Electrical and Mechanical Properties of Grafted and Ungrafted Polyacrylamide–Rubber Blends

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ABSTRACT: A systematic dielectric and mechanical study was carried out on an ethylene propylene diene monomer (EPDM) and a nitrile rubber (NBR) blended with polyacrylamide (PAM). From the compatibility investigations, it was found that EPDM/PAM is incompatible while NBR/PAM is semicompatible. To overcome the problem of phase separation between rubber and PAM, PAM was grafted with two different monomers, acrylonitrile (AN) and acrylic acid (AA), and added with 10 phr to both EPDM and NBR. Poly(vinyl chloride) (PVC) was also added as a compatiblizing agent to both types of blend. It was concluded that the addition of either a grafted polymer or PVC to the rubber–plastic blend could improve to some extent the compatibility of such blends. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2053–2059, 1998

Key words: EPDM; polyacrylamide; rubber; acrylonitrile; acrylic acid

INTRODUCTION

Intensive work has been recently carried out in the field of polymer blends with several published articles and issued patents.[1–3] This new interesting field of research allowed a great deal of progress in commercial exploitation of polymer blending as an approach for the preparation of materials with newly described properties absent in the component polymers.[1–4] The production of such polymer blends makes it possible to improve the physical properties of the investigated polymers. Blending rubber with plastic to achieve good mechanical properties is not an easy process due to the incompatibility of most of these blends.[5] Several strategies have been employed to minimize the phase separation and to increase the interfacial adhesion that include the addition of physical or chemical comatibilizers.[6,7] Even though blending is an easy method for the preparation of thermoplastic elastomers (TPEs), most of the TPE blends are immiscible. Very often, the resulting materials exhibit poor mechanical properties due to the poor adhesion between the phases. Over the years, different techniques have been developed to solve this problem. These include the addition of a third homopolymer, a graft or block copolymer, which is miscible with the two phases, and the introduction of covalent bonds between the homopolymer phases.

The electrical and mechanical properties of the ethylene propylene diene monomer (EPDM) and nitrile rubber (NBR) blended with polyacrylamide (PAM) were studied. The properties of such blends when PAM is grafted with two different monomers (acrylonitrile and acrylic acid) were also investigated.

EXPERIMENTAL

Materials

Material	Designation	Characteristics
Nitrile rubber	NBR	Butadiene acrylonitrile—copolymer with 32%—acrylonitrile
Ethylene propylene diene monomer	EPDM	Ethylene norbornene—with ethylene weight—content 70% propylene—ratio DB/100c 8% and—22% propylene
Peroxide	Perkadox	1,3-Bis(isoopropyl butyl)—benzene (peroxide)—on calcium carbonate—having trade name—Perkadox 14/10 and—molecular weight of 338

Polyacrylamide (PAM) (MW over 5,000,000) and poly(vinyl chloride) (PVC) emulsion, K value = 70, from BDH were used as received. Acrylonitrile (AN) and acrylic acid (AA) from BDH were distilled just before use. Potassium persulfate was obtained from Merck.

Techniques

Blend Preparation

The melt mixing was carried out in a Brabender Plasticorder at 170°C and a rotor speed of 30 rpm. The mixing was continued for 5 min, and then the peroxide was added to the mix on a laboratory two-roll mill (470-mm diameter, 300-mm working distance, speed of the slow roll 24 rev/min, gear ratio 1 : 1.4). The compounded blends were left overnight before vulcanization.

Vulcanization

The vulcanization was carried out in a heated platten press under a pressure of about 40 kg/cm^2 and temperature of 172 $\pm$ 1°C.

Testing of Blend Mixes and Vulcanizate

The rheometric characteristics, M_L, M_H, t_{c90}, t_{s2}, and CRI using a Monsanto oscillating disc rheometer 100 were determined according to ASTM.

Method of Grafting

The appropriate amount of PAM and distilled water was placed in a round-bottomed flask, and the mixture was refluxed for 48 h to dissolve the PAM. Potassium persulfate of 0.05 mol/L as the initiator and a suitable amount of AN or AA were added to the polymer solution. The solution was placed in a water thermostat at 40°C, with occasional stirring for about 24 h. When the grafting time was over, the grafted PAM solution was precipitated in methanol to get rid of the ungrafted PAM and PAA homopolymer formed and in DMF to be purified from any PAN homopolymer present. Then, the precipitate was filtered and dried in an oven at 50°C for 10 h and kept in a vacuum desiccator for use.

The percent grafting was calculated as follows:

$$\%Gr = \frac{W - W_0}{W_0} \times 100$$

where W_0 and W are the weights of the initial and grafted samples, respectively. The percent grafting was 350% for PAM-g-AN and 360% for PAM-g-AA.

