	40 (PP ^a)	10	2	10	125
EP ^b ₋₈₀	60	40 (PP ^b)	0	0	10	80
EP ^b ₋₉₅	60	40 (PP ^b)	0	0	10	95
EP ^b ₋₁₁₅	60	40 (PP ^b)	0	0	10	115
EP ^b ₋₁₂₅	60	40 (PP ^b)	0	0	10	125
EP ^b _{v10-80}	60	40 (PP ^b)	10	2	10	80
EP ^b _{v10-95}	60	40 (PP ^b)	10	2	10	95
EP ^b _{v10-115}	60	40 (PP ^b)	10	2	10	115
EP ^b _{v10-125}	60	40 (PP ^b)	10	2	10	125
EP ^c ₋₈₀	60	40 (PP ^c)	0	0	10	80
EP ^c ₋₉₅	60	40 (PP ^c)	0	0	10	95
EP ^c ₋₁₁₅	60	40 (PP ^c)	0	0	10	115
EP ^c ₋₁₂₅	60	40 (PP ^c)	0	0	10	125
EP ^c _{v10-80}	60	40 (PP ^c)	10	2	10	80
EP ^c _{v10-95}	60	40 (PP ^c)	10	2	10	95
EP ^c _{v10-115}	60	40 (PP ^c)	10	2	10	115
EP ^c _{v10-125}	60	40 (PP ^c)	10	2	10	125

The letters E, P^a, P^b, and P^c represent the EPDM, PP^a, PP^b, and PP^c resins, respectively.

Preparation of dynamically vulcanized EPDM/PP resins

The EPDM/PP blends were prepared via reactive extrusion using a Nanjing Jiant SHJ-36 corotating twin-screw extruder; the length-to-diameter ratio of the screw was 40. For every 60 parts by weight of EPDM, 40 parts of the PP resin (various melt indexes) were melt-blended twice to shear and disperse the EPDM resins in the twin-screw extruder, which was operated at 185°C in the feeding zone and at 190°C toward the extrusion die with a constant screw rate within the range 80–125 rpm. The pre-blended EPDM/PP resins were then quenched in cold water at 25°C and cut into pellets. In the second step, the pre-blended EPDM/PP resins were melt-blended with dimethylol phenolic resin (10 parts), SnCl₂ (two parts), and naphthenic process oil (10 parts) for further dynamic vulcanization of the EPDM resin. During the dynamic vulcanization process, the extruder was operated under the same conditions as those used in the pre-blending process. The vulcanized EPDM/PP resins were then quenched in cold water at 25°C and cut into pellets. Table II summarizes the compositions and specimen designations of the resulting dynamically vulcanized EPDM/PP resins.

Rheological properties

The melt shear viscosities (η_s) of the PP and EPDM resins were measured at 195°C and shear rates rang-

ing from 30 to 180 1/s using a Rosand precision advanced capillary extrusion rheometer equipped with a capillary having a diameter of 1 mm and a length of 16 mm. The measured values of η_s were correlated to the deformation behavior of the EPDM and PP resins during their melt-blending and dynamic vulcanization processes in the twin-screw extruder.

Morphologies and surface compositions of the un-vulcanized and dynamically vulcanized EPDM/PP specimens

The morphologies of the un-vulcanized and dynamically vulcanized EPDM/PP samples were examined using a JEOL JSM-5200 scanning electron microscope (JEOL Technics, Tokyo, Japan). The hot-pressed samples were sectioned using a scalpel and etched with cyclohexane at 50°C for 24 h to dissolve the un-vulcanized EPDM resins present on the surfaces. The samples were fractured in liquid nitrogen before etching, and then gold-coated before examination using scanning electron microscopy (SEM). The compositions of the surfaces of these specimens were determined using a Siemens D5000S EDX spectrometer equipped on the SEM instrument.

Mechanical properties

The tensile properties of the un-vulcanized and dynamically vulcanized EPDM/PP samples were

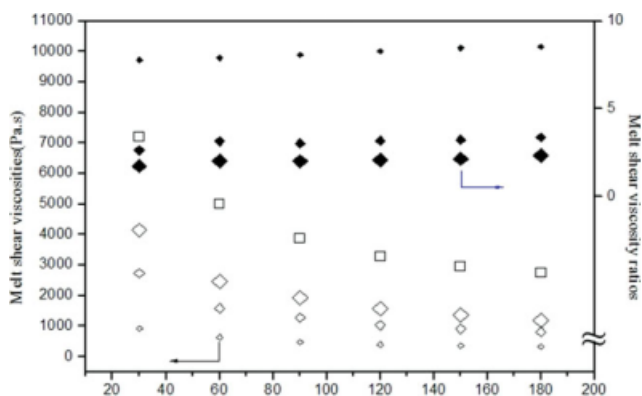


Figure 1 Melt shear viscosities of PP^a (\diamond), PP^b (\circ), PP^c (\triangle), and EPDM (\square) and EPDM-to-PP melt shear viscosity ratios of PP^a (\blacklozenge), PP^b (\blacklozenge), and PP^c (\blacklozenge), measured at 195°C using various shear rates. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

determined at 25°C using an HT-9112 Hungta Instron testing machine operated at a crosshead speed of 100 mm/min. The specimens were prepared and tested according to the ASTM D638 Type IV standard. Rectangular samples having dimensions of 50 × 10 × 0.4 mm were used. The experiment was per-

formed using a Chun Yen CY-6458 impact tester according to ISO 179. At least five samples were measured in each test; the results were averaged.

