Dielectric Properties of Isotactic Polypropylene/Nitrile Rubber Blends: Effects of Blend Ratio, Filler Addition, and Dynamic Vulcanization

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ABSTRACT: The dielectric properties of isotactic polypropylene/acrylonitrile-butadiene rubber blends have been investigated as a function of frequency with special reference to the effect of blend ratio. The dielectric properties measured were volume resistivity, dielectric constant (ϵ'), dissipation factor (tan δ), and loss factor (ϵ''). At high frequencies, a transition in relaxation behavior was observed whereby the dielectric constant of the blends decreased with frequency, whereas the loss tangent and loss factor increased on reaching a maximum. The variation of the dielectric properties with blend composition was correlated with blend morphology, and relationships were established with reference to blend composition. Experimental ϵ' values were compared with theoretical predictions. The effect of the addition of fillers on the dielectric properties was also investigated for different fillers and filler loadings. It was found that silica filler increases the dissipation factor, whereas carbon black and cork gave a reverse trend. The variation in dielectric properties upon dynamic vulcanization of the rubber phase using different vulcanizing agents (such as sulfur, peroxide, and mixed systems) was also investigated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 255–270, 1999

Key words: polypropylene; nitrile rubber; blends; dielectric properties

INTRODUCTION

During the last few decades, thermoplastic elastomers (TPEs) replace usual thermoset rubbers in many areas like the automotive and electrical sector. This replacement is due to the fact that TPEs possess the excellent processing characteristics of thermoplastics with the properties of vulcanized rubbers and that the products from TPEs can be prepared at a lesser cost than that required for vulcanized rubbers.^{1–3}

Many of the TPEs are used in various electrical applications (e.g., wire and cable), and as insula-

tion and jacketing materials due to their unique combination of properties (such as low temperature flexibility, excellent insulating characteristics, and resistance to moisture absorption).⁴ By blending suitably selected plastics with elastomers, materials with desirable final properties can be prepared. Electrical properties of various polymer blends have been investigated by different researchers.^{5–11} In their publications, it has been shown that the dielectric properties of polymers and blends in general depend on structure, crystallinity, morphology, and the presence of fillers or other additives. The dielectric constant of the blends is found to increase with an increase in the effective dipole moment. In styrene-butadiene rubber/acrylonitrile-butadiene rubber (NBR) blends, the permittivity ϵ' was found to

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Ingredients	Sulfur System (PS)	DCP System (PC)	Mixed System (PM)
PP	70.0	70.0	70.0
NBR	30.0	30.0	30.0
ZnO	5.0	_	5.0
Stearic acid	2.0	_	2.0
CBS	2.0	_	2.0
TMTD	2.5	_	2.5
S	0.2	_	0.1
DCP	_	2.0	1.0

 Table I
 Formulation of Dynamic-Vulcanized PP/NBR Blends

ZnO-Zinc oxide; CBS, N-cyclohexyl benzothiazyl sulfenamide; TMTD, tetramethyl thiuram disulfide; S, sulfur.

increase with an increase in concentration of C=N dipoles.¹¹ The incorporation of polar components into polyethylene increased the dielectric constant and dielectric loss of the blends.¹² The measurement of dielectric properties as a function of temperature was used as a way to study the miscibility of different polymer blend systems.⁵ Dielectric monitoring of thermosets and their blends have been used for the monitoring of curing.⁷ In heterogeneous polymer blends, the dielectric constants of the polymers are influenced by interfacial effects (i.e., due to the polarization arising from difference in conductivities of the two phases).¹² The volume resistivity of various polymer blends on incorporation of filler was also studied.^{13–17} The addition of conductive black into different polymer blends to make conducting polymers was reported.

Polypropylene (PP) has excellent electrical properties like low dielectric constant, low loss factor, high volume resistivity, and high surface resistivity, and is used as high-frequency insulator.^{18,19} NBRs have moderate insulating properties and good oil resistance. Therefore, by blending PP with NBR material with easy processability, good flexibility and excellent oil resistance can be achieved. Earlier, we investigated the mechanical, dynamic mechanical, and rheological properties of these blends.²⁰⁻²² In the present article, we report on the effect of blend ratio and dynamic vulcanization on dielectric constant, dissipation factor, loss factor, and volume resistivity of PP/NBR blends. The effect of different fillers on the dielectric properties is also investigated.