The physicomechanical properties were measured at room temperature on a tensile testing machine[8] (Zwick 1101). Swelling[9] was carried out in toluene at room temperature (25°C) for 24 h, and the percentage soluble fraction[10] was determined.

The permittivity ε' and dielectric loss ε'' in the frequency range 100 Hz to 50 kHz were measured using an LCR meter type AG-4311B Ando electric LTD. The capacitance C and the loss tangent tan δ were obtained directly from the bridge from which ε' and ε'' were calculated. The cell was calibrated using standard materials with known permittivity according to the method discussed before.[11]

The resistance R was measured using the same bridge used for ε' and ε''. The dipole moment μ was measured using a dipolemeter type DMO1 from Wiss. Tech. Werkstatten GMBH (WTW), Germany, with a sample holding cell type DFL1. Scanning electron microscopy was done using a Nanolape 7 Semco with an applied voltage 15 kV and a magnification of 1000.

RESULTS AND DISCUSSION

PAM–Rubber Blends

In this study, two synthetic rubbers were chosen: the ethylene propylene diene monomer (EPDM)

Table I   Physicomechanical Properties of PAM–Rubber Blends

Ingredients	Sample No.							
	I_a	I_b	I_c	I_d	II_a	II_b	II_c	II_d
NBR	100	90	80	70	—	—	—	—
EPDM	—	—	—	—	100	90	80	70
PAM	—	10	20	30	—	10	20	30
Perkodex	4	4	4	4	4	4	4	44
Rheometric characteristics at $172 \pm 1°C$								
M_L (dN m)	5.00	3.00	3.00	2.50	11.75	6.50	6.50	7.50
M_H (dN m)	48.00	48.00	44.50	44.50	61.00	59.50	60.00	56.00
t_{s2} (min)	1.50	1.75	1.75	1.75	1.37	1.75	1.50	1.50
t_{c90} (min)	11.00	10.50	9.50	10.00	13.50	11.50	10.00	9.00
CRI (min^{-1})	10.52	11.42	12.90	12.12	8.24	10.25	11.76	13.33
Mechanical properties								
M-100 (MPa)	0.95	0.60	—	—	0.47	0.85	0.64	0.63
Tensile strength (MPa)	1.50	0.85	0.73	0.76	1.15	1.10	1.02	0.81
Elongation (%)	175.00	125.00	83.00	55.00	263.00	190.00	163.00	120.00
Equilibrium swelling (%)	170.00	168.00	150.00	131.00	182.00	173.00	159.00	146.00

as a nonpolar type and nitrile rubber (NBR) as a polar one to be blended with (10–30 phr) polyacrylamide (PAM). The rheometric characteristics were determined at $172 \pm 1°C$ and the obtained mixes were vulcanized at their optimum cure time. The physicomechanical properties were determined and the obtained data were calculated and are reported in Table I. From the obtained data, it is clear that the addition of PAM to NBR (group I) decreases both the maximum and minimum torque. This could be attributed to the thermoplastic properties of PAM which increase the plasticity of rubber at high temperature. However, the addition of PAM to NBR slightly decreases the optimum cure time and increases the cure rate index. On the other hand, the tensile strength and the elongation at break are decreased with increase of the PAM content. The high reduction in elongation and tensile strength could be due to the uncompatibility of these polymer blend systems.

The equilibrium swelling of both groups was determined and is listed in Table I. It is clear that the increase of PAM content decreases both the swelling in toluene due to the addition of a polar compound.

Scanning electron microscopy offers the simplest procedure,[12] since it reveals surface features. The internal structure of the blends was investigated by viewing the fracture surface created at ambient temperatures. Figure 1(a) shows the morphology of the NBR/PAM (90/10) blend. No significant etching is apparent for this sample, as the micrograph shows dark and bright regions (holes). The holes on the surface correspond to the PAM phase, which exists as domains in the continuous NBR matrix. On the other hand, for the

Figure 1   Scanning electron micrograph with magnification 1000 of (a) NBR/PAM blend (90/10), (b) NBR/PAM blend (90/10) containing 10% PVC, (c) NBR/PAM blend (90/10) grafted with AN, and (d) NBR/PAM blend (90/10) grafted with AA.

Figure 2 Scanning electron micrograph with magnification 1000 of (a) EPDM/PAM blend (90/10), (b) EPDM/PAM blend (90/10) containing 10% PVC, (c) EPDM/PAM blend (90/10) grafted with AN, and (d) EPDM/PAM blend (90/10) grafted with AA.

EPDM/PAM (90/10) blend, scanning electron microscopy shows that it consists of separated short fibrils, as is clear from Figure 2(a).