RESULTS AND DISCUSSION

Rheological properties of EPDM and pp samples

Figure 1 summarizes the melt shear viscosities (η_s) of EPDM and the PP resins and the EPDM-to-PP viscosity ratios measured at various shear rates (γ). The melt shear viscosity of each base resin decreased upon increasing the shear rate. Among these base resins, EPDM always exhibited higher melt shear viscosities than did the PP resins (i.e., the PP^a, PP^b, and PP^c resins). The melt shear viscosities of the virgin PP resins measured at varying shear rates increased upon decreasing their melt indexes (see Table I and Fig. 1); the values of η_s of the PP resins followed the order PP^a > PP^b > PP^c. Figure 1 reveals that the values of η_s of EPDM remained slightly higher than those of the PP^a resin and significantly higher than those of the PP^b and PP^c resins when measured at various shear rates. In contrast, the EPDM-to-PP melt shear viscosity ratios increased even further from 1.74 to 2.32 (PP^a), 2.63 to 3.37

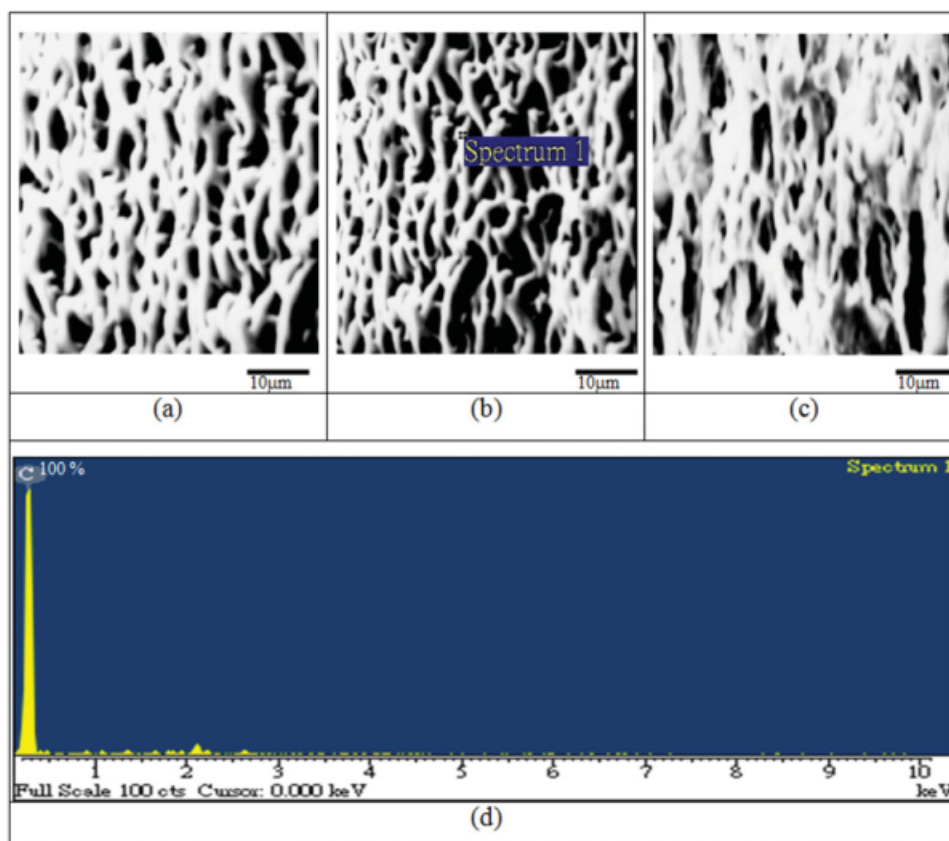


Figure 2 Fracture surface morphologies of (a) EP₋₁₁₅^a, (b) EP₋₁₁₅^b, and (c) EP₋₁₁₅^c specimens and (d) EDX spectrum (elemental composition) of spectrum 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

