Influence of Various Crosslinking Systems on the Mechanical Properties of Gas Phase EPDM/PP Thermoplastic Vulcanizates

Madhuchhanda Maiti, Jaydeep Patel, Kinsuk Naskar, Anil K. Bhowmick

Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, West Bengal, India

ABSTRACT: Dynamically cured thermoplastic elastomers or thermoplastic vulcanizates (TPVs) are widely used nowadays for their unique characteristics. In this paper, gas phase ethylene–propylene–diene terpolymer (GEPDM)/Polypropylene (PP) TPVs with various crosslinking systems have been extensively studied to optimize the curative level in each crosslinking system with special reference to their mechanical properties. Optimized systems were compared for heat aging, recyclability, crosslink density, morphology studies, and dynamic mechanical analysis. Crosslinking by peroxide in the presence of triallyl cyanurate as a coagent gives best overall performance with reference to excellent heat aging behavior, tension set, and compatibility between GEPDM and PP. Conventional EPDM/PP system was also compared with GEPDM/PP system. GEPDM/PP system was found to exhibit better behavior in all respects. Significant correlations were obtained between delta torque values obtained from Moving Die Rheometer and modulus or crosslink density of TPVs irrespective of the nature of crosslinking agent. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5463–5471, 2006

Key words: thermoplastic vulcanizates; TPVs; Crosslinking; EPDM; Mechanical properties; PP

INTRODUCTION

In the last two decades conventional ethylene–propylene–diene terpolymer/polypropylene (EPDM/PP) thermoplastic elastomers (TPEs) and especially thermoplastic vulcanizates (TPVs) or dynamic vulcanizates have been extensively studied because of their commercial importance. The gas phase process technology for the production of EPDM rubber came in the market by DuPont Dow Elastomers in early 2002. Gas phase EPDM (GEPDM) is generally produced by using carbon black during the polymerization step itself to prevent the EPDM particles from agglomeration. The granular nature of GEPDM having high surface area is unique, which leads to significant cost saving when applied to the production of TPVs by (1) eliminating cutting steps, (2) easing the feeding, (3) easing the mixing with lower mixing time, and (4) taking less time to absorb oil.[1,2]

Extensive work has already been done that deals with the mechanical and rheological properties of dynamically cured PP/EPDM TPVs.[3–7] A few studies have also been carried out mainly to characterize the morphology of TPVs based on different rubber–plastic blend systems.[8–11] Attempts have been made to study the effect of carbon black and silica as filler in dynamically cured EPDM/PP blends. Bhowmick et al. have also reported a series of TPEs and TPVs from different rubber–plastic combinations.[12–20] However, limited studies have been pursued so far focusing on GEPDM/PP based TPVs comparing different crosslinking systems. Preliminary work in our laboratory showed that GEPDM exhibits better mechanical properties (tensile strength, elongation at break, tension set etc.) over conventional EPDM in blends with PP. Williams et.al.[21] reported that GEPDM could offer compounders of TPVs lower cost, higher production rates, and competitive performance to current commercial materials.

Thus the main objectives of the present investigation were (1) to investigate in detail the effects of various crosslinking systems in GEPDM/PP TPVs, (2) to select the crosslinking system with optimum level of processing and properties, and finally (3) to compare the optimized GEPDM/PP TPVs with the existing conventional EPDM/PP TPVs. The results of the crosslinking studies are expected to provide new direction in understanding many other thermoplastic vulcanizates from rubber–plastic blends.

EXPERIMENTAL

Materials

Materials used for the present study are shown in Table I.

<div align="center">

TABLE I
Materials Used and Their Suppliers

</div>

Material	Trade name/abbreviation	Supplier
Gas phase EPDM (ENB = 4.7 wt %, Ethylene = 67 wt %)	NDR 47130/GEPDM	Dupont Dow Elastomers, Geneva
Conventional EPDM (ENB = 4.7 wt %, Ethylene = 67 wt %)	Royalene-563	DSM Elastomers, The Netherlands
Polypropylene	PP	Basell Polymers
Stannous chloride	$SnCl_2 \cdot 2H_2O$	Advance In-Organics, Bombay, India
N,N-m-phenylenedimaleimide	HVA-2	Dupont Dow Elastomers, Wilmington
Vinyl trimethoxy silane	Vinyl trimethoxy silane/VTMOS	Dowcorning Chemicals, Wilmington
Polyethylene glycol	Polyethylene glycol/PEG	Aldrich Chemicals, USA
Phenolic resin	Chemmould	Bombay Chemicals, Bombay, India
Dibutyltin dilaurate	Dibutyltin dilaurate/ DBTDL	Bombay Chemicals, Bombay, India
Dicumyl peroxide	DCP	Bombay Chemicals, Bombay, India
Tetramethyl thiuram disulfide	TMTD	Bombay Chemicals, Bombay, India
Mercapto dibenzothiazole disulphide	MBTS	Bombay Chemicals, Bombay, India
Triallyl cyanurate	TAC	Bombay Chemicals, Bombay, India

Preparation of various TPVs

All the blends were prepared by a batch process in a Brabender Plasti-Corder PLE-330, having a mixing chamber volume of 70 cm³. The batch size was 65 cm³. The mixer temperature was always kept at 190–200°C. A constant rotor (cam type) with a speed of 60 rpm was applied.