EXPERIMENTAL

Isotactic PP having a melt flow index (MFI) of 3 g/10 min was supplied by IPCL Baroda. Acryloni-

trile-co-butadiene rubber, having an acrylonitrile content of 34%, was obtained from Synthetics and Chemicals (Bareli, UP). The fillers used were high abrasion furnace black (HAF) (N 330), silane, treated silica, and cork powder. The silica was prepared by the treatment of silica (100 g) with a Union Carbide A174 silane coupling agent (5 g).

Blends of isotactic PP/NBR was prepared in different blend ratios by melt mixing PP and NBR in a Brabender plasticorder PLE-330 at a temperature of 180°C. The rotor speed was 60 rpm, and time of mixing was 6 min. The dynamically vulcanized blends were prepared by using the formulation given in Table I. The binary blends were denoted P₁₀₀, P₇₀, P₅₀, P₃₀, and P₀, where the subscripts indicate the weight percentage of PP in the blend. In the case of filled blends, the filler loading was varied from 10 to 30 phr and is designated as $P_x Tsi_v$, $P_x K_v$, and $P_x C_v$, respectively, for silane-treated silica, cork, and carbon black loading, where x denotes the weight percentage of PP in the blends and y denotes the weight percentage of filler with respect to the rubber phase in the blends.

The samples for electrical property measurements were prepared by compression molding the samples into 2-mm-thick sheets in a hydraulic press at a temperature of 200°C. Samples for volume resistivity measurements were prepared by compression molding the samples into 0.3-mmthick films.

The volume resistance of the samples were measured with a Twenty Million Megohmmeter model 29A at room temperature. The volume resistivity (ρ_v) was calculated using

$$\rho_v = R \cdot A/t \ \Omega \ \mathrm{cm} \tag{1}$$

where R is the volume resistance, A is the area, and t is the thickness of the sample.

The capacitance and tan δ of the blends were measured at frequencies ranging from 31.6 Hz–10 MHz at room temperature using a 4192 Impedance Analyzer of Hewlett–Packard. The dielectric constant was obtained from the capacitance using

$$\epsilon' = C \cdot t/\epsilon_0 \cdot A \tag{2}$$

where *C* is capacitance, *t* is thickness, *A* is area, and ϵ_0 is 8.85 × 10⁻¹² F/m and

Loss factor:
$$\epsilon'' = \epsilon' \cdot \tan \delta$$
. (3)

The weight percentage crystallinity of PP was determined using differential scanning calorimetry from the ratio of the heat of fusion of the blend to that of the 100% crystalline PP ($\Delta H_{pp} = 138 \text{ J} \text{ g}^{-1}$).²³ Samples for scanning electron microscopic studies were prepared by cryogenically fracturing in liquid nitrogen. From the fractured samples, the NBR phase was preferentially extracted with chloroform. The morphology of PP/NBR blends was examined using a JEOL scanning electron microscope.

RESULTS AND DISCUSSION

Volume Resistivity

Resistivity studies are important for insulating materials, because the most desirable characteristic of an insulator is its ability to resist the leakage of electrical current. Figure 1 shows the variation of volume resistivity (ρ_n) of PP/NBR blends as a function of NBR concentration. PP is a good insulator, with a volume resistivity in the order $10^{16} \Omega$ cm, whereas the volume resistivity of nitrile rubber is in the order of $10^{10} \Omega$ cm. In the case of blends the ρ_v has intermediate values in between that of PP and NBR. As the concentration of NBR increases, the ρ_v values decrease. This decrease is due to the introduction of low resistivity NBR material. The curve shows a sharp change after 50 wt % NBR. This change can be correlated with the morphology of the blends. In $P_{\rm 70}$ and $P_{\rm 50}\,\rm NBR$ is dispersed as domains in the continuous PP matrix, whereas in P₃₀, NBR also forms a continuous phase resulting in a co-continuous morphology (Figure 2). The change of NBR from the dispersed phase to the continuous phase



Figure 1 Variation of volume resistivity of PP/NBR blends with NBR content.

should cause a sharp change in the electrical properties.