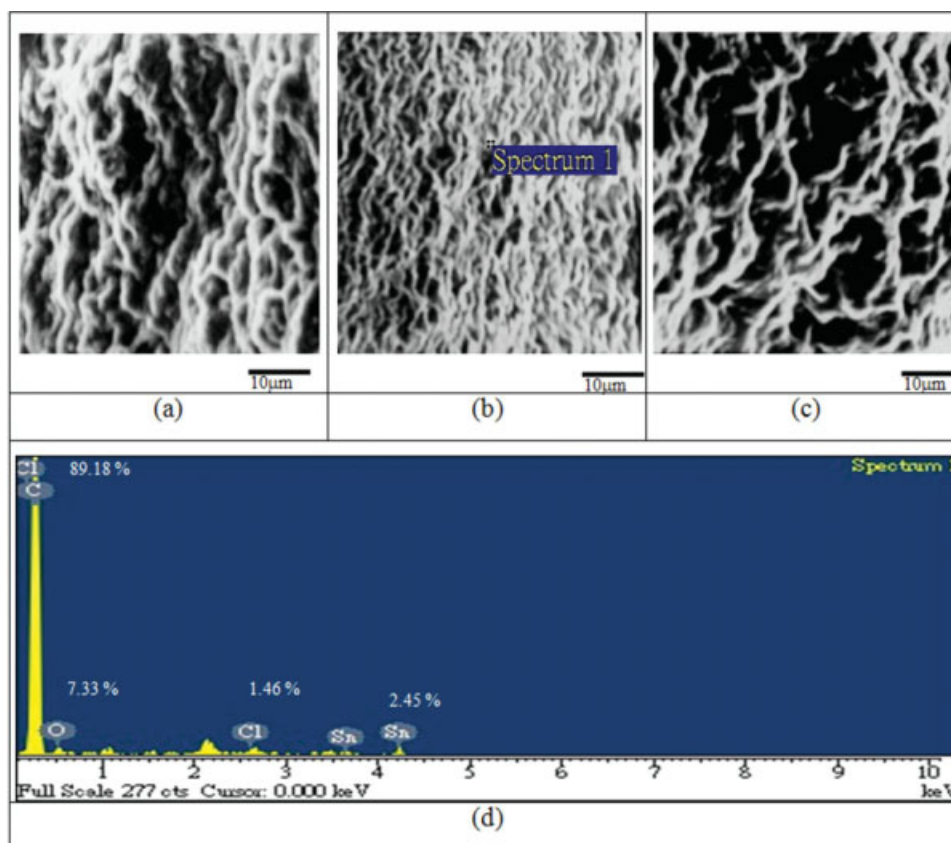


Figure 3 Fracture surface morphologies of (a) EP_{v10-80}^a , (b) $EP_{v10-115}^a$, and (c) $EP_{v10-125}^a$ specimens and (d) EDX spectrum (elemental composition) of spectrum 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(PP^b), and 7.78 to 8.54 (PP^c), respectively as their shear rates increased from 30 to 180 s^{-1} (Fig. 1).

Morphology of dynamically vulcanized EPDM/PP

Figures 2–5 present typical SEM micrographs of the fracture surfaces of un-vulcanized and dynamically vulcanized EPDM/PP specimens. Figure 2(a) reveals many dispersed black domains, having sizes ranging from about 0.5 to $10 \mu\text{m}$, on the cyclohexane-etched surfaces of the un-vulcanized EPDM/PP specimens prepared at a screw rate of 115 rpm. Because virgin EPDM resins can be dissolved in cyclohexane, the black and white domains on the surface of the un-vulcanized EPDM/PP specimens most likely correlated to the dispersed virgin EPDM and PP resins, respectively. EDX spectroscopic analysis of the compositions of the un-vulcanized EPDM/PP specimens revealed that only C atoms were present on the cyclohexane-etched surfaces of these un-vulcanized EPDM/PP specimens [Fig. 2(d)]; i.e., the crosslinking O atoms present in the EPDM resin were absent. These results suggest that the white domains on the surfaces of the un-vulcanized EPDM/PP specimens corresponded to the PP resin. We observed similar morphologies on the cyclohexane-etched surfaces of

the other un-vulcanized EPDM/PP specimens prepared using PP samples having lower values of η_s . The average sizes of the dispersed black domains decreased significantly upon increasing the value η_s of the PP resin [cf. Figs. 2(a–c)].

In contrast, after dynamic vulcanization of the EPDM resins, many finely dispersed black domains were present on the surfaces of the dynamically vulcanized EPDM/PP specimens (cf. Figs. 3–5); the relative size of the black domains reached a minimum when the vulcanized EPDM/PP specimens were prepared at the optimal screw rate (115 rpm). In fact, at this screw rate, the relative sizes of the black domains decreased further upon increasing the values of η_s of the PP resins used to prepare the vulcanized EPDM/PP specimens. Figure 3(b), 4b, and 5b reveal that the sizes of the black domains of the $EP_{v10-115}^a$ specimens ranged from about 0.1 to $1 \mu\text{m}$ —significantly smaller than those of the other vulcanized EPDM/PP specimens (i.e., $EP_{v10-115}^b$ and $EP_{v10-115}^c$). In addition to C atoms, small amounts of O atoms present in the EPDM resin, and Sn or Cl atoms from the SnCl_2 catalyst used to crosslink the EPDM, were also evident in the EDX spectra of the cyclohexane-etched surfaces of the vulcanized EPDM/PP specimens (cf. Fig. 3(d), 4d, and 5d).