GEPDM was added first and softened for 2 min followed by the addition of PP. After 6 min of mixing, crosslinking agents were added and mixed for another 4 min, so that total mixing time was 10 min. In the case of conventional EPDM (Royalene-563)/PP blends, carbon black (same amount as present in GEPDM) was added after the addition of rubber, which was followed by addition of PP and crosslinking agents. Immediately after mixing, the composition was removed from the mixer and while still molten, passed once through a cold two-roll mill to have a sheet of about 2 mm thickness. The sheet was then cut and pressed in a compression-molding

<div align="center">

TABLE II
Formulation of Various Thermoplastic Vulcanizates and Comparison of Physical Properties with Different Crosslinking Systems at Optimized Level

</div>

	S2a	R2	SH3a	EPD$_{1.0}$	DH2	SI7	UV30	EB10
System								
GEPDM	100	100	100	100	100	100	100	100
PP	40	40	40	40	40	40	40	40
Sulphur	1.8	–	1.5	–	–	–	–	–
ZnO	5.0	3.0	–	–	–	–	–	–
Stearic acid	1.0	–	–	–	–	–	–	–
MBTS	0.45	–	0.5	–	–	–	–	–
TMTD	0.90	–	–	–	–	–	–	–
$SnCl_2 \cdot 2H_2O$	–	1.0	–	–	–	–	–	–
Phenolic Resin	–	1.5	–	–	–	–	–	–
HVA-2	–	–	0.5	–	2.0	–	–	–
DCP	–	–	–	1.0	1.0	0.1	–	–
TAC	–	–	–	2.0	–	–	–	–
DBTDL	–	–	–	–	–	0.2	–	–
VTMOS	–	–	–	–	–	3.0	–	–
PEG	–	–	–	–	–	3.0	–	–
Heating in boiling water for 10 min	–	–	–	–	–	Yes	–	–
Benzophenone								–
Peroxide	–	–	–	–	–	–	1.0	–
Exposure time (s)	–	–	–	–	–	–	0.5	–
EB radiation dose (Mrad)	–	–	–	–	–	–	–	10
Mechanical properties								
Tensile strength (MPa)	19.2	5.9	24.1	15.7	10.2	11.5	7.0	7.3
Elongation at break (%)	202	180	245	221	123	154	113	250
Modulus at 100% (MPa)	18.5	4.9	16.2	9.4	8.4	7.1	6.4	5.3
Hardness (Shore D)	40	36	43	38	36	39	36	36
Tension set at 25°C (%)	6.9	21.0	7.3	8.3	9.5	7.9	9.5	8.5

TABLE III
Optimization of Resin Concentration. Formulations in phr and Properties

	R1	R2	R3
System			
GEPDM	100	100	100
PP	40	40	40
$SnCl_2 \cdot 2H_2O$	1.0	1.0	1.0
ZnO	3.0	3.0	3.0
Phenolic resin	0.5	1.5	3.0
Mechanical properties			
Tensile strength (MPa)	2.8	5.9	4.5
Elongation at break (%)	130	180	164
Modulus at 100% (MPa)	2.2	4.9	3.6
Hardness (Shore D)	34	36	35
Tension set at 25°C (%)	21.0	21.0	21.1

machine (Moore Press, Birmingham, UK) at 210°C, for 3 min at 5 MPa pressure. Aluminum foils were placed between the mold platens. The sheet was then cooled down to room temperature under same pressure. Test specimens were die-cut from the compression molded sheet and used for testing after 24 h of storage at room temperature. TPE samples for rheometric studies were also prepared in a Brabender Plasticorder but the crosslinking agents were mixed on a two roll mixing mill. TPVs requiring water (for silane crosslinking) were put in boiling water for another 10 min after mixing.

Testing procedures

MDR (moving die rheometer) [Monsanto Instruments and Equipment, USA] was used to study the cure characteristics.

Tensile test of the samples was carried out according to ASTM D412-98 on dumb-bell shaped specimens using a Zwick Tensile Testing machine 1445 at a constant cross-head speed of 500 ± 5 mm/min. Hardness of the samples was measured by a Durometer (Shore D Type, ASTM D2240). Tension set test

of the samples was performed at room temperature with a stretched condition for 10 min at 100% elongation following ASTM D412-98 method.

The crosslink density of EPDM was determined by equilibrium solvent-swelling method in cyclohexane at room temperature, by the application of Flory–Huggins[22] equation, which can be represented approximately as

$$\ln(1 - \upsilon_2) + \upsilon_2 + \chi \upsilon_2{}^2 + \rho \frac{V_1}{M_c} \upsilon_2{}^{1/3} = 0 \qquad (1)$$

Where υ_2 is the volume fraction of the rubber in the swollen gel, ρ is the density of the material, V_1 is the molar volume of the solvent, and M_c is the molecular weight between the two crosslinks. However, in case of TPVs where EPDM is embedded in relatively less swellable matrix like PP, it swells against the compressive force exerted by the PP-matrix. The situation is then equivalent to the restricted swelling of the rubber phase under a hydrostatic pressure p', and extent of the swelling can be given by

$$\ln(1 - \upsilon_2') + \upsilon_2' + \chi \upsilon_2'^2 + \rho \frac{V_1}{M_c} \upsilon_2'^{1/3} + p' \frac{V_1}{RT} = 0 \qquad (2)$$

