

Properties and Morphologies of Elastomer Blends Modified with EPDM-*g*-Poly[2-dimethylamino ethylmethacrylate]

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ABSTRACT: The graft copolymerization of 2-dimethylamino ethylmethacrylate (DMAEMA) onto ethylene propylene diene monomer rubber (EPDM) was carried out in toluene via solution polymerization technique at 70°C, using dibenzoyl peroxide as initiator. The synthesized EPDM rubber grafted with poly[DMAEMA] (EPDM-*g*-PDMAEMA) was characterized with ¹H-NMR spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). The EPDM-*g*-PDMAEMA was incorporated into EPDM/butadiene acrylonitrile rubber (EPDM/NBR) blend with different blend ratios, where the homogeneity of such blends was examined with scanning electron microscopy and DSC. The scanning electron micrographs illustrate improvement of the morphology of EPDM/NBR rubber blends as a result of incorporation of EPDM-*g*-PDMAEMA onto that blend. The DSC trace exhibits one glass transition temperature (T_g) for EPDM/NBR blend

containing EPDM-*g*-PDMAEMA, indicating improvement of homogeneity. The physico-mechanical properties after and before accelerated thermal aging of the homogeneous, and inhomogeneous EPDM/NBR vulcanizates with different blend ratios were investigated. The physico-mechanical properties of all blend vulcanizates were improved after and before accelerated thermal aging, in presence of EPDM-*g*-PDMAEMA. Of all blend ratios under investigation EPDM/NBR (75/25) blend possesses the best physico-mechanical properties together with the best (least) swelling (%) in brake fluid. Swelling behavior of the rubber blend vulcanizates in motor oil and toluene was also investigated. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2547–2554, 2009

Key words: EPDM; blend; 2-dimethylamino ethylmethacrylate; graft copolymerization; physico-mechanical properties; homogeneity

INTRODUCTION

Ethylene propylene diene monomer rubber (EPDM) is known of its ability to improve weather resistance of high diene rubbers via blending. Unfortunately other physical properties of the rubber–rubber blend are often poorer than those of either parent elastomer alone because of thermodynamic incompatibility, which results due to the absence of the physical and the chemical interactions across the phase boundaries and poor interfacial adhesion.^{1–5} Nitrile rubber (NBR) is hard rubber, it is known of its high solvent and oil resistance. The extremely strong intermolecular hydrogen bonding makes it one of the most difficult rubbers to compound with other rubbers and/or plastics.⁶ It has been reported⁷ that NBR has a solubility parameter higher than that of EPDM by $2.53 \text{ (J/m}^3)^{1/2}$, and the compatibility between polymers reduces as the difference in solubility parameters of the respective polymers approaches a value of 0.5 or greater. In case of

blending NBR with EPDM one of them will form large domains distributed in the continuous phase of the other. The difference in solubility parameters of NBR and EPDM and consequently the immiscibility arise from size of the molecular chains, leading to small entropy of mixing, and from chemical characteristics of the segments.⁸ Great research efforts have been made to improve homogeneity of the polymer blends as well as their corresponding ultimate properties by means of phase compatibilization.^{9–12} Several approaches have been reported to improve the compatibility of NBR/EPDM blends. The use of liquid elastomers, such as transpolyoctylene, results in blends with more homogenous morphology and better mechanical properties.¹³ Polar polymers such as polychloroprene,¹⁴ chlorinated polyethylene, chlorosulfonated polyethylene,¹⁵ and bromobutyl rubber¹⁶ have also been employed as a third component to improve the compatibility of that blend. Another procedure to improve the interfacial adhesion between incompatible rubber phases is the addition of graft copolymers, whose segments are identical or miscible with each blend domain.¹⁷ Functionalization of EPDM with mercapto groups has improved the poor

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compatibility of EPDM with high diene content rubbers.¹⁸ Mercapto-modified ethylene vinyl acetate has been employed as a reactive compatibilizing agent for EPDM/NBR blends vulcanized with a sulfur/mercapto benzothiazole disulfide (MBTS) single accelerator system and a sulfur/MBTS/tetramethylthiuram disulfide binary accelerator system.¹⁹ The graft copolymer of acrylonitrile or acrylic acid onto EPDM has been used as compatibilizing agent for EPDM/NBR blend.²⁰ Maleic anhydride grafted EPDM has also been used successfully as a compatibilizer for the same blend.²¹ The morphology of this blend has been improved by the addition of epoxidized EPDM in a small amount. Of all the blend ratios investigated, the 75/25 EPDM/NBR blend ratio compatibilized with aminated epoxidized EPDM has shown the best mechanical properties, heat resistance, and stability against UV irradiation.²² In continuation of our group research interest in the compatibility of NBR containing rubber blends,²³ we are introducing in this work a new graft copolymer namely EPDM grafted with poly[(2-dimethylamino) ethylmethacrylate] EPDM-*g*-PDMAEMA as a third component in the EPDM/NBR blend to study its ability to increase the interfacial adhesion between the two domains in different blend ratios. PDMAEMA was chosen because of its polar character.