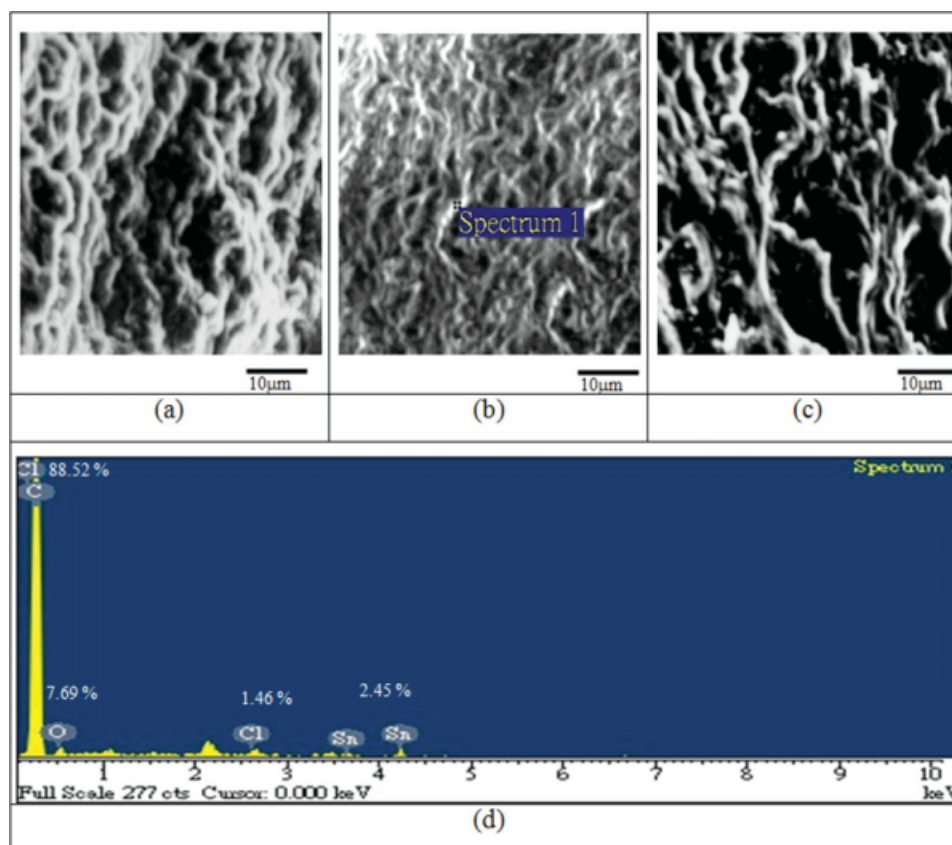


Figure 4 Fracture surface morphologies of (a) EP_{v10-80}^b , (b) $EP_{v10-115}^b$, and (c) $EP_{v10-125}^b$ specimens and (d) EDX spectrum (elemental composition) of spectrum 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Based on these findings, we suggest that the finely dispersed black domains corresponded to the un-vulcanized or slightly vulcanized EPDM resins and the white domains corresponded to the PP and/or vulcanized EPDM resins that did not dissolve in the cyclohexane.

We are not completely sure of the cause of the interesting morphologies of these un-vulcanized and vulcanized EPDM/PP specimens. It is generally recognized, however, that EPDM melts can be sheared by PP melts during the melt-blending process of un-vulcanized and vulcanized EPDM/PP specimens if the PP melts are not too soft or "strong" enough to shear the EPDM melts with relatively high values of η_s .⁴⁰⁻⁴³ As we mentioned above, the values of η_s of the EPDM samples measured at various shear rates in this study were higher than those of the PP resins. It is, therefore, reasonable that the EPDM domains present in the EPDM/PP blends were sheared better and into smaller sizes by the PP melts upon increasing the values of η_s of the PP melts. Moreover, we also expected the blending speed to have a great influence on the sizes of the EPDM domains during the melt-blending and/or vulcanization processes of the EPDM/PP melts, because we expected the

degrees of melt-blending of the EPDM/PP resins to improve upon increasing the screw rate (shear rate) in the melt-blending process. As mentioned above, however, the values of the EPDM-to-PP melt shear viscosity ratios of the PP^a, PP^b, and PP^c resins all increased significantly upon increasing the shear rates. This behavior can compromise the beneficial blending effect of the screw rate on reducing the sizes of EPDM domains. Therefore, the relative sizes of the EPDM domains reached a minimum when the un-vulcanized and vulcanized EPDM/PP specimens were prepared at the optimal screw rate (115 rpm).

On the other hand, we expected the vulcanized EPDM molecules to separate gradually from the virgin EPDM phases during the dynamic vulcanization processes of the EPDM/PP specimens, because vulcanized EPDM molecules flow more poorly and have significantly higher values of η_s than do the virgin EPDM molecules. Under such circumstances, the virgin EPDM phases can be further sheared by the PP melts and separate from the vulcanized EPDM molecules during the dynamic vulcanization processes, thereby causing more finely dispersed EPDM domains than those in the un-vulcanized EPDM/PP specimens.