Here υ_2' represents the volume fraction of the rubber in the swollen vulcanizates under the constrained swelling condition. If we replace p' by an equivalent quantity G, the shear modulus of PP phase [eq. (2)], becomes

$$\ln(1 - \upsilon_2') + \upsilon_2' + \chi \upsilon_2'^2 + \rho \frac{V_1}{M_c} \upsilon_2'^{1/3} + G \frac{V_1}{RT} = 0 \qquad (3)$$

Equation (3) gives an approximate value of the crosslink density (μ) of the EPDM rubber in a EPDM/PP TPV from the following equation

$$\mu = \frac{\rho}{2M_c} \qquad (4)$$

TABLE IV
Effect of Different Concentrations of DCP in Various Blend Compositions: Formulations in phr

	EP	EPD$_{0.5}$	EPD$_{1.0}$	EPD$_{1.5}$	EPD$_{2.0}$	EPD$_{2.5}$	EPD$_{3.0}$	EPD*$_{1.0}$
System								
GEPDM	100	100	100	100	100	100	100	–
PP	40	40	40	40	40	40	40	40
DCP	–	0.5	1.0	1.5	2.0	2.5	3.0	1.0
TAC	–	2.0	2.0	2.0	2.0	2.0	2.0	2.0
ROYALENE–563	–	–	–	–	–	–	–	73
CARBON BLACK	–	–	–	–	–	–	–	27
Mechanical properties								
Tensile strength (MPa)	6.3	9.5	15.7	14.8	13.4	12.8	9.1	9.3
Elongation at break (%)	39	62	221	177	159	121	68	116
Modulus at 100% (MPa)	–	–	9.4	10.2	10.7	11.3	–	8.9
Hardness (Shore D)	33	36	38	39	39	40	40	30
Tension set at 25°C (%)	29.9	9.1	8.3	7.5	2.4	1.6	0.4	6.9

	DH1	DH2	DH3
System			
GEPDM	100	100	100
PP	40	40	40
DCP	1.0	1.0	1.0
HVA-2	1.0	2.0	3.0
Mechanical properties			
Tensile strength (MPa)	8.1	10.2	9.8
Elongation at break (%)	90	123	131
Modulus at 100% (MPa)	–	8.4	8.7
Hardness (Shore D)	35	36	34
Tension set at 25°C (%)	10.7	9.5	9.2

A 2 mm thick TPV sample was first submerged in cyclohexane. After 24 h, the cyclohexane was refreshed to remove the extracted oil. After another 24 h, the swollen sample was weighed, dried, and weighed again.

The phase morphology of various blends with different crosslinking systems was investigated by a JEOL JSM 5800 Digital Scanning Electron Microscope (SEM). The samples were cut into small pieces using a sharp knife and then sputter-coated with gold before examination under the SEM. The images were obtained at a tilt angle of 0° with an operating voltage of 20 kV.

The phase morphology of various blends with different crosslinking systems was also investigated by a Multimode Scanning Probe Microscope model with a Nanoscope IIIa controller by Digital Instruments (Veeco Metrology Group), Santa Barbara, CA. The AFM measurements were carried out in air at ambient conditions (25 °C) using tapping mode probes with constant amplitude (40 mV). The rotated tapping mode etched silicone probe (RTESP) [square pyra-

mid in shape with a spring constant of $20N/m$, nominal radius of curvature of 10nm] with resonance frequency of 270 kHz was used. Height and phase images were recorded simultaneously at the resonance frequency of the cantilever with a scan rate of 1 Hz and a resolution of 256 samples per line. This allowed the resolution of individual primary particle measurements. The images were analyzed using a nanoscope image processing software (5.30r1).

Dynamic mechanical analysis was carried out in a DMA 2980 Dynamic Mechanical Analyzer (TA Instruments, New Castle, DE) at an amplitude of 20 µm, frequency of 1 Hz and at a heating rate of 5°C/min under dual cantilever mode. Temperature range was kept from −40°C to +175°C. The temperature corresponding to the peak in tan δ versus temperature plot was taken as the glass to rubber transition temperature (T_g).

RESULTS AND DISCUSSION

Optimization of curative level in various crosslinking systems

Several crosslinking agents can be tried to crosslink the EPDM phase in EPDM/PP blends: coagent assisted peroxides, activated phenol-formaldehyde resins (resols), commonly known as resol-resins; platinum catalyzed hydrosiloxane; vinyltrialkoxysilane/moisture; catalyzed quinonedioxime, bisazides, and bisthiols; etc. Each and every crosslinking system has got its own merits and demerits. The cure rate, the final crosslink density, the thermal stability of the crosslinks formed, the safety, health and environmental characteristics of the chemicals used and the cost price are relevant parameters for the final choice of the crosslinking system. In this particular study, the main focus was on GEPDM as one of the compo-

TABLE VI
Effect of Different Concentrations of Silane and PEG on Physical Properties