The effect of dynamic vulcanization on ρ_{v} values of PP/NBR blends is given in Table II. On dynamic vulcanization of the blends using sulfur, the resistivity of the blends decreases for different blend compositions. Among the various vulcanized systems, the dicumyl peroxide (DCP) system shows the highest resistivity value and sulfur the lowest. The mixed system shows an intermediate value. The difference in conductivity among the different vulcanizing systems may arise because of the difference in the type of crosslinks formed during vulcanization. In the sulfur-vulcanized system, S—S linkages are formed; whereas in the DCP crosslinked system, C-C linkages are formed (Figure 3). In a mixed vulcanized system, a combination of both C—C and S—S linkages are formed. Compared with C-C linkages, S-S linkages have ionic character, which may further increase the conductivity of the system. On vulcanization of blends, some ionic impurities are incorporated into the blend system as vulcanizing ingredients; thus, conductivity of the final system increases upon vulcanization. In the case of peroxide, vulcanization free radicals are present, which arise due the degradation of PP that may also increase the conductivity.

The effect of incorporation of fillers on the resistivity values is shown in Figure 4. It is seen that the incorporation of 10 wt % carbon black,



(a)

(b)



(c)

Figure 2 Scanning electron micrographs of the morphology of PP/NBR blends. (a) 70/30, (b) 50/50, and (c) 30/70 PP/NBR blends.

silane-treated silica, and cork into P_{50} blend decreases the resistivity values. In the case of carbon black and silica, a further increase in the loading decreases the resistivity; whereas, in the case of cork, as the loading increases, the resistivity rather increases. The decrease in resistivity for silica and carbon black may arise from the presence of ionic groups present in silica and carbon black, which facilitates the conducting process. The nonconducting nature of the cork filler

accounts for the increase in resistivity of the PP/ NBR blend at higher loadings of cork. By the incorporation of the conducting filler into polymers and blends, the resistivity generally decreases and there is a critical loading of filler (i.e., percolation threshold at which the polymer composites change from insulating to conducting material). Hashem and colleagues¹⁵ have reported that, in semi-reinforcing furnace (SRF) blackloaded butyl rubber, the percolation threshold is

Sample	Volume Resistivity $ imes 10^{-13} \ \Omega \ { m cm}$
P ₇₀	24.00
PS70	3.52
PC70	8.65
PM70	5.82

Table IIVolume Resistivity Values ofUnvulcanized and Dynamic-Vulcanized P70Blends

at 30 wt % carbon black. In PP/NBR blends, the change in resistivity on increasing the loading up to 30 wt % is less, and no percolation threshold is observed up to this loading.

Dielectric Constant, Loss Factor, and Dissipation Factor

Effect of Blend Ratio

The dielectric constant and loss tangent are important parameters in the selection of an insulating material. The variation of dielectric constants of pure PP and the blends of PP/NBR as a function of frequency is shown in Figure 5. The dielectric constant values of pure PP, NBR, and their blends were decreased with increase in frequency. Generally the dielectric constant of a material arises due to polarization of molecules, and the dielectric constant increases with increase in polarizability. The different types of polarizations possible in a material are the polarizations arising from: (1) electronic polarization, (2) atomic polarization, and (3) orientation polarization due to the orientation of dipoles parallel to the applied field.²⁴ For heterogeneous materials, there is also the possibility for interfacial polarization that arises due to the differences in conductivities of the two phases.²⁵ The time required for each type of polarization to reach the equilibrium level varies with the nature of the polarization.

The orientation polarization requires much more time, compared with electronic and atomic polarization to reach static field value. Therefore, the orientation polarization decreases with increase in frequency, at a lower frequency region, compared with electronic and atomic polarizations. Interfacial polarization generally occurs at still lower frequencies. In the dielectric constant vs. frequency plot of PP/NBR blends, it is seen that the reduction in ϵ' occurs in three stages. In the first stage, the high values of dielectric constant can be attributed to the interfacial polarization effects. The high value of ϵ' for PP indicates the presence of impurities in the PP. It may also due to the fact that the impurities in such polymers may cause some oxidation at structural defects that lead to the formation of oxidized centers that then causes interfacial polarization.⁴

In the case of blends, due to the presence of two phases of NBR and PP with different conductivities, interfacial polarization occurs leading to an increase in dielectric constant. Because interfacial polarization decreases with an increase in frequency, as the frequency increases to 100 Hz,



Figure 3 Schematic representation of various crosslinks formed during vulcanization using: (a) sulfur, (b) peroxide, and (c) mixed system.