EXPERIMENTAL

Materials

2-Dimethylamino ethylmethacrylate (DMAEMA, Aldrich, Milwaukee, WI) was purified from inhibitor by stirring over aluminum silicate for 4 h at an ambient temperature. Paraffin oil ($d = 0.861 \text{ g/cm}^3$) supplied by Prolabo Chemicals (Briare, France), was used as the dispersing phase. Sorbitan monooleate (Span 80) a nonionic surfactant of HLB value of 4.3, supplied by Sigma Chemical Co. (St. Louis, MO), was used as received. Dibenzoyl peroxide, a product of Acros, (Morris Plains, NJ), was recrystallized from chloroform/methanol (50/50) v/v twice. Toluene, chloroform, and methanol products of El Nasr Chemical Company, Cairo, Egypt, were used as received. Vistalon-6505 (EPDM) of 9% ethylidene norbornene content and of 50 Mooney viscosity [$M_L (1+4)$ at 100°C] is a product of Esso Chimie, London, UK. Krynac-3450 (NBR) of 34% acrylonitrile content and 50 Mooney viscosity [$M_L (1+4)$ at 100°C] is a product of Bayer Company, Leverkusen, Germany.

Techniques

Synthesis of EPDM-*g*-PDMAEMA

EPDM-*g*-PDMAEMA was synthesized via solution polymerization technique. EPDM, 5 g was dissolved

in 300 mL toluene. DMAEMA 20 g was added dropwise over 4 h to the EPDM solution. The solution polymerization reaction was carried out in 1 L, three neck-round bottom flask, using mechanical stirrer rotating at 100 rpm. The polymerization system was flushed with nitrogen for 30 min and kept in water bath at 70°C. Benzoyl peroxide 27 mmol was dissolved in 10 mL toluene where 2.5 mL were added per hour. The copolymerization reaction product was precipitated in methanol overnight, decanted, and washed several times with water and methanol. The resulting copolymers were precipitated in methanol/water (50/50) v/v from their THF solution. Finally EPDM-*g*-PDMAEMA copolymers were dried in a vacuum oven at 40°C for a week. The grafted material (EPDM-*g*-PDMAEMA) was purified from PDMAEMA homopolymer by soxhlet extraction with dioxane for 24 h.

Synthesis of PDMAEMA

Polymerization reaction for a total recipe of 62.5 g was carried out in a 150 mL round bottom flask fitted with a mechanical stirrer, a thermometer, a nitrogen inlet/outlet and a rubber septum cap for injection of the redox initiators. The aqueous/oil phase ratio and the total monomer concentration were 60/40 and 25 wt %, respectively. Span 80 (7.0 mmol) was solubilized in paraffinic oil (20 g). DMAEMA (159 mmol) were solubilized in distilled water (30 g) at 30°C with mild stirring. The aqueous phase was poured drop-wise over the oil phase under stirring rate of 7000 rpm of Ultra Turax homogenizer. The mixture was left under this stirring rate for 15 min. The formed w/o emulsion was polymerized in a batch reaction mode using sodium persulfite (0.42 mmol) and sodium metabisulfite (0.263 mmol) redox initiating system at 20°C.

Characterization techniques

¹H-NMR spectroscopy

EPDM-*g*-PDMAEMA molecular composition was analyzed; 5 mg of EPDM-*g*-PDMAEMA was solubilized in CDCl₃ (1 mL) and detected at an ambient temperature using JEOL, 500 MHz NMR Spectroscopy, JEOL, Akishima, Tokyo 196-8558, Japan, with Delta NMR software.

Gel permeation chromatography

The number average molecular weights (M_n 's), weight average molecular weights (M_w 's), and MWDs (M_w/M_n)'s were obtained using Agilent gel permeation chromatography (GPC) instrument. The instrument is equipped with a series of three styragel columns (10², 10³, and 10⁴ Å), and calibrated

TABLE I
Formulations and Rheological Properties of EPDM/NBR Rubber Blends of Different Blend Ratios With and Without EPDM-g-PDMAEMA, at 162°C

Ingredients/Designation	S1	S2	S3	S4	S5	S6	S7	S8
EPDM	100	75	50	25	75	50	25	0
NBR	0	25	50	75	25	50	75	100
EPDM-g-PDMAEMA	0	0	0	0	10	10	10	0
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
HAF ^a	40	40	40	40	40	40	40	40
Processing oil	5	5	5	5	5	5	5	5
CBS ^b	1	1	1	1	1	1	1	1
Sulfur	2	2	2	2	2	2	2	2
Rheological properties								
Minimum torque, Nm	16	13	11	10.5	9.5	9.5	8	8
Maximum torque, Nm	86	91	79	77	78	72	60	71
Cure time (t _{c90}), min	16.5	11.5	11.5	5.5	13	12	7	10
Scorch time (t _{s2}), min	3	2	2	1.5	2	2	1.5	1.75
Cure rate index (CRI), min ⁻¹	7.4	10.5	10.5	25	9	10	18	12

^a High abarasion furnace black.