	SI1	SI2	SI3	SI4	SI5	SI6	SI7	SI8
System								
GEPDM	100	100	100	100	100	100	100	100
PP	40	40	40	40	40	40	40	40
DCP	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
DBTDL	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
VTMOS	–	–	2.0	3.0	4.0	3.0	3.0	3.0
PEG	–	–	–	–	–	2.0	3.0	3.0
Heating in boiling water for 10 min.	Yes	–	–	–	–	–	Yes	–
Mechanical properties								
Tensile strength (MPa)	10.7	12.5	9.4	9.4	8.3	7.9	7.9	8.3
Elongation at break (%)	5.3	3.9	6.3	9.1	8.4	9.8	11.5	10.8
Modulus at 100% (MPa)	60	54	110	121	121	133	154	137
Hardness (Shore D)	–	–	5.9	8.8	6.3	6.5	7.1	6.8
Tension set at 25°C (%)	35	34	39	39	40	40	39	43

TABLE VII
Recyclability Tests of Various Blends with Different Curing Systems

	No. of recycling	S2a	R2	SH3a	EPD$_{1.0}$	DH2	SI7	UV30	EB10	EPD$_{1.0}$*
Mechanical Properties										
Tensile strength (MPa)	0	19.2	5.9	24.1	15.7	10.2	11.5	7.0	7.8	9.3
	1	15.1	4.1	24.5	15.4	6.8	8.2	6.9	7.4	8.7
	2	13.9	4.1	21.5	13.2	5.9	6.2	6.1	7.3	7.9
	3	12.5	3.9	20.1	12.0	4.9	5.9	5.5	6.9	6.7
Elongation at break (%)	0	202	180	245	221	123	154	113	250	124
	1	182	325	477	211	60	111	110	221	112
	2	171	322	397	198	50	90	99	190	109
	3	160	290	380	177	48	85	80	177	90
Modulus at 100% elongation	0	18.5	4.9	16.2	9.4	8.4	7.1	6.4	5.3	8.7
	1	15.6	4.2	7.9	9.3	–	6.9	6.2	5.2	8.3
	2	14.3	3.9	7.7	8.5	–	–	–	5.0	7.6
	3	11.2	3.7	6.4	8.0	–	–	–	4.5	–
Tension set at 25°C (%)	0	6.9	21.0	7.3	5.9	9.5	10.7	9.5	8.5	6.9
	1	8.2	22.4	6.3	6.5	11.0	11.2	11.2	8.5	9.5
	2	9.3	23.3	6.2	8.2	12.5	13.7	11.2	10.7	11.2
	3	10.1	23.3	6.2	8.4	13.7	15.4	13.4	11.2	13.4

nents of TPVs and the mechanical properties of different crosslinking systems were compared.

Variation of tensile strength, elongation at break and tension set with curative concentrations for different crosslinking systems namely, S (sulfur/accelerator), R (phenolic resin), SH (sulfur/HVA-2), EPD (peroxide/triallyl cyanurate), DH (peroxide/HVA-2), SI (silane), UV irradiation, and electron beam (EB) irradiation have been studied. Each curing system shows optimum level of physical properties at particular dose of curatives, which are represented in Table II. Tensile properties are usually used for quality check in rubber and TPE industry. Hence, optimum formulations have been chosen based on these. For example, 1.5 phr phenolic resin, 3.0 phr ZnO, and 1.0 phr SnCl$_2$, 2H$_2$O or 1.0 phr dicumyl peroxide, and 2.0 phr of TAC in GEPDM/PP blend offer best tensile strength and elongation at break (Tables III and IV). Similarly, 1.0 phr DCP with 2.0 phr HVA-2 display maximum values of the earlier-mentioned properties (Table V). Beyond this level the properties start to deteriorate because of (1) saturation limit of polymer by curative (in the case of sulfur containing systems) and (2) detrimental effect of curative on polymer (especially in the case of peroxide curing). In the silane based systems (Table VI) SI7 system shows optimum level of properties over other SI systems because of (1) proper dose of curatives (silane)

and (2) optimum time given to facilitate the condensation reaction in boiling water and PEG. Without silane, the crosslinking occurs only via free radical mechanism whereas presence of silane additionally forms *in situ* alkoxy-silyl groups, which in turn reacts with water and PEG via condensation reaction. Improvement in tensile strength is very low when samples were vulcanized with EB or UV irradiation, which might be due to simultaneous degradation of polymer chains by free radicals as generated by UV or EB. Table II shows the comparison of physical properties with different crosslinking systems at optimized level. SH3a system shows the highest value of tensile strength followed by S2a, EPD$_{1.0}$, SI7, DH2, EB10, UV30, and R2. The 100% modulus value of S2a and SH3a is much above those of other compositions. The elongation at break is above 200% for S2a, SH3a, EPD$_{1.0}$, and EB10. The tension set value is lowest for the S2a system.