It may be concluded that the decrease in tensile strength and elongation of these blends upon adding a second phase can be attributed to the dispersed polymer which does not adhere to the surrounding matrix. During the deformation of the blends, holes are formed that contain the loosely dispersed polymer particles. Accordingly, the stress-bearing cross section of the tensile bar is dimensioned by the presence of the dispersed polymer and, also, the presence of the second phase (polymer or holes) gives rise to stress concentrations around the inclusions.[13]

The values of the permittivity ε' and dielectric loss ε'' obtained for the EPDM–PAM and NBR–PAM blends with three different PAM ratios (10, 20, and 30 phr) are illustrated graphically in Figure 3 versus the log of the applied frequency. The whole measurements were carried out at room temperature (25°C) in the frequency range from 100 Hz to 50 kHz. From this figure, it is clear that the values of ε' decrease by increasing the applied frequency and show anomalous dispersion. From this figure, it is also clear that the ε' for the blends lies between those of rubber and PAM for both investigated types of blends.

To study the compatibility between both types of rubber and PAM through the three investigated concentrations, the permittivity ε' is plotted graphically versus the content of PAM in the blend at two different frequencies (1 and 10 kHz)

Figure 3 Permittivity ε' and dielectric loss ε''. (A) EPDM/PAM blends: (○) 100/0; (X) 90/10; (□) 80/20; (●) 70/30; (△) 0/100. (B) NBR/PAM blends: same notations as (A).

as shown in Figure 4. From this figure, it is interesting to find that NBR is nearly compatible with PAM through the three investigated concentrations as ε' coincides with the line connecting NBR and PAM with fluctuations not exceeding

Figure 4 Relation between the permittivity ε' and rubber content in the blend: (A) EPDM; (B) NBR.

Table II   Physicomechanical Properties of Grafted PAM–Rubber Blends

Ingredients	Sample No.							
	I_b	I_1	I_2	I_3	II_b	II_1	II_2	II_3
NBR	90	90	90	90	—	—	—	—
EPDM	—	—	—	—	90	90	90	90
PAM	10	—	—	10	10	—	—	10
PAM/AN	—	10	—	—	—	10	—	—
PAM/AA	—	—	10	—	—	—	10	—
PVC	—	—	—	10	—	—	—	10
Perkodex	4	4	4	4	4	4	4	4
Rheometric characteristics at 172 ± 1°C								
M_L (dN m)	3.00	3.75	4.00	5.00	6.50	8.00	8.50	7.00
M_H (dN m)	48.00	48.00	44.00	51.00	59.50	57.50	57.00	57.00
t_{s2} (min)	1.750	1.75	2.00	2.00	1.75	1.25	1.25	1.13
t_{c90} (min)	10.50	9.50	10.50	11.50	11.50	11.00	11.00	15.00
CRI (min^{-1})	11.42	12.90	11.75	10.52	10.25	10.25	10.25	7.20
Mechanical properties								
M-100 (MPa)	0.60	0.29	0.53	0.88	0.85	0.57	0.52	1.05
Tensile strength (MPa)	0.85	0.69	0.76	1.41	1.10	1.11	1.31	2.20
Elongation (%)	125.00	215.00	127.00	125.00	190.00	175.00	229.00	195.00
Equilibrium swelling (%)	168.00	235.00	149.00	143.00	173.00	176.00	182.00	159.00

2.5%. On the other hand, no compatibility is expected for the EPDM–PAM blend as the permittivity values for the investigated blends are somewhat far from the line connecting EPDM and PAM as shown in Figure 4.

The absorption curves given in Figure 3 relating the dielectric loss ε'' and the log of the applied frequency are found to be flatter than the Debye curve, indicating that more than one relaxation mechanism is present. These expected mechanisms ascribe the orientation of the main chain and its related motions. From this figure, it is also noticed that the values of ε'' in the whole range of frequency increase by the addition of PAM to EPDM while they decrease by adding PAM to NBR. This is an expected result as the value of ε'' of PAM is much higher than that of EPDM while it is lower than that of the polar one of NBR.

For both blends and through the three investigated concentrations, it is interesting to find that the values of the dielectric loss at frequencies to 10^4 Hz are lower when compared with those at the higher-frequency range. This could give a good expectation that the blends under investigation are characterized by promising insulating properties at that range of frequency.