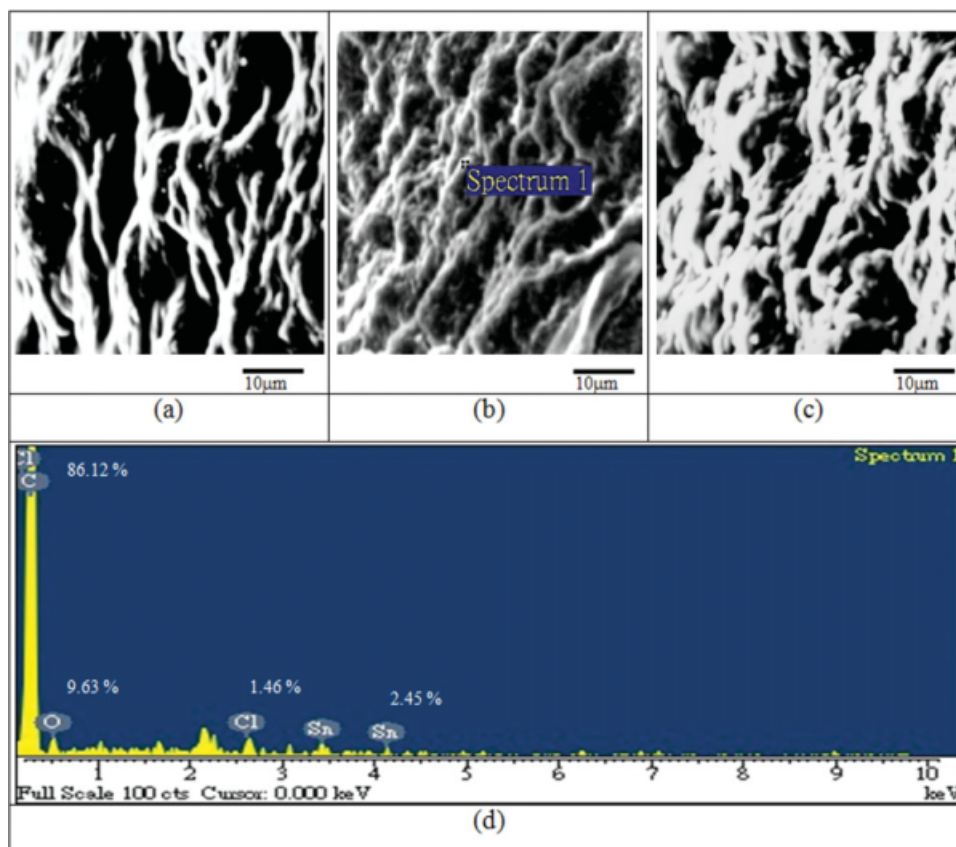


Figure 5 Fracture surface morphologies of (a) EP_{v10-80}^c , (b) $EP_{v10-115}^c$, and (c) $EP_{v10-125}^c$ specimens and (d) EDX spectrum (elemental composition) of spectrum 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Tensile properties of un-vulcanized and vulcanized EPDM/PP specimens

Table III and Figure 6 summarize the tensile properties of EPDM, PP, and the un-vulcanized EPDM/PP series of samples. The tensile strengths (σ_f) of the virgin PP specimens were approximately three times greater than that of the virgin EPDM specimen, increasing slightly upon increasing the values of η_s of the PP resins. In contrast, the elongation at break (ϵ_f) of the virgin EPDM specimen reached 1233%—at least 30 times greater than those of the virgin PP specimens—and those of the virgin PP specimens increased significantly upon increasing their values of η_s . After melt-blending the EPDM and PP resins twice in the twin-screw extruder, the values of the un-vulcanized EP_{-x}^a , EP_{-x}^b , and EP_{-x}^c series of samples were at most equal to that of the pure EPDM specimen (i.e., 9.1 MPa)—they were much lower than that of the virgin PP specimens—even though the values of σ_f and ϵ_f of each of the un-vulcanized EPDM/PP series samples reached a maximum when the screw rate approached the optimal value (115 rpm). Figure 6 reveals that the values of σ_f and ϵ_f of the un-vulcanized EPDM/PP samples (i.e., EP_{-115}^a , EP_{-115}^b , and EP_{-115}^c) prepared at the optimal screw

rate (115 rpm) improved significantly upon increasing the values of η_s of the PP resins. The values of ϵ_f of the un-vulcanized EP_{-115}^a , EP_{-115}^b , and EP_{-115}^c

TABLE III
Compositions and Sample Tensile Properties of EPDM, PP, and the EPDM/PP Blends

Composition and screw rate/sample	Tensile properties		Screw rate (rpm)
	Tensile strength (MPa)	Tensile strain (%)	
EPDM	9.1	1233.3	–
PP ^a	30.2	39.6	–
EP ₋₈₀ ^a	9.1	236.8	80
EP ₋₉₅ ^a	9.1	240.3	95
EP ₋₁₁₅ ^a	9.1	254.3	115
EP ₋₁₂₅ ^a	8.9	234.1	125
PP ^b	29.6	31.9	–
EP ₋₈₀ ^b	7.6	200.5	80
EP ₋₉₅ ^b	7.6	213.5	95
EP ₋₁₁₅ ^b	7.7	233.1	115
EP ₋₁₂₅ ^b	7.6	183.5	125
PP ^c	29.4	10.4	–
EP ₋₈₀ ^c	6.2	68.2	80
EP ₋₉₅ ^c	6.3	73.9	95
EP ₋₁₁₅ ^c	6.5	85.2	115
EP ₋₁₂₅ ^c	6.1	69.3	125

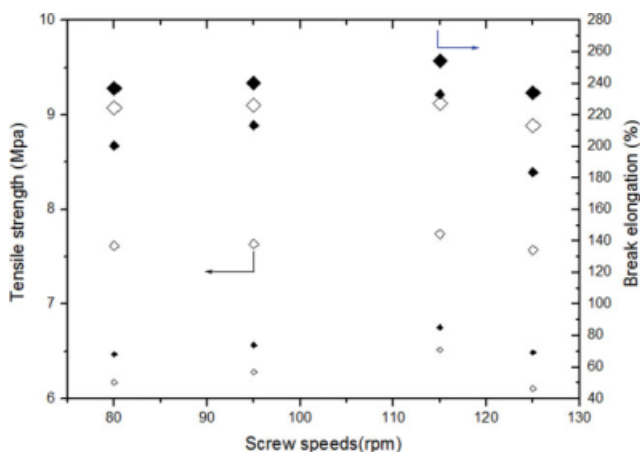


Figure 6 Tensile strengths (open symbols) and elongations at break (solid symbols) of EP_{-x}^a (\diamond , \blacklozenge), EP_{-x}^b (\diamond , \blacklozenge), and EP_{-x}^c (\diamond , \blacklozenge) specimens prepared at various screw rates. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