Figure 4 Variation of volume resistivity of 50/50 PP/ NBR blends with wt % of filler for different fillers. C-black, carbon black.

the dielectric constant decreases considerably. In the region $3.16 \times 10^2 - 10^5$ Hz frequency, the dielectric constant has contribution from orientation and atomic and electronic polarization. Here, the dispersion region spreads over a wide range of frequencies. Above 3.16×10^5 Hz frequency the ϵ' further reduces, which may be due to the drop in orientation polarization. At this frequency, the drop in ϵ' increases with the increase in the rubber content. It is due to the increase in dipoles in the materials at a high rubber concentration, which leads to a decrease in orientation polarization at a higher rate, compared with the blends with a lesser number of dipoles.

The variation of dielectric constant with weight percentage of NBR at three different frequencies is shown in Figure 6. PP shows the lowest ϵ' value, similar to a nonpolar material, and nitrile rubber shows the highest value. Generally, for a nonpolar material, the dielectric constant equals the square of refractive index (n^2) . The refractive index of PP is 1.47 and hence $\epsilon' = 2.16$. The experimental value is 2.805. The higher values may be due to the presence of interfacial polarization due to the presence of impurities. For polar materials, the ϵ' values are generally greater than n^2 and ϵ' increases with an increase in polarity. In the case of blends, the dielectric constant increases as the rubber content increases. This increase in ϵ' with the incorporation of rub-



Figure 5 Variation of dielectric constant of PP/NBR blends with frequency.

ber is due to an increase in C = N dipoles, which increase the orientation polarization and also due to the presence of interfacial polarization. Again, the orientation of dipoles depends on the crystallinity of the medium. Upon the introduction of rubber, the crystallinity of the system decreases (Table III). As the crystallinity decreases, the di-



Figure 6 Variation of dielectric constant of PP/NBR blends with NBR content.

Composition	Crystallinity (%) from DSC
P ₁₀₀	55.3
P_{70}^{100}	33.9
P_{50}	20.9
P ₃₀	13.7

Table III Crystallinity of PP/NBR Blends

DSC, differential scanning calorimetry.

poles can orient more easily. Such an increase in dielectric constant on incorporation of polar polymers was reported.¹² The dielectric constant depends on resistivity by the equation²⁶

$$\log R_{10}(298 \text{ K}) = 23 - 2 \cdot \epsilon' (298 \text{ K}) \qquad (4)$$

(i.e., the electrical resistance of polymers decreases exponentially with increasing dielectric constant). In PP/NBR blends, as the dielectric constant increases with an increase in rubber content, the volume resistivity decreases (Figure 1). The increase in ϵ' is more pronounced above 50 wt % NBR (Figure 6). This can be correlated with blend morphology. In PP/NBR blends at 30 and 50 wt % NBR, NBR forms the dispersed phase; while in blend with 70 wt % NBR, both NBR and PP forms continuous phases leading to a co-continuous morphology (Figure 2). The continuous nature of the NBR phase leads to a better orientation of dipoles and results in a high dielectric constant.

Experimental data can be compared with model calculations. The dielectric constant of a composite containing two components can be expressed in the general form:

$$\boldsymbol{\epsilon}_{c}^{\prime} = V_{1}\boldsymbol{\epsilon}_{1}^{\prime} + \boldsymbol{\epsilon}_{2}^{\prime}(1 - V_{1}), \text{ (Model I)} \tag{5}$$

where ϵ' and ϵ'_2 are dielectric constants of components 1 and 2, and V_1 and $V_2 = 1 - V_1$ are the volume fractions of components 1 and 2, respectively. The logarithmic variation of dielectric constant was also expressed by the equation:

$$\log \epsilon_c' = V_1 \log \epsilon_1' + (1 - V_1) \log \epsilon_2' \text{ (Model II)} \quad (6)$$