^b N-cyclohexyl 2-benzothiazole sulfenamide.

with a series of narrow molecular weight polystyrene standards and a refractive index detector (Agilent 1100 differential refractometer).

Thermal analysis

Glass transition temperatures (T_g 's) of EPDM-g-PDMAEMA copolymer were determined using a Shimadzu (Model DSC-50) calorimeter, Foster City, CA. The specimens were cooled to -100°C and heated up to 110°C to remove their thermal history. The second runs were measured at a heating rate of 10 min^{-1} under nitrogen atmosphere. Thermal degradation was studied with thermal gravimetric analyzer (Model TGA- 50) by heating the samples from ambient temperature to 700°C .

Homogeneity investigation

Scanning electron microscopy

Morphology of EPDM/NBR rubber blends with different blend ratios, in presence and absence of EPDM-g-PDMAEMA, was studied using scanning electron microscope, Model JXA-840A, JEOL, Technics, Tokyo, Japan, at magnification $M = 500\times$. The surface of the polymer was mounted on a standard specimen stub. Thin coating 10 \AA of gold was deposited onto the polymer surface and attached to the stub before examination in the microscope to enhance conductivity.

Differential scanning calorimetry

Glass transition temperatures (T_g 's) of EPDM/NBR (50/50) rubber blends, in presence and absence of

EPDM-g-PDMAEMA, were determined using a Shimadzu (Model DSC-50) calorimeter as indicated above.

Mixing and vulcanization

For physico-mechanical properties determination and swelling behavior investigation, the rubber blends were mixed with curatives and other compounding ingredients, for 20 min, on an open two roll-mill of 170 mm diameter and 300 mm working distance at 24 rpm speed of slow roll and 1 : 1.25 of gear ratio at 90°C . EPDM-g-PDMAEMA was first mixed with EPDM then NBR was added onto the mill followed by the other compounding ingredients. The rheometric characteristics²⁴ of the rubber mixes were assessed with an Oscillating Disc Rheometer R-100, (Monsanto, Akron, OH) at $162^\circ\text{C} \pm 1^\circ\text{C}$. The blends were then cured for their respective optimum cure time, in a hydraulic press at the same temperature and pressure of 4 MPa on the mold. The formulations and rheological characteristics of EPDM/NBR/EPDM-g-PDMAEMA blends are shown in Table I.

Physico-mechanical test

The physico-mechanical properties were determined with a Zwick-1425 tensile tester²⁵ at $25^\circ\text{C} \pm 1^\circ\text{C}$ and cross-head speed of 500 mm min^{-1} . Accelerated thermal aging of rubber vulcanizates was carried out in an air-circulated oven at 90°C for 7 days. The physico-mechanical data were measured after and before thermal aging in five replicates.

Swelling test

Weight swell test of rubber blend vulcanizates in toluene was carried out at $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$ for 48 h²⁶; however, swelling test in motor oil and brake fluid was conducted at $100^{\circ}\text{C} \pm 1^{\circ}\text{C}$ for 7 days, in a thermo stated electric oven. The swelling data were measured in five replicates.

RESULTS AND DISCUSSION

Grafting efficiency

Efficiency of the graft polymerization was determined based on the copolymer composition using ¹H-NMR spectroscopy.^{27,28} The relative concentration of each copolymer was determined from the integrated area of the corresponding protons. Figure 1 shows the ¹H-NMR spectrum of EPDM-g-PDMAAEMA together with the proposed structure and the peaks assignment. The two *N*-methyls (6H) of PDMAEMA appear at $\delta = 2.3$ PPM with integration value of 1.361. When divided by double the integration value of methyl protons (3H) of EPDM backbone at $\delta = 0.75$ PPM; results in 3.402% grafting efficiency and grafting yield percentage of 0.00176 DMAEMA onto EPDM backbone according to the following equation:

$$\text{Grafting Efficiency} = \frac{\sum N - \text{CH}_3 \times 1/2}{\sum \text{CH}_3_{\text{EPDM}} \times 100} \quad (1)$$