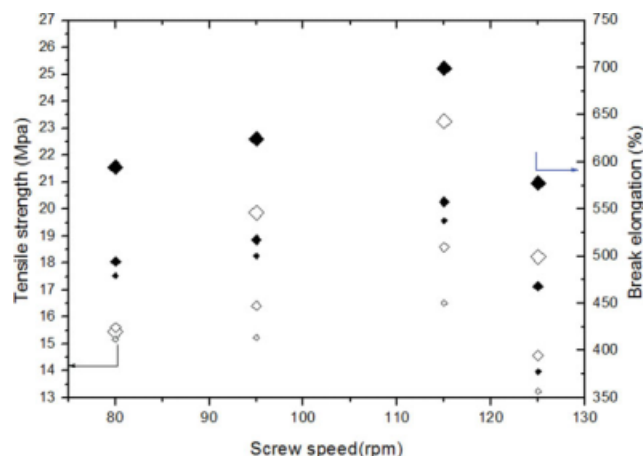


Figure 7 Tensile strengths (open symbols) and elongations at break (solid symbols) of EP_{v10-x}^a (\diamond , \blacklozenge), EP_{v10-x}^b (\diamond , \blacklozenge), and EP_{v10-x}^c (\diamond , \blacklozenge) specimens prepared at various screw rates. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

samples were, however, dramatically higher than those of their respective virgin PP resins, and they improved significantly upon increasing the values of η_s of the PP resins. In fact, the value of ε_f of the EP_{-115}^a specimen was more than 250%, approximately six times of that of the pure PP^a specimen.

Figure 7 and Table IV displays the tensile properties of EPDM, PP, and the dynamically vulcanized EPDM/PP series of samples. The tensile properties of the dynamically vulcanized EPDM/PP samples (i.e., EP_{v10-x}^a , EP_{v10-x}^b , and EP_{v10-x}^c) were significantly better than those of their corresponding un-vulcanized EPDM/PP specimens. For example, the values of σ_f and ε_f of EP_{v10-80}^a were about 1.7 and 2.5 times greater, respectively, than those of the un-vulcanized EP_{-80}^a specimen. Similar to the behavior of the un-vulcanized EPDM/PP specimens, the tensile properties of the dynamically vulcanized EP_{v10-x}^a , EP_{v10-x}^b , and EP_{v10-x}^c specimens also reached their highest values when they were prepared at the optimal screw rate (115 rpm). Moreover, the values of σ_f and ε_f of the dynamically vulcanized EPDM/PP samples (i.e., $EP_{v10-115}^a$, $EP_{v10-115}^b$, and $EP_{v10-115}^c$) prepared at the optimal screw rate improved significantly upon

increasing the values of η_s of the PP resins. In fact, the values of σ_f and ε_f of the dynamically vulcanized $EP_{v10-115}^a$, $EP_{v10-115}^b$, and $EP_{v10-115}^c$ specimens reached 23.2 MPa/700%, 18.6 MPa/558%, and 16.5 MPa/538%, respectively, about 2.6/2.8, 2.4/2.4, and 2.5/6.3 times greater than those of the un-vulcanized EP_{-115}^a , EP_{-115}^b , and EP_{-115}^c specimens, respectively.

The significantly improved mechanical properties of dynamically vulcanized EPDM/PP blends are generally attributed to the presence of fine particles of the vulcanizates dispersed in continuously thermoplastic matrices.^{9,11-14} Oderkerk and Groeninckx³⁰ further suggested that the values of σ_f and ε_f improve significantly upon decreasing the relative dimensions of the EPDM domains. It is not completely clear, however, what it is that causes the interesting tensile properties of our un-vulcanized and dynamically vulcanized EPDM/PP specimens. As mentioned above, we observed more finely dispersed EPDM domains on the surfaces of the dynamically vulcanized EPDM/PP specimens relative to those of the un-vulcanized EPDM/PP specimens, with the relative sizes of the un-vulcanized and vulcanized EPDM domains all reaching a

TABLE IV
Tensile Properties of Dynamically Vulcanized EPDM/PP Blends Prepared at Various Screw Rates and Blend Ratios and After the Addition of 10 Parts of Dimethylol Phenolic Resin

Sample/screw rate (rpm)	EP_{v10}^a		EP_{v10}^b		EP_{v10}^c	
	Tensile strength (MPa)	Tensile strain (%)	Tensile strength (MPa)	Tensile strain (%)	Tensile strength (MPa)	Tensile strain (%)
80	15.4	594.3	15.6	494.4	15.2	479.4
95	19.9	624.6	16.4	517.5	15.2	500.3
115	23.3	699.2	18.6	557.8	16.5	537.8
125	18.2	577.5	14.6	468.2	13.2	377.8

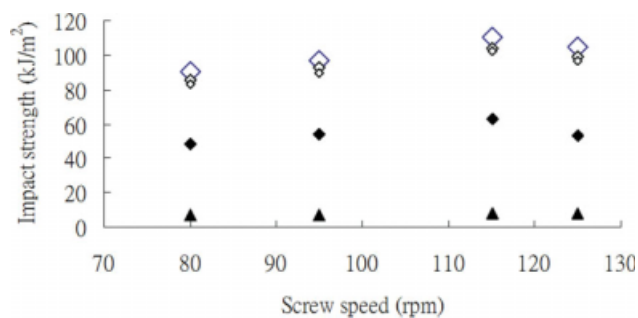


Figure 8 Impact strengths of PP_{-x}^a (▲), EP_{-x}^a (◆), EP_{v10-x}^a (◇), EP_{v10-x}^b (◇) and EP_{v10-x}^c (◇) specimens prepared at various screw rate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

minimum when we prepared the vulcanized EPDM/PP specimens at the optimal screw rate (115 rpm). As a result, it is understandable that the values of σ_f and ε_f of the dynamically vulcanized specimens were significantly higher than those of the corresponding un-vulcanized EPDM/PP specimens prepared at the same screw rate.