Recyclability tests

Table VII shows tensile strength, modulus, elongation at break, and tension set values for various crosslinking systems after recycling. All the systems show a decrease in tensile strength and modulus after recycling three times. The elongation at break decreases after recycling for all the samples except

TABLE VIII
Effect of Aging for Different Optimized Crosslinking Systems

System	S2a	R2	SH3a	EPD$_{1.0}$	DH2	SI7	UV30	EB10	EPD$_{1.0}$*
% Change in tensile strength	−37	−28	−10	−6	−20	−23	−22	−17	−8
% Change in Elongation at break	−18	−32	−28	−11	−17	−16	−15	−11	−10
% Change in Modulus at 100%	−41	−22	−15	−9	−1	−2	–	−6	−13

TABLE IX
Crosslink Density and ΔTorque Values of Various TPVS

System	$\Delta \text{Torque} = (T_{max} - T_{min})$ from MDR	Crosslink density, $\mu \times 10^4 = \frac{\rho}{2M_c}$ (mol/cm^3)
S2a	3.7	259
R2	0.1	199
SH3a	3.9	262
EPD$_{1.0}$	1.7	245
DH2	1.2	220
SI7	1.2	228
EPD$_{1.0}$*	1.4	206

R2 and SH3a. Tension set shows an increasing trend after recycling for all the systems. EPD$_{1.0}$ shows best overall retention of properties (24 and 15% decrease in tensile strength and 100% modulus, respectively), even after recycling for three times. This observation could be explained by the fact that C—C linkages as formed by peroxide crosslinking system can sustain more shear forces and heat aging during repeated mixing cycles as compared to C—S or S—S or other linkages. It may be noted that these changes in tension set would make these qualify for good TPVs.

Effect of heat aging

Table VIII shows % decrease in tensile strength and modulus at 100% elongation respectively, for various systems after aging in hot air oven at 100°C for 7 days. EPD$_{1.0}$ shows best retention of tensile strength followed by EPD$_{1.0}$*, SH3a, EB10, DH2, UV30, SI7, R2, and S2a. Peroxide curing provides stronger C—C linkages as crosslinks, which are more stable even at higher temperature, which is reflected in better aging

behavior. Conversely, sulfur curing provides poly, di, or monosulfide linkages, which are more susceptible to degradation during the aging experiment, exhibiting poor retention of properties.

Correlation between delta torque values and properties of TPVs

Table IX shows the values of crosslink densities as calculated from modified Flory–Huggins equation and delta torque ($T_{max} - T_{min}$ during vulcanization, as obtained from MDR (Moving Die Rheometer), which represents the crosslinking formation in EPDM/PP phase under dynamic condition). SH3a shows highest value of crosslink density followed by S2a, EPD$_{1.0}$, SI7, DH2, and EPD$_{1.0}$*. HVA-2 as a coagent for sulfur shows higher efficiency than conventional accelerators system. Hence, SH3a shows higher value of tensile strength over S2a. Furthermore, the type of crosslinks formed during dynamic vulcanization affects the strength of the TPVs. Although, peroxide curing system forms less crosslinks per unit volume, it forms C—C linkages, which are stronger than C—S and S—S linkages. In addition, there is a possibility of the formation of *in situ* graft-link structures of PP with GEPDM at the interface during the process of dynamic vulcanization in coagent assisted peroxide-cured PP/EPDM blends.[22,23] These *in situ* graft-links can also act as a compatibilizer in such a system, which in turn can improve final mechanical properties. As a result, EPD$_{1.0}$ system has almost same tensile strength as S2a. SI7, DH2 and resin curing systems are relatively less effective in gas phase EPDM/PP blend, perhaps
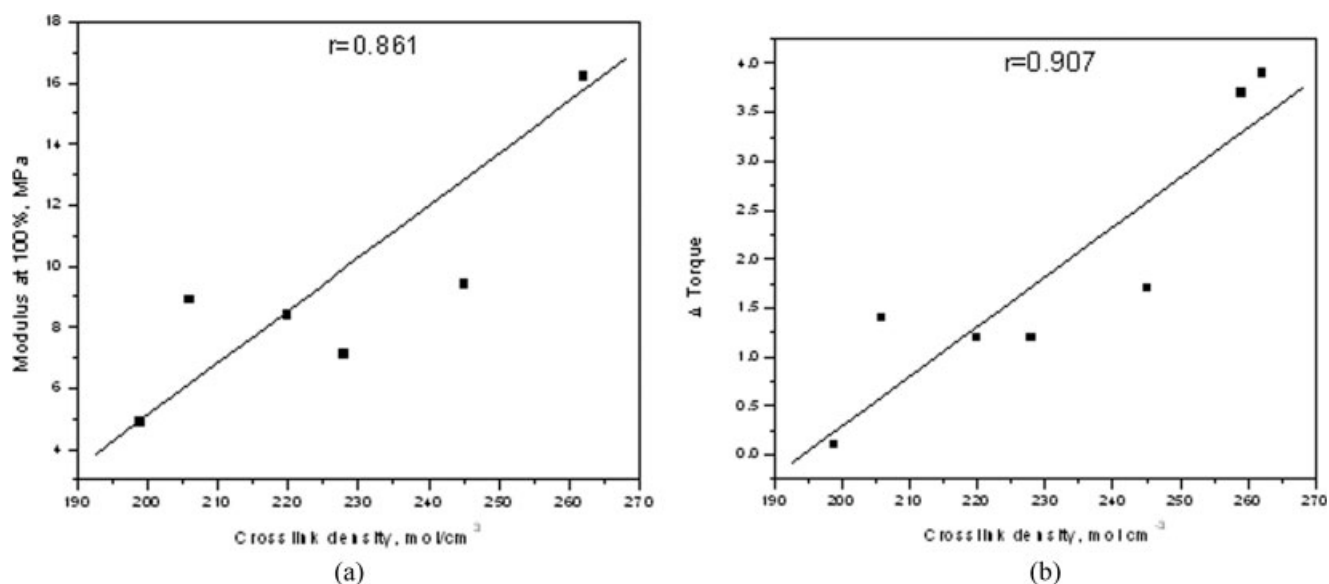