This result is very close to our previous grafting efficiency measurements²⁹ of other acrylates onto rubber materials via other analytical techniques such as titration and/or elemental analysis. The GPC trace of the modified EPDM is shown in Figure 2. The M_n and PI of EPDM-g-PDMAAEMA were found to be 435 K and 4.12, respectively. The modified EPDM has a higher PI than that of EPDM (3.85) due to branching caused by PDMAEMA moieties. From

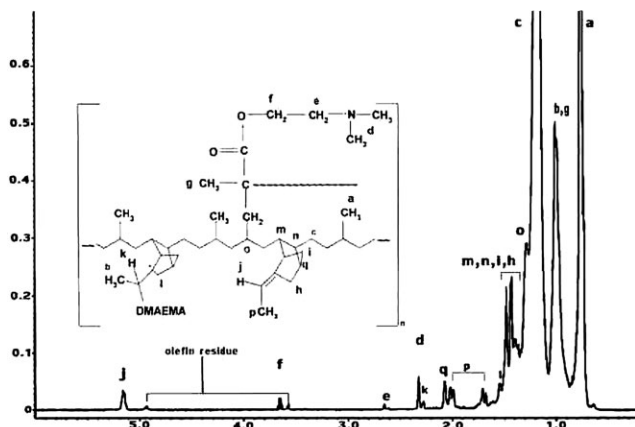


Figure 1 ¹H-NMR spectrum of EPDM-g-PDMAAEMA.

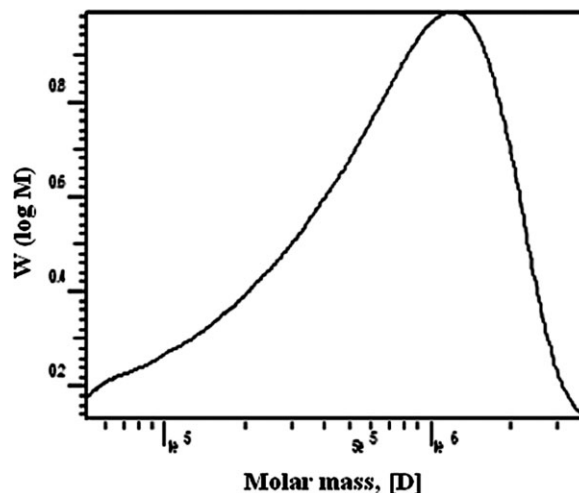


Figure 2 GPC trace of EPDM-g-PDMAAEMA. W: refractive index of polymer solution, M: minus mvolt.

¹H-NMR spectroscopy and GPC measurements we can calculate the M_n of PDMAEMA as:

$$M_n \text{ PDMAEMA} = [3.402/100] \times 435 \times 10^3 = 18.283 \times 10^3 \quad (2)$$

The T_g of PDMAEMA homopolymer which corresponds to a weight average molecular weight of 52,000 appears at 146°C in Figure 3; however, in Figure 4, the T_g s of molecular segments in the graft copolymer show up at -49.91°C for EPDM and at 114°C for PDMAEMA. The T_g of PDMAEMA segment is lower than its respective homopolymer due to the reduction in molecular weight of PDMAEMA in the graft copolymer which is attributed to the insolubility of the polar homopolymer in the graft polymerization reaction medium. The explanation discussed is based on Fox and Flory³⁰ empirical equation to express the dependence of T_g on M_n for different linear polymers.

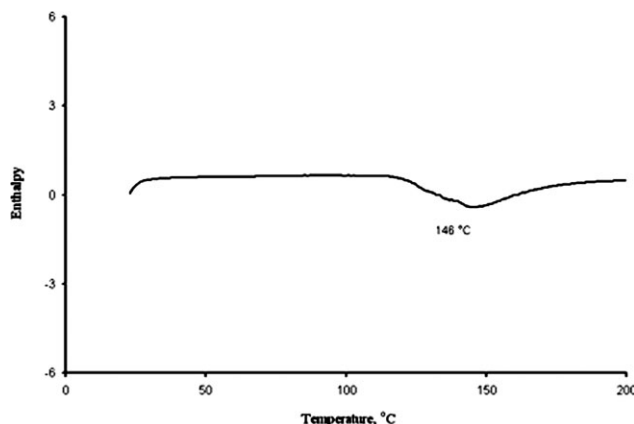


Figure 3 DSC scan of PDMAEMA.