Figure 8 displays the impact strength properties of the dynamically vulcanized EPDM/PP series of samples. The impact strengths of the dynamically vulcanized EPDM/PP samples (i.e., EP_{v10-x}^a, EP_{v10-x}^b, and EP_{v10-x}^c) were significantly better than those of the corresponding PP_{-x}^a and EP_{-x}^a specimens. For example, the values of EP_{v10-80}^a were about 90 and 1.9 times greater, respectively, than those of the un-vulcanized EP₋₈₀^a specimen. Similar to the behavior of the un-vulcanized EPDM/PP specimens, the impact strengths of the dynamically vulcanized EP_{v10-x}^a, EP_{v10-x}^b, and EP_{v10-x}^c specimens also reached their highest values when they were prepared at the optimal screw rate (115 rpm).

CONCLUSIONS

EDX spectroscopic analysis of the cyclohexane-etched surfaces of un-vulcanized and dynamically vulcanized EPDM/PP specimens revealed the presence of finely dispersed black domains that most likely correlated to un-vulcanized or slightly vulcanized EPDM resins and white domains that correlated to PP and/or vulcanized EPDM resins that did not dissolve in the cyclohexane. Many finely dispersed black domains were evident on the surfaces of the dynamically vulcanized EPDM/PP specimens; the relative sizes of the black domains reached a minimum when the vulcanized EPDM/PP specimens were prepared at the optimal screw rate of 115 rpm. In fact, at this screw rate, the average sizes of the dispersed black domains decreased upon increasing the values of η_s of PP resins used to prepare the vul-

canized EPDM/PP specimens. We suspect that the vulcanized EPDM molecules separated gradually from the virgin EPDM phases during the dynamic vulcanization of the EPDM/PP specimens and that the virgin EPDM phases were further sheared by the PP melts and separated from the vulcanized EPDM molecules during the dynamic vulcanization processes, thereby causing more finely dispersed EPDM domains than those in the un-vulcanized EPDM/PP specimens. Moreover, we expected the EPDM domains present in the EPDM/PP blends to be sheared better and into smaller sizes by the PP melts upon increasing the values of η_s of the PP melts and/or the screw rate. The decreases in the EPDM-to-PP viscosity ratios of the resins can, however, compromise the beneficial blending effect of the screw rate on reducing the sizes of the EPDM domains. As a result, the relative sizes of the EPDM domains reached their minima when we prepared the un-vulcanized and vulcanized EPDM/PP specimens at the optimal screw rate (115 rpm).

After melt-blending the EPDM and PP resins twice in the twin-screw extruder, the values of σ_f of the un-vulcanized EP_{-x}^a, EP_{-x}^b, and EP_{-x}^c series of samples were at most equal to that of the pure EPDM specimen, but much lower than those of the virgin PP specimens, although the values of σ_f and ε_f of each un-vulcanized EPDM/PP sample reached their maxima when the screw rate approached the optimal value (115 rpm). The values of ε_f of the un-vulcanized EP₋₁₁₅^a, EP₋₁₁₅^b, and EP₋₁₁₅^c samples were, however, dramatically higher than those of their respective virgin PP resins, and they improved significantly upon increasing the values of η_s of the PP resins. In fact, the value of ε_f of the EP₋₁₁₅^a specimen was greater than 250%, approximately six times higher than that of the pure PP^a specimen. Notably, the tensile properties of the dynamically vulcanized EPDM/PP samples were significantly better than those of their corresponding un-vulcanized EPDM/PP specimens. Similar to the behavior of the un-vulcanized EPDM/PP specimens, the tensile properties of each dynamically vulcanized EP_{v10-x}^a, EP_{v10-x}^b, and EP_{v10-x}^c specimen also reached their maxima when prepared at the optimal screw rate (115 rpm). Moreover, the values of σ_f and ε_f of the dynamically vulcanized EPDM/PP samples prepared at the optimal screw rate improved significantly upon increasing the values of η_s of the PP resins. In fact, the values of σ_f and ε_f of the dynamically vulcanized EP_{v10-115}^a, EP_{v10-115}^b, and EP_{v10-115}^c specimens were 23.2 MPa/700%, 18.6 MPa/558%, and 16.5 MPa/538%, respectively, about 2.6/2.8, 2.4/2.4, and 2.5/6.3 times greater than those of the un-vulcanized EP₋₁₁₅^a, EP₋₁₁₅^b, and EP₋₁₁₅^c specimens, respectively. We attribute the significantly improved tensile properties of the dynamically vulcanized samples

prepared at the optimal screw rate to the significantly reduced dimensions of the EPDM domains present in the vulcanized EPDM/PP specimens.