Figure 1 (a) Relation between calculated crosslink density and modulus at 100% elongation. (b) Relation between calculated crosslink density and ΔTorque.
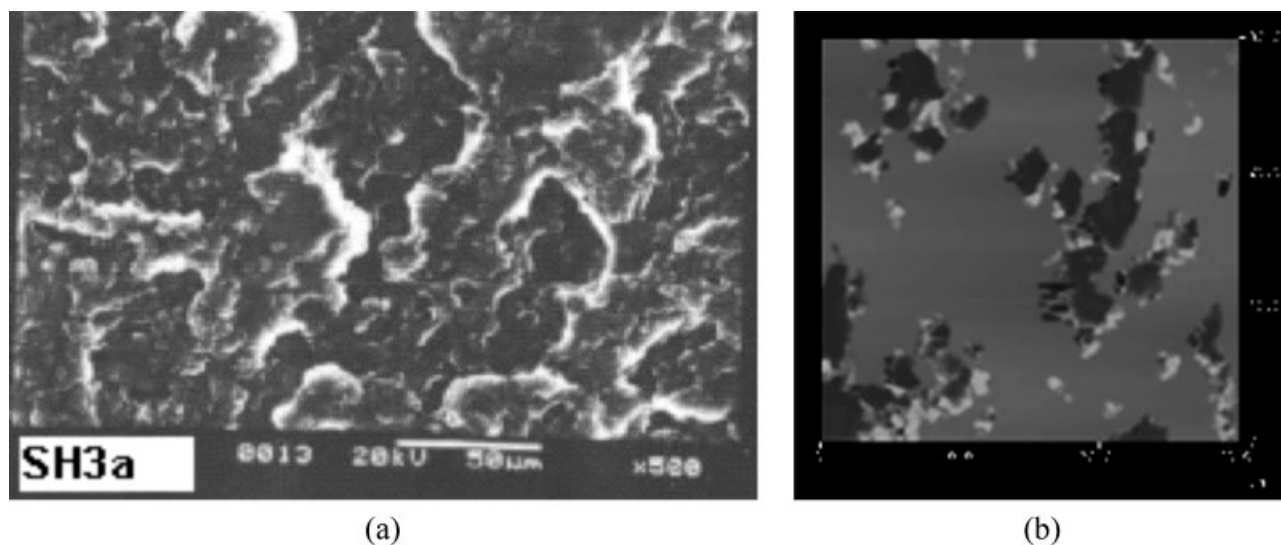
Figure 2 (a) SEM photomicrograph of SH3a system. (b) AFM photomicrograph of SH3a system.

due to the interference with the carbon black as present in GEPDM. Figure 1(a) shows a plot between modulus of TPVs and values of crosslink densities as calculated from modified Flory–Huggins equation. There is an overall trend of increasing modulus with increasing crosslinking density. Similarly, correlation also exists between ΔTorque as obtained from MDR and crosslink density. Figure 1(b) shows a linear relation between ΔTorque of TPVs obtained from MDR and theoretical values of crosslink densities as calculated from modified Flory–Huggins equation. SH3a system shows highest ΔTorque value, while R2 exhibits the lowest value. This may be due to the

fact that phenolic resin system is not an effective curative package for the crosslinking of GEPDM.

Morphology studies

Figure 2(a) shows representative SEM photomicrograph of the SH3a system. White continuous phase highlights PP, whereas approximately circular black domains represents the EPDM phase surrounded by carbon black. All the other systems exhibit similar morphology (and hence not shown here). As crosslink density increases, rubber domains are reduced in size and get separated from the PP phase. SH3a
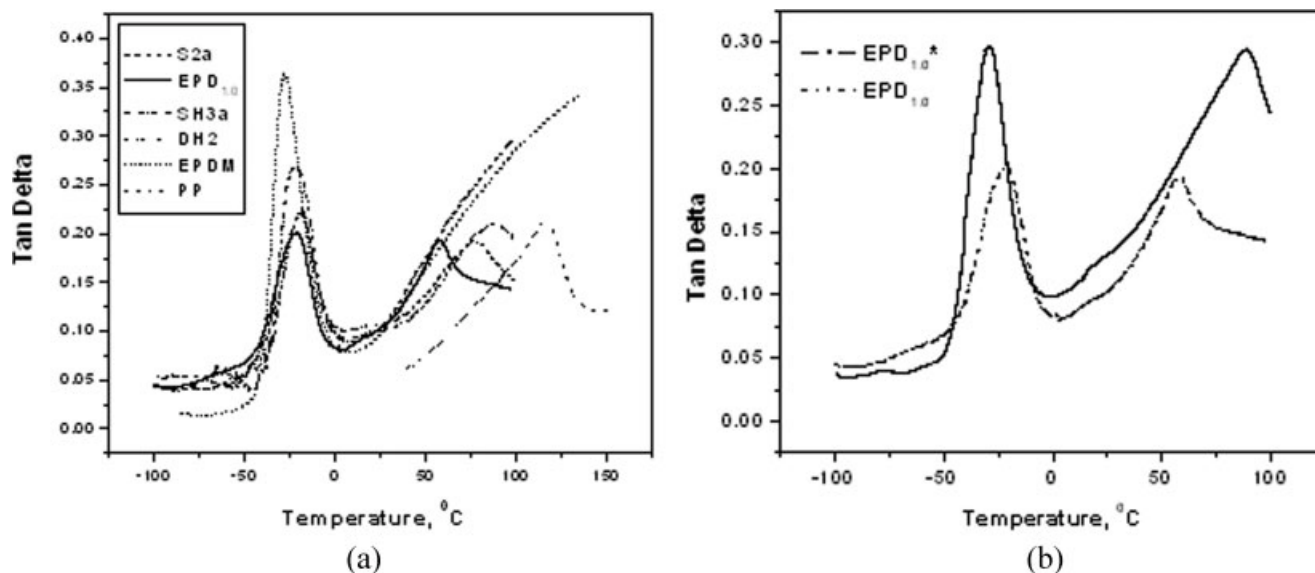