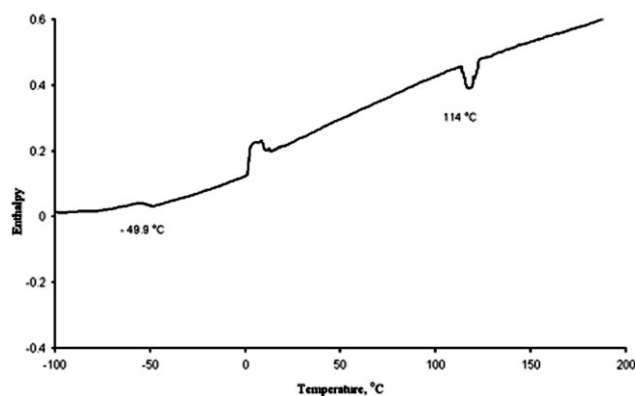


Figure 4 DSC scan of EPDM-g-PDMAEMA.

$$T_g = T_g\infty - K/M_n \quad (3)$$

Figure 5 represents the TGA scan of EPDM-g-PDMAEMA. It is obvious that the material is stable up to 150°C as it loses only 4.9% of its original weight.

Homogeneity of EPDM/NBR blend

Differential scanning calorimetry (DSC) traces of EPDM/NBR (50/50) blends with and without EPDM-g-PDMAEMA (10 phr) are illustrated in Figure 6(a,b). Glass transition temperatures (T_g 's) of EPDM and NBR in the blend without EPDM-g-PDMAEMA appear at -30 and -60 °C, respectively with T_g difference of 30°C. However, T_g of EPDM/NBR rubber blend with EPDM-g-PDMAEMA appears at -50 °C. These data illustrate that EPDM/NBR rubber blend possessed one T_g upon incorporation of EPDM-g-PDMAEMA. This can be attributed to the reduction of interfacial energy and to the increase of adhesion between phases³¹; as a result of

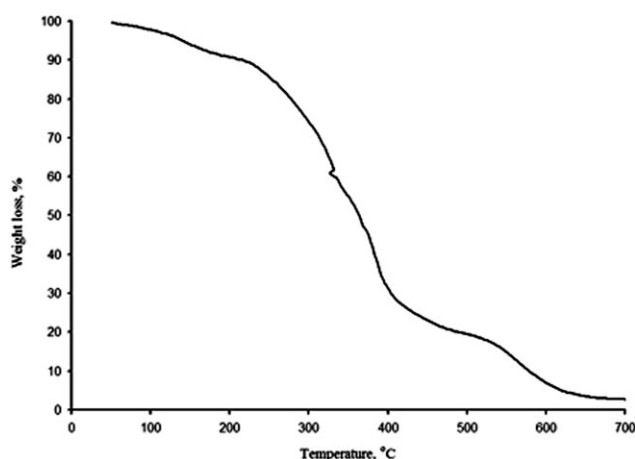


Figure 5 TGA scan of EPDM-g-PDMAEMA.

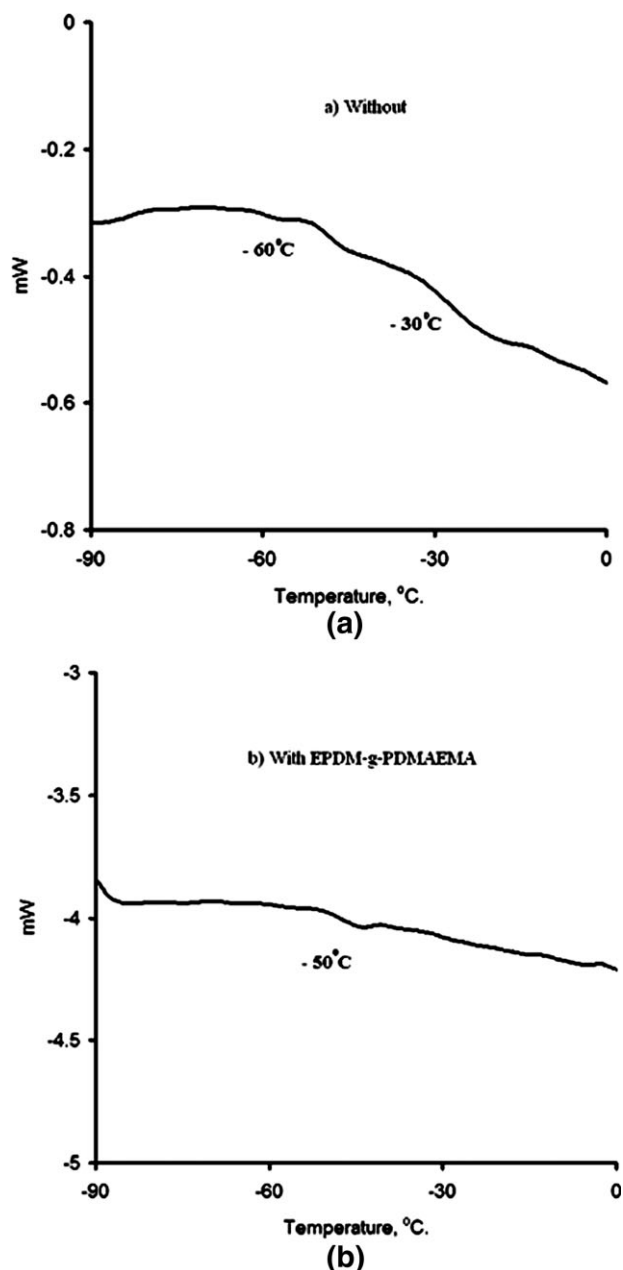


Figure 6 DSC traces of EPDM/NBR (50/50) blends with and without EPDM-g-PDMAEMA.