The dielectric constant of two phase mixtures based on spherical particle, which consider all the possible interaction, was also calculated for PP/ NBR in which NBR is dispersed as spherical domains in the continuous PP matrix using²⁷

$$\epsilon'_{c} = 1/4(H + (H^{2} + 8\epsilon'_{1}\epsilon'_{2})^{1/2}) \text{ (Model III)}$$
 (7)

where

$$H = (3V_1 - 1)\epsilon'_1 + (3V_2 - 1)\epsilon'_2.$$
(8)

The Maxwell–Wagner–Sillars equation was also used to predict the ϵ' values that are given as²⁸

$$\epsilon_{c}' = \epsilon_{2}' \frac{2\epsilon_{2}' + \epsilon_{1}' + 2V_{1}(\epsilon_{1}' - \epsilon_{2}')}{2\epsilon_{2}' + \epsilon_{1}' - V_{1}(\epsilon_{1}' - \epsilon_{2}')}$$
(Model IV) (9)

Figure 7 gives the experimental and the theoretical variations of dielectric constants with blend composition. The experimental values are lower than that of the parallel model and is close to logarithmic mixing rule. The Maxwell–Wagner–Sillars equation gives a better correlation of dielectric constants with experimental results.

The measurement of dissipation factor $(\tan \delta)$ and loss factor (ϵ'') of insulating material is important because the loss tangent is a measure of the alternating current electrical energy that is converted to heat. This heat raises the temperature and accelerates deterioration. The variation of dissipation factor and loss factor (ϵ'') with frequency of PP and PP/NBR blends is shown in Figure 8. Frequency increases the dissipation factor and increases the loss factor for pure PP and



Figure 7 Experimental (at 31.6 KHz) and theoretical variations of ϵ' values with wt % of NBR.



Figure 8 Variation of dissipation factor tan δ and loss factor ϵ'' of PP/NBR blends with frequency.

the blends. A relaxation region is observed in the frequency range of 3.16 \times 10⁵–3.16 \times 10⁶ Hz, which may be due to a lag in dipole orientation behind the alternating electric field. Also, it is seen from Figure 8 that the dissipation factor and magnitude of relaxation increase with an increase in rubber content. In the case of PP, which is nonpolar, relaxation is not due to dipole orientation. But, on the incorporation of nitrile rubber, dipoles are introduced into the system; this leads to a lag in orientation of dipoles on the application of the electric field. Hence, the dissipation factor increases with an increase in rubber content. Blends of NBR with PP show the presence of a relaxation peak maximum at a frequency 10^6 Hz. As the concentration of NBR increases, the relaxation peak maximum shifts to higher frequency (i.e., to 3.16 \times 10⁶ Hz). This suggests that the relaxation time decreases with increase in rubber content.

In polar polymer, it was reported that the increase in crystallinity reduces the tan δ values and also leads to an increase in relaxation time (i.e., their peaks corresponding to α and β relaxation process shifted to lower frequency), because the relaxation time τ is given by

$$\tau = 1/2 \pi f_m \tag{10}$$

where f_m is the frequency corresponding to the maximum in relaxation peak. In PP/NBR, as the

concentration of NBR increases, the crystallinity in PP/NBR blends decreases. Hence, the observed shift in relaxation frequency or reduction in relaxation time is due to the reduction in crystallinity. As the crystallinity of the system decreases, the rotatory motion of the dipoles becomes more easy, which leads to higher values of tan δ .

The sharp increase in tan δ beyond 50 wt % NBR is due to a change in morphology of the blend (i.e., the phase inversion of NBR from the dispersed to the continuous phase). It is seen that the incorporation of rubber into PP did not increase the value of tan δ by > 3%, which is frequently desired to avoid problems leading to failure of the insulator.

Effect of Fillers

Fillers are generally incorporated into TPEs to modify physical and electrical properties. The effect of the addition of carbon black on ϵ' values in 50/50 PP/NBR blend is shown in Figure 9. The incorporation of carbon black into the P₅₀ blend increases the dielectric constant. This increase is due to the conducting nature of the black that is associated with a conjugated bonding structure present in the crystalline regions and also due to the presence of polar groups in carbon black. It is again seen that, as the loading of carbon black increases, the dielectric constant increases, and



Figure 9 Variation of dielectric constant of carbon black-loaded P_{50} blends with frequency.