References

1. Gessler, M. U.S. Pat. 3,037,954, 1962.
2. Fisher, K. U.S. Pat. 3,758,643, 1973.
3. Coran, A. Y.; Patel, R. P. *Rubber Chem Technol* 1980, 53, 141.
4. Coran, A. Y.; Patel, R. P.; Williams, D. *Rubber Chem Technol* 1982, 55, 116.
5. Zhang, X.; Xie, H.; Zhang, M.; Fang, L. *Proceedings of the 1998 International Symposium on Electrical Insulating Materials, Japan, 1998*; 301.
6. Coran, A. Y.; Patel, R. P. *Rubber Chem Technol* 1981, 54, 91.
7. Folt, V. L.; Smith, R. W. *Rubber Chem Technol* 1973, 46, 1193.
8. Chang, H. S.; Dong, I. J.; Sung, K. C. *J Appl Polym Sci* 1986, 32, 6281.
9. Bucknall, C. B. *Toughened Plastics*; Applied Science: London, 1977; 188.
10. Dao, K. C. *Polymer* 1984, 25, 1527.
11. Kresge, E. N.; Lohse, D. J.; Datta, S. *Makromol Chem Macromol Symp* 1992, 53, 173.
12. Krulis, Z.; Fortenlly, I.; Kovar, J. *Collect Czech Chem Commun* 1993, 58, 2642.
13. Inouse, T. *J Appl Polym Sci* 1994, 54, 723.
14. Kocsis, J. K.; Kallo, A.; Szafner, A.; Bodor, G.; Senyei, Z. S. *Polymer* 1979, 20, 37.
15. Jang, B. Z.; Uhlmann, D. R.; Sande, J. B. *J Appl Polym Sci* 1985, 30, 2485.
16. Hoppner, D.; Wendorff, J. H. *Colloid Polym Sci* 1990, 288, 500.
17. Punkaszky, B.; Tudos, F.; Kallo, A.; Bodor, G. *Polymer* 1989, 30, 1399.
18. Karger-Kocsis, J.; Kallo, A.; Kuleznev, N. *Polymer* 1984, 25, 279.
19. Jain, A. K.; Gupta, N. K.; Nagpal, A. K. *J Appl Polym Sci* 2000, 77, 1488.
20. Jain, A. K.; Nagpal, A. K.; Singhal, R.; Gupta, N. K. *J Appl Polym Sci* 2000, 78, 2089.
21. Xiao, H. W.; Huang, S. Q.; Jiang, T.; Cheng, S. Y. *J Appl Polym Sci* 2002, 83, 315.
22. Coran, A. Y. *Thermoplastic Elastomers Based on Elastomer/Thermoplastic Blends Dynamically Vulcanized*; Al-Malaika, S., Ed. Blackie Academic and Professional: London, 1997; p 349.
23. Ghosh, P.; Chakrabarti, A. *Eur Polym J* 2000, 36, 607.
24. Olayo, R.; Manzur, A.; Llamas, J. H.; Escobar, A. *Polym Bull* 1988, 41, 99.
25. Coran, A. Y.; Patel, R. P. *Rubber Chem Technol* 1980, 53, 781.
26. Koshy, A. T.; Kuriakose, B.; Premalatha, C. K.; Thomas, S. *J Appl Polym Sci* 1993, 49, 901.
27. Varughese, K. T.; De, P. P.; Nando, G. B.; De, S. K. *J Vinyl Technol* 1987, 9, 161.
28. Huang, H.; Yang, J.; Liu, X.; Zhang, Y. *Eur Polym J* 2002, 38, 857.
29. Wu, S. *Polym Eng Sci* 1987, 27, 335.
30. Oderkerk, J.; Groeninckx, G. *Polymer* 2002, 43, 2219.
31. Coran, A. Y.; Patel, R. P. *Rubber Chem Technol* 1983, 56, 211.
32. Favis, B. D.; Chalifoux, J. P. *Polym Eng Sci* 1987, 27, 1591.
33. Favis, B. D.; Willis, J. M. *J Polym Sci Part B: Polym Phys* 1990, 28, 2259.
34. Kuriakose, B.; De, S. K. *Polym Eng Sci* 1985, 25, 630.
35. Favis, B. D. *J Appl Polym Sci* 1990, 39, 285.
36. Silva, D. A.; Nazareth, A. L. *Polym Test* 1990, 15, 1.
37. Silva, D. A.; Marisa, C. G.; Nazareth, A. L. *Polym Test* 2002, 21, 3.
38. Zaharescu, T.; Chipara, M.; Postolache, M. *Polym Degrad Stab* 1999, 66, 1.
39. Dai, Y. Q.; Wang, B.; Wang, S. J.; Jiang, T.; Cheng, S. Y. *Radiat Phys Chem* 2003, 68, 3.
40. Ponsard-Fillette, M.; Barres, C.; Cassagnau, P. *Polymer* 2005, 46, 23.
41. Sengers, W. G. F.; Sengupta, P.; Noordermeer, J. W. M.; Picken, S. J.; Gotsis, A. D. *Polymer* 2005, 45, 26.
42. Chen, Y.; Li, H. *Polymer* 2005, 46, 18.
43. Yang, H.; Li, B.; Wang, K.; Sun, T.; Wang, X.; Zhang, Q.; Fu, Q.; Dong, X.; Han, C. *Eur Polym J* 2008, 44, 1.