the dipole-dipole interaction between the acrylonitrile groups of nitrile rubber and the amino groups of EPDM-g-PDMAEMA. EPDM/NBR blends of different blend ratios with and without EPDM-g-PDMAEMA (10 phr) were prepared for microscopy examination. The micrographs [Fig. 7(a-c)] of the blends without EPDM-g-PDMAEMA illustrate two different phases for the individual rubbers indicating phase separation and incompatibility of EPDM/NBR blends. However, the micrographs [Fig. 7(d-f)] of the blends containing EPDM-g-PDMAEMA show one phase and no phase separation takes place

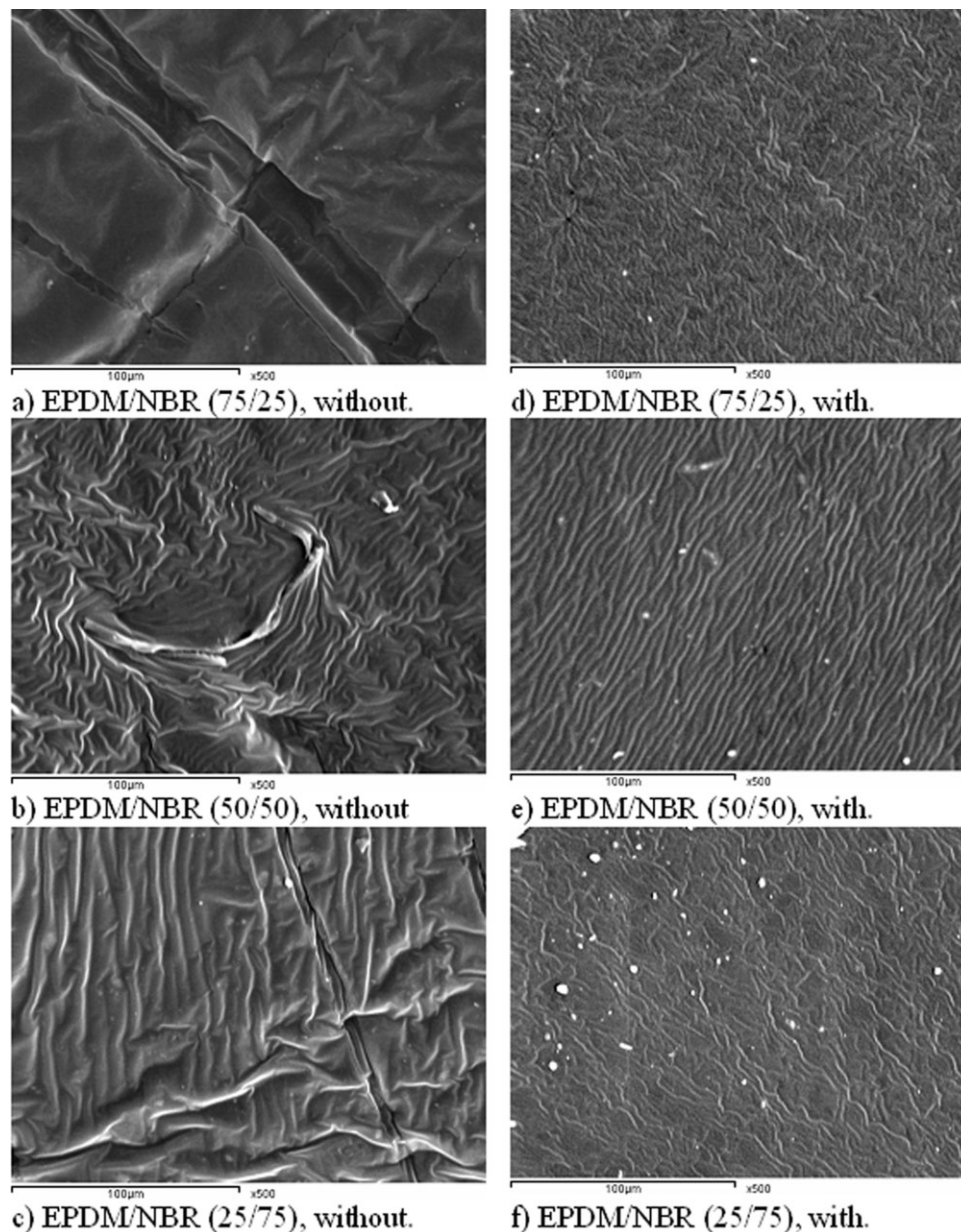


Figure 7 SEM micrographs of EPDM/NBR rubber blends of different blend ratios, with and without EPDM-g-PDMAEMA, $M = 500\times$.

indicating change in the morphology and enhancement of the homogeneity of EPDM/NBR rubber blends.