Figure 10 Variation of dielectric constant of 30 wt % carbon black-loaded PP/NBR blends with frequency.

this increase is more pronounced for 30% carbon black. Figure 10 depicts the variation of the dielectric constant of PP/NBR blends at 30 wt % loading of carbon black. Upon the incorporation of carbon black, the dielectric constants of all the blends are increased, and this increase becomes more pronounced with an increase in rubber content. It is seen from the figure that, at 70 wt % NBR, the dielectric constant shows a sharp increase in size, compared to P_{70} and P_{50} . This can be explained in terms of the morphology of the system. The morphology of filled blends can be schematically represented as shown in Figure 11. In P_{70} and P_{50} , NBR forms a dispersed phase in a continuous PP phase, whereas in P_{30} , NBR also forms a continuous phase resulting in a co-continuous morphology. Again, at this black concentration (30%), the carbon black forms a continuous network in the continuous nitrile rubber phase. This leads to an increase in conductivity of system and an increase in dielectric constant. Carbon black is predominantly dispersed in the NBR phase due to its high polarity. Generally, in thermoplastic elastomers, the fillers locate in the rubber phase.⁴

The variation of dielectric constant with the incorporation of silane-treated silica is shown in Figure 12. In these samples, also the ϵ' values decrease with frequency in three steps, due to the relaxation in interfacial and dipole polarizations.

It is seen from Figure 12 that, upon incorporation silica, the dielectric constant increases up to 20 wt % loading. However, at 30 wt % of loading, the ϵ' value decrease. The increase in ϵ' on the addition of silica may be due to the presence of polar groups present in the filler. As the filler loading increases, the density of the system is also increased and the extent of orientation of dipoles is retarded; thus the ϵ' shows a decrease at this concentration. Figure 13 shows the variation of ϵ' with frequency for the P_{70} , P_{50} , and P_{30} blends containing 30 wt % treated silica. As the concentration of rubber increases, the ϵ' increases and it is seen that the incorporation of silica increases the dielectric constant. The increase is more in the case of the P_{70} blend, whereas in P_{50} and P_{30} , the silica only slightly affects the ϵ' values.



70/30 PP/NBR BLEND: NBR DISPERSED IN CONTINUOUS PP PHASE CARBON BLACK DISPERSED IN NBR DOMAINS



50/50 PP/NBR BLEND: NBR DISPERSED IN CONTINUOUS PP PHASE CARBON BLACK DISPERSED IN NBR DOMAINS



CARBON BLACK DISPERSED IN CONTINUOUS NBR PHASE

Figure 11 Schematic representation of the morphology of carbon black-loaded PP/NBR blends.



Figure 12 Variation of dielectric constant of silanetreated, silica-loaded P_{50} blends with frequency.

Figure 14 depicts the variation of ϵ' with frequency for the P₅₀ blend containing a varying concentration of cork. Up to 10 wt % cork, the ϵ' increases while further loading decreases the ϵ' values. The increase in ϵ' on the addition of cork is due to interfacial polarization. The variation of



Figure 14 Variation of dielectric constant of corkloaded P_{50} blends with frequency.

dielectric constant with 30 wt % cork-loaded P_{70} , P_{50} , and P_{30} blends are shown in Figure 15. The nature of relaxation spectra is not affected by the presence of cork. Here, too, the dielectric constant increases with an increase in rubber content, but the difference is less than those with the other



Figure 13 Variation of dielectric constant of 30 wt % silane-treated, silica-loaded PP/NBR blends with frequency.



Figure 15 Variation of dielectric constant of 30 wt % cork-loaded PP/NBR blends with frequency.



Figure 16 Variation of loss factor of carbon blackloaded P_{50} blends with frequency.

two fillers, which may be due to the nonconducting character of cork.

The variation of loss factor with frequency for carbon black, cork, and silane-treated silica-filled 50/50 PP/NBR blends is shown in Figures 16–18, respectively, for different filler loadings. Figure 16 shows the variation of loss factor, ϵ'' , with



Figure 17 Variation of loss factor of cork-loaded P_{50} blends with frequency.