Figure 3 (a) Tan δ versus temperature plot of various crosslinking systems. (b) Tan δ versus temperature plot of $EPD_{1.0}$ and $EPD_{1.0}$* systems.

TABLE X
T_{g1} and T_{g2} Positions in Different Crosslinking Systems

System	S2a	R2	SH3a	$EPD_{1.0}$	DH2	$EPD_{1.0}*$	GEPDM	PP
T_{g1}	−19	−22	−17	−21	−19	−29	−30	–
T_{g2}	88	98	77	58	97	88	–	115
$T_{g2} - T_{g1}$	107	120	94	79	116	117	–	–

system shows finer rubber domains followed by S2a, $EPD_{1.0}$, SI7, and DH2. AFM phase diagram [Fig. 2(b)] displays the morphology of SH3a blend system. The black regions are small rubber domains dispersed in the continuous gray plastic phase. The hard small white color regions may be the carbon black surrounding the rubbery phase and some unreacted curatives.

DMA analysis

The DMA curves of the GEPDM/PP TPVs with various crosslinking systems are shown in Figure 3(a). All the blends exhibit two distinct peaks, indicating the thermodynamic immiscibility between the two components of these blends: PP and GEPDM. Value and position of tan δ peak in both phases represent the degree of crosslinking. The higher degree of crosslinking prevents the alignment of chains in a crystal lattice, hinders crystallization, and leads to decrease the degree of crystallinity of PP. Table X shows the T_{g1}, T_{g2} and $T_{g2} - T_{g1}$ values for various crosslinking systems. T_{g1}, T_{g2} correspond to the glass transition temperature of rubbery and plastic phase respectively. SH3a shows most increase in the rubbery phase T_g. It indicates that dynamic vulcanization has been taken place most efficiently in this system, which can be confirmed by the observed highest crosslink density for this system (Table IX). The plastic phase T_g has been drastically decreased in $EPD_{1.0}$ system.

TABLE XI
Comparison of Blends of GEPDM and Conventional EPDM (ROYALENE-563) on the Basis of Different Curing Systems

	$EPD_{1.0}$	$EPD_{1.0}*$
System		
GEPDM	100	–
ROYALENE-563	–	73
Carbon black	–	27
PP	40	40
DCP	1.0	1.0
TAC	2.0	2.0
Mechanical properties		
Tensile strength (MPa)	15.7	9.3
Elongation at break (%)	221	116
Modulus at 100% (MPa)	9.4	8.9
Hardness (Shore D)	38	30
Tension set at 25°C (%)	5.9	6.9

$EPD_{1.0}$ system also shows lowest difference followed by SH3a, S2a, SI7, DH2, and R2. DCP/TAC combination provides efficient free radicals that crosslink EPDM phase. Additionally, it forms *in situ* EPDM-PP graft-links, which in turn enhances the compatibility between EPDM and PP. It also affects the T_g of PP. tan δ peak related to GEPDM phase shifts significantly with different crosslink systems.

Comparison of $EPD_{1.0}$ with $EPD_{1.0}*$

In line with the goal of our study, conventional Royalene-563 EPDM rubber with similar content of diene (4.7 wt %) was chosen for comparison with GEPDM. Table XI shows that excellent tensile strength, elongation at break, modulus at 100% elongation and tension set were obtained for $EPD_{1.0}$ when compared with $EPD_{1.0}*$. $EPD_{1.0}$ shows better retention of tensile strength, elongation at break, and modulus at 100% elongation as well as better tension set over conventional $EPD_{1.0}*$ system.

$EPD_{1.0}*$ shows lower value of crosslink density (Table IX) when compared with $EPD_{1.0}$ possibly due to improper dispersion of curatives and carbon black throughout the matrix. Granular nature of the GEPDM provides finer morphology with excellent distribution of carbon black throughout the matrix over conventional $EPD_{1.0}*$ system. As a result $EPD_{1.0}$ shows very good overall properties over $EPD_{1.0}*$ system.