Effect of EPDM-g-PDMAEMA on the physico-mechanical properties of EPDM/NBR blends

EPDM/NBR rubber blends with different blend ratios, namely 100/0, 75/25, 50/50, 25/75, and 0/100, were prepared in presence and absence of EPDM-g-PDMAEMA. The formulations and the rheological properties of EPDM, NBR and their blends are listed in Table I. Cure times (t_{c90}) of the EPDM/NBR (25/75) blends with and without

EPDM-g-PDMAEMA were shorter and cure rate indices were greater than those of the individual rubbers. The rubber mixes were then vulcanized at their cure times. Physico-mechanical properties of EPDM, NBR and their blends with different blend ratios in presence and absence of EPDM-g-PDMAEMA were measured after and before thermal aging and plotted vs. NBR content in the blend (Figs. 8 and 9). It is clearly seen from Figure 8 that the tensile strength and elongation at break (%) of EPDM/NBR blends decrease with increasing of NBR content in the blends till EPDM/NBR ratio of 50/50, beyond which (25/75 blend) the physico-mechanical properties remain unchanged. However,

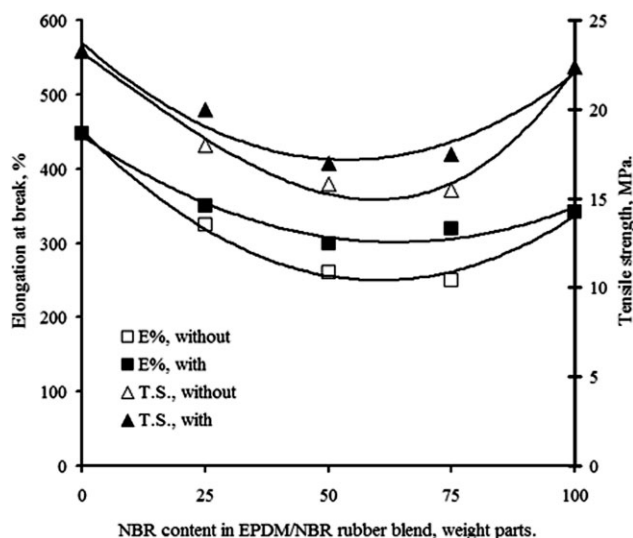


Figure 8 Tensile strength, MPa and elongation at break, % of EPDM/ NBR rubber blend vulcanizates with and without EPDM-g-PDMAEMA vs. NBR content in the blend.

both tensile strength and elongation at break (%) increase with further increase of NBR content up to 100 parts (NBR vulcanizate). From the same Figure 8, it is obvious that both tensile strength and elongation at break (%) of EPDM/NBR blend vulcanizates with different blend ratios were improved as a result of incorporation of EPDM-g-PDMAEMA (10 phr). The improvement in the mechanical properties can be attributed to the improved interfacial adhesion of EPDM/NBR blends by reducing the interfacial energy between phases as a result of incorporation

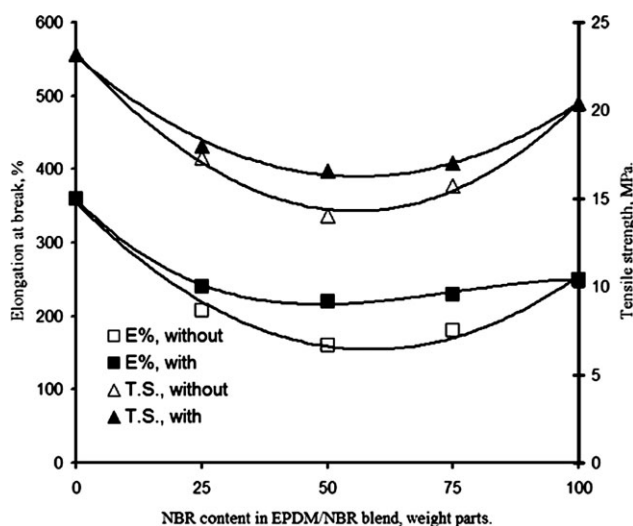


Figure 9 Tensile strength, MPa and elongation at break, % of EPDM/NBR rubber blend vulcanizates, with and without EPDM-g-PDMAEMA vs. NBR content in the blend, after thermal aging at 90°C for 7 days.

of EPDM-g-PDMAEMA. As shown in Figure 9, the tensile strength and elongation at break (%) of EPDM/NBR homogeneous blends, after 7 days of thermal aging, showed superior performance to that of the inhomogeneous blends. In other words, the elongation at break and tensile strength results agree with one another and confirm homogeneity of EPDM/NBR blend as a result of incorporation of EPDM-g-PDMAEMA. It should be noted here that EPDM/NBR (50/50) blend as well as 25/75 blend showed more pronounced effect of EPDM-g-PDMAEMA than 75/25 blend did. This could be attributed to the increase in the number of polar acrylonitrile groups as the NBR content increased in these blends, which enhances the dipole-dipole interaction with the dimethylamino groups in the EPDM-g-PDMAEMA.