Figure 18 Variation of loss factor of silane-treated, silica-loaded P_{50} blends with frequency.

frequency for carbon black-loaded samples. The loss factor shows an increase with filler loading. The addition of carbon black did not alter the relaxation process; however, the peak height corresponding to the relaxation of C=N dipole increases. At 30 phr loading, the peak maximum shifts to a lower frequency of 10^6 Hz, compared with 3.16×10^6 Hz for the other loadings. The incorporation of filler into the blend system increases the dielectric loss, and this may be due to the presence of some oxidized groups in carbon black and also due to the increase in conductance loss. The shift in relaxation frequency to low values (i.e., reduced relaxation time) indicates that the resistance for relaxation of C=N dipoles increases at 30 phr loading. This indicates that the filler is mainly located in the rubber phase.

Figure 17 shows the change in loss factor with frequency for different loadings of cork filler in the P_{50} system. The incorporation of cork into the blend system slightly decreases the loss factor. As the loading of cork increases, the loss factor also decreases. The lowest value is obtained for the blend with 30 phr filler loading. The reduction in loss factor for the cork filler is due to the hindrance for the orientation of C=N dipoles in the presence of filler. As the loading of filler increases, the orientation of dipoles is retarded by the presence of the cork. The width of the relaxation peak also decreases with increase in filler loading.



Figure 19 Variation of loss factor of 30 wt % carbon black-loaded PP/NBR blends with frequency.

In the case of treated silica filler, the variation of loss factor with frequency is depicted in Figure 18. Here, the loss factor increases up to 20 phr loading for 30 phr loading of silica filler, the loss factor shows a decrease. The silica filler contains polar groups; this also contributes to the loss factor due to the increase in effective dipole moment. This, in fact, leads to an increase of ϵ'' values on incorporation of treated silica filler to the P₅₀ blend. However at 30 phr loading, although there is an increase in the effective dipole moment, the relaxation process is retarded due to an increase in viscosity. In effect, the loss factor shows a decrease at this loading.

The variations in loss factor with NBR content for different fillers are shown in Figures 19-21. As the rubber content in the blend increases, the loss factor (ϵ'') increases in all cases. The increase in loss factor (ϵ'') with rubber content is low up to 50 wt % and after that the loss factor (ϵ'') increases sharply. This sharp increase in ϵ'' above 50 wt % NBR is due to the change in morphology (i.e., phase inversion of NBR from the dispersed phase to the continuous phase > 50 wt % NBR leads to a better orientation of dipoles). Among the filled blends, in carbon black-loaded samples, the relaxation peak is observed at a frequency of 10^6 Hz in all composition, whereas in silanetreated silica-filled samples, the peak is observed at 3.16 \times 10⁶ Hz. In cork-loaded samples, the peak is at 10^6 Hz for 70/30 composition; and, at



Figure 20 Variation of loss factor of 30 wt % corkloaded PP/NBR blends with frequency.

higher NBR content, the peak is shifted to higher frequency.

Effect of Dynamic Vulcanization

Vulcanization of the rubber phase during mixing, known as dynamic vulcanization, is reported to be an efficient technology to improve the properties



Figure 21 Variation of loss factor of 30 wt % silanetreated, silica-loaded PP/NBR blends with frequency.



Figure 22 Schematic representation of the morphology of dynamic-vulcanized thermoplastic elastomers.

of thermoplastic elastomers.^{29,30} Dynamic vulcanization leads to a uniform distribution of rubber particles in the thermoplastic matrix. The morphology is also stabilized. This is schematically represented in Figure 22. Figure 23 depicts the variation of dielectric constant ϵ' with frequency for unvulcanized, sulfur, peroxide, and mixed-system vulcanized P_{70} blends. It is seen that vulcanization of the rubber phase leads to an increase in dielectric constant. The variation in ϵ' is marginal in the case of the sulfur crosslinked system, compared with the other systems. Among the different systems used, the peroxide system shows the highest ϵ' values, whereas the sulfur system shows the lowest value. The mixed (S + peroxide)system shows ϵ' values in between. The higher values of peroxide and mixed system may be due to the increased interfacial polarization, but also due to the degradation of the PP phase in the presence of DCP. The degradation of the PP phase may decrease the crystallinity, which leads to better dipole orientation. Because the rubber particles are finely dispersed upon dynamic vulcanization, the interfacial area increases and this leads to an increase in interfacial polarization. Therefore, the dielectric constant increases. The phase morphologies of the 70/30 blend vulcanized with sulfur, peroxide, and mixed system are shown in Figure 24. It is seen that, in the DCP vulcanized system, the rubber is more finely and uniformly distributed, compared with mixed and sulfur vulcanized systems. The size of NBR domains increase in the order sulfur > mixed > peroxide systems. Although the DCP-vulcanized system has the highest crosslink density, the effect is not observed in the properties due to the degradation of PP.