Figure 3(b) shows the tan δ versus temperature plots of $EPD_{1.0}$ and $EPD_{1.0}*$. $EPD_{1.0}$ shows very low value of $T_{g2} - T_{g1}$ over $EPD_{1.0}*$ because of excellent compatibility. Granular nature of GEPDM facilitates the excellent distribution of curative and carbon black over conventional EPDM/PP TPVs. Also, tan δ peaks for both the phases decrease significantly because of very low damping behavior.

Table XII shows the evaluation of overall performance of various crosslinking systems, which gives an impression about the selection of the crosslinking agent depending on the final property requirements.

CONCLUSIONS

1. GEPDM/PP TPVs with various crosslinking systems have been studied extensively to optimize the curative level in each crosslinking sys-

TABLE XII
Overall Performance of Different Crosslinking Systems

System	Strength of product	Processibility	Aging	Recyclability	Tension set property	Appearance of product	Cure time for dynamic vulcanization (minutes)
S2a	Good	Poor	Poor	Ok	Excellent	Poor	Low
R2	Poor	Ok	Ok	Ok	Poor	Good	High
SH3a	Excellent	Poor	Good	Ok	Ok	Poor	Very high
$EPD_{1.0}$	Good	Excellent	Excellent	Good	Excellent	Excellent	Very low
DH2	Ok	Ok	Ok	Poor	Ok	Good	Very low
SI7	Ok	Ok	Ok	Poor	Ok	Excellent	High
UB30	Poor	–	Ok	Ok	Ok	Excellent	Very low
EB10	Poor	–	Good	Good	Ok	Excellent	Very low
$EPD_{1.0}*$	Ok	Good	Ok	Ok	Good	Excellent	Low

tem with special reference to their physical properties.

2. Optimized systems as obtained from the earlier-mentioned studies were compared for heat aging, recyclability, crosslink density, morphology studies, and DMA analysis.

3. Peroxide curing with TAC as a coagent gives better overall performance with reference to excellent heat aging resistance, tension set, and compatibility between EPDM and PP.

4. Conventional EPDM/PP system was compared with GEPDM/PP system for heat aging, processibility, crosslink density, morphology studies, and physical properties. GEPDM/PP system was found to exhibit better behavior in all respect.

5. Significant correlations were obtained between MDR delta torque value or modulus and crosslink density of TPVs.

References

1. Martin, S.; Denton, D.; Candy, L.; Ramage D. Presented at the ACS Rubber Division Fall Meeting, Pittsburg, PA, Oct. 8–12, 2002.
2. Grant, C.; Vara, R.; Tang S. Presented at the ACS Rubber Division Fall Meeting, Pittsburg, PA, Oct. 8–12, 2002.
3. Coran, A. Y.; Patel, R. P. Rubber Chem Technol 1981, 54, 892.
4. Coran, A. Y.; Patel, R. P. Rubber Chem Technol 1981, 54, 91.
5. Abdou-Sabet, S.; Patel R. P. Rubber Chem Technol 1991, 54, 769.
6. Ghosh, P.; Chattopadhyay, B.; Sen, A. K. Polymer 1994, 35, 18.
7. Danesi, S.; Porter, R. S. Polym 1978, 19, 448.
8. Kresge, E. N. Rubber Chem Technol 1991, 64, 469.
9. Abdou-Sabet, S.; Puydak, R. C.; Patel R. P. Rubber Chem Technol 1996, 69, 479.
10. Kresge, E. N. In Polymer Blends; Paul, D. R., Newman, S., Eds.; Academic: New York, 1978; Chapter 20, p 20.
11. Bhowmick, A. K.; Inoue, T. J Appl Polym Sci 1993, 49, 1893.
12. Roychoudhury, N.; Bhowmick, A. K. J Appl Polym Sci 1989, 38, 1091.
13. Jha, A.; Dutta, B.; Bhowmick, A. K. J Appl Polym Sci 1999, 74, 1490.
14. De Sarkar, M.; De, P. P.; Bhowmick, A. K. Polymer 1999, 40, 1201.
15. Naskar, A. K.; Bhowmick, A. K.; De, S. K. Polym Eng Sci 2001, 41, 1087.
16. Chattopadhyay, S.; Chaki, T. K.; Bhowmick, A. K. J Appl Polym Sci 2001, 79, 1877.
17. Kader, A.; Bhowmick, A. K. Rubber Chem Technol 2001, 74, 662.
18. Anadhan, S.; De, P. P.; De, S. K.; Bandyopadhyay, S.; Bhowmick, A. K.; Rubber Chem Technol 2003, 76, 1145.
19. De, S. K.; Bhowmick, A. K. Eds. Thermoplastic Elastomers from Rubber-Plastic Blends; Ellis Horwood: London, 1990.
20. Jha, A.; Bhowmick, A. K. J Appl Polym Sci 2004, 92, 2000.
21. William, G.; Clayfield, T.; Johnston, R. In TPE 2003, 6th International Conference on New Opportunities for Thermoplastic Elastomers, Brussels, Belgium, Sept. 16–17, 2003; pp 59–71.
22. Naskar, K.; Noordermeer, J. W. M. Rubber Chem Technol 2004, 77, 955.
23. Naskar, K.; Noordermeer, J. W. M. Rubber Chem Technol 2003, 76, 1001.