Swelling behavior

Weight swell (%) in toluene, motor oil and brake fluid of the EPDM/NBR rubber blend vulcanizates vs. NBR content in those blends, in presence and absence of EPDM-g-PDMAEMA, are illustrated in Figure 10. Weight swell (%) in toluene, in absence of EPDM-g-PDMAEMA, shows S shape behavior. However, it shows linear behavior with incorporation of EPDM-g-PDMAEMA, this linearity in turn confirms the homogeneity of EPDM/NBR rubber blends as a result of incorporation of EPDM-g-PDMAEMA. Also, Figure 10 illustrates that weight swell (%) of the EPDM/NBR rubber blend vulcanizates

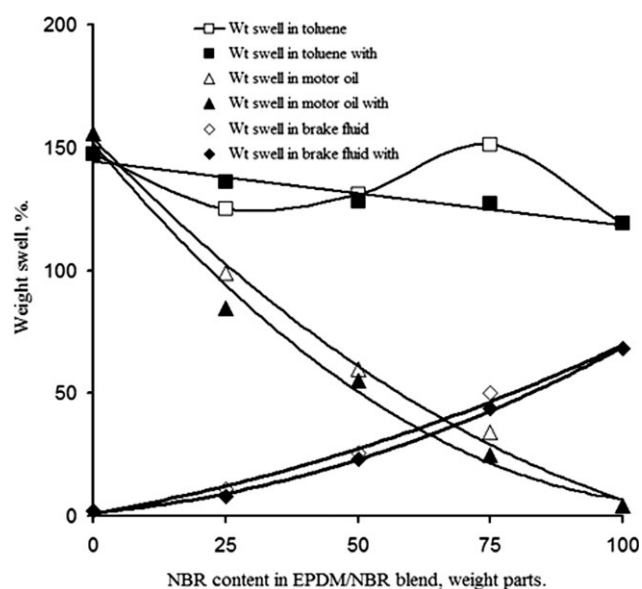


Figure 10 Weight swell, % of EPDM/NBR rubber blend vulcanizates with and without EPDM-g-PDMAEMA in toluene, motor oil and brake fluid, vs. NBR content in the blend.

decreased in motor oil while increased in brake fluid with increasing NBR content in the blend. This can be attributed to the increase of number of the polar acrylonitrile groups due to the increase of NBR content. Generally, weight swell (%) of the homogeneous EPDM/NBR blends in motor oil and in brake fluid is less than that of the inhomogeneous blends (desired phenomenon). Of all blend ratios explored, EPDM/NBR (25/75) exhibited the best swelling behavior in motor oil while EPDM/NBR (75/25) possessed the best swelling behavior in brake fluid. Therefore, EPDM/NBR blends (25/75) and (75/25) can be recommended to be used in industry of oil seal and hose subjected to motor oil and brake fluid respectively.

CONCLUSIONS

1. EPDM-g-PDMAEMA was successfully synthesized in toluene via solution polymerization technique at 70°C, using dibenzoyl peroxide as initiator. The EPDM grafted rubber was characterized with ¹H-NMR, GPC, DSC, and TGA.
2. The SEM micrographs illustrate change in the morphology and enhancement of the homogeneity of EPDM/NBR rubber blend upon incorporation of EPDM-g-PDMAEMA. This can be attributed to the reduction of interfacial energy and to the increase of adhesion between phases as a result of the dipole-dipole interaction between the acrylonitrile groups of nitrile rubber and the amino groups of EPDM-g-PDMAEMA.
3. The results obtained from DSC traces confirmed that EPDM-g-PDMAEMA (10phr) can be used successfully to improve the homogeneity of EPDM/NBR rubber blends.
4. EPDM/NBR (75/25) rubber blend possesses good mechanical properties together with the best swelling behavior in brake fluid.
5. NBR and NBR rich blend showed the best weight swell (%) in toluene and motor oil. This can be attributed to the great number of polar acrylonitrile groups.
6. The physico-mechanical properties of EPDM/NBR blend vulcanizates were improved after

and before accelerated thermal aging upon incorporation of EPDM-g-PDMAEMA.

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