Grafted PAM–Rubber Blends

To overcome the problem of phase separation between the rubber and PAM, trials were made to improve the compatibility of PAM with both types of rubber under investigation. For this purpose, PAM was grafted by two different monomers, namely, AN and AA, before mixing with the rubber. Also, PVC was used as a compatablizing agent in a ratio of 10 parts per 100 parts of the polymer rubber/PAM blend. The formulations of the prepared samples and the rheometric characteristics at 172 ± 1°C as well as their mechanical properties are given in Table II. From the obtained data, it is clear that grafting with AA has no remarkable effect on both the rheometric characteristics and the mechanical properties of NBR, while grafting with AN slightly increases the rate of curing of the vulcanizate as deduced from the decrease in the optimum cure time and the increase of the cure rate index. PAM grafted with AN decreases both the modulus and tensile strength and also increases both the elongation at break and the equilibrium swelling in toluene. On the other hand, the addition of PVC slightly decreases the rate of curing but highly improves the mechanical properties.

In the case of EPDM, the grafted PAM has no remarkable effect on the rheometric characteristics while slightly enhancing the mechanical properties. Also, it is noticed that the addition of PVC decreases the cure rate but enhances the mechanical properties as shown from the high increase in tensile strength and modulus—100%.

The morphology using scanning electron microscopy of EPDM/PAM (90 : 10) after the addition of 10 phr PVC loosened the fibrils as noticed from Figure 2(b), while the addition of PVC to the NBR/PAM (90 : 10) blends leads to the reduction of the particle size of the dispersed phase (holes) [Fig. 1(b)]. After grafting PAM with AN, the micrographs showed that there was some degree of surface homogeneity distribution when it was blended with NBR [Fig. 2(c)], while when PAM was grafted with AN and added to EPDM, some degree of surface homogeneity distribution or dispersion of the particles encased within the blending matrix was observed. Actually, of course, the particles have regular shapes as is clear from Figure 1(c). Figure 1(d) represents the morphology of NBR/AA-grafted PAM (90 : 10). The micrograph shows the phase boundary of the dispersed PAM particles and the formation of holes from which the particles are pulled out and coverd with small globules. The total volume of these irregularities agrees well with the type of graft copolymer.[13] On the other hand, in the case of EPDM/AA-grafted PAM, the particles have regular shapes and sharp fine grains which are distributed homogeneously [Fig. 2(d)].

The permittivity ε' and dielectric loss ε'' for the two types of rubber blended with 10 parts of grafted PAM with both AN and AA were measured at the same range of frequency used in the previous investigatin and also at the same temperature (25°C). The data obtained are illustrated graphically in Figure 5. It is noticed that the presence of grafted PAM in the blend increases the values of ε' at the whole range of investigated frequency.

This increase is found to be higher in the case of AN, which may be due to its higher polarity in comparason with AA. To confirm this assumption, the dipole moment μ was measured using the equation of Guggenheim[14] for both AN and AA in dilute solutions of carbon tetrachloride at 20°C and the obtained values were found to be 3.43 and 1.24 respectively.

In the case of the dielectric loss measurements ε'', the data indicate that ε'' increases by the same trend as ε' in the case of the EPDM blend, while in the case of the NBR blend, it was found that it

Figure 5 Permittivity ε' and dielectric loss ε''. (A) EPDM/PAM blends: (○) 100/0; (X) 90/10; (▲) 90/10 grafted with AN; (●) 90/10 grafted with AA; (△) 0/100. (B) NBR/PAM blends: same notations as (A).

behaves with the same trend only up to about 5 kHz, while an opposite trend is noticed at higher frequencies. On the other hand, it is clear from Figure 5 that after the addition of the grafted polymer with either AN or AA an absorption region in the lower-frequency range was pronouncedly detected at about 400 Hz in addition to the expected regions in the available range of investigated frequencies. This region is considered to be due to the Maxwell Wagner effect, the origin of which is an ac current which is in-phase with the applied potential. This current results from the difference in permittivity and resistivity of the grafted polymer and rubber in the blend. To confirm this, the permittivity ε' and the resistivity ρ were measured for the two grafted polymers and the data obtained show that the permittivity of PAM when grafted with either AN or AA were 60.1 and 21.4 at $f = 100$ Hz, which are higher than those of the two types of rubber ($\varepsilon' = 2.8$ and 12.7) for EPDM and NBR, respectively. On the other hand, the resistivities ρ of PAM grafted with AN and AA are found to be 0.2 $\times 10^{-8}$ and 3.8×10^{-8} ohm cm, respectively, which are found to be lower than those for the two types of rubber ($\rho > 10^{-10}$ ohm cm).

Figure 4 represents the variation of ε' of the two investigated types of rubber and PAM after the addition of PVC to both of them. It is clear that the value of ε' of the blend containing PVC lies on the straight line connecting the two individuals for the two types of rubber. This means that the addition of PVC as a compatibilizer improves the compatibility to some extent, especially for the incompatible EPDM–PAM blend.

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