Figure 25 shows the variation of dielectric constant with frequency for P_{70} , P_{50} , and P_{30} blends vulcanized with sulfur. As the concentration of rubber increases, the dielectric constant of the crosslinked blends are found to be slightly higher than that of the uncrosslinked ones at low frequencies; whereas, at high frequencies, the trend is reversed. The increase in dielectric constant for vulcanized blends at low frequencies may be due to the increase in interfacial polarization, which reduces with an increase in frequency; at high frequencies, the effect from orientation polarization predominates. On vulcanization of the rubber phase, the relaxation of C=N dipoles is retarded due to the presence of crosslinks between the chains. This leads to a low value of dielectric constant that arises from orientation polarization.

The variations of dissipation factor $(\tan \delta)$ and loss factor with frequency are shown in Figures 26 and 27. It is seen that the dissipation factor is not affected much by vulcanization. But, at the high-frequency region of 10^7 Hz, the sulfur system shows the highest tan δ value, and the peroxide system showed the lowest. The mixed vulcanized system takes an intermediate position. On dynamic vulcanization, the magnitude of ϵ'' increases slightly. However, as the concentration of rubber increases to 50 and 70 wt % NBR, the relaxation peak frequency is shifted to a lower value (i.e., the relaxation time increases). The increase in relaxation time arises due to the in-



Figure 23 Variation of dielectric constant of unvulcanized and dynamic-vulcanized 70/30 PP/NBR blends with frequency.



(a)





(c)

Figure 24 Scanning electron micrographs of the morphology of dynamic-vulcanized 70/30 PP/NBR blends. (a) Sulfur, (b) peroxide, and (c) mixed system.

crease in viscosity that leads to more constraints to the relaxation of $C \equiv N$ dipoles. The relaxation spectra of 70/30 blends vulcanized with different vulcanizing systems are shown in Figure 27. The peroxide and mixed system vulcanized blends have higher peak heights, compared with unvulcanized and sulfur-vulcanized systems. In the presence of DCP, the PP phase is degraded, and this may lead to the presence of some oxidized centers. The dielectric constant is also affected by the decrease in crystallinity. This will increase the dielectric relaxation and hence the peroxide and mixed-vulcanized systems show higher values of ϵ'' . It is seen that the relaxation peak width increases upon dynamic vulcanization.

CONCLUSIONS

The dielectric properties (such as volume resistivity, dielectric constant and tan δ of PP/NBR



Figure 25 Variation of dielectric constant of dynamic-vulcanized PP/NBR blends with frequency.

blends) were investigated over a wide range of frequencies. The dielectric constant of the pure components and blends decreases with an increase in frequency. Variation in dielectric constant is in three stages due to the relaxation in interfacial and orientation polarization. Upon the increase of NBR content, the dielectric constant



Figure 26 Variation of dissipation factor and loss factor of unvulcanized and dynamic-vulcanized 70/30 PP/NBR blends with frequency.



Figure 27 Variation of dissipation factor and loss factor of dynamic-vulcanized PP/NBR blends with frequency.

increased and showed a sharp change after 50 wt % loading. This sharp change was correlated with the morphology of the blend. The experimental dielectric constant values were compared with theoretical models. It was found that experimental data fit well with data obtained from the Maxwell-Wagner-Sillars equation. The effects of various fillers (such as HAF black, silane-treated silica, and cork) on dielectric properties were also investigated. The fillers affect the dielectric properties. The dielectric constant increases on the addition of carbon black, and the increase is more pronounced in the P_{30} blend. The change is correlated with the formation of a network of carbon black particles in the continuous NBR phase at 70 wt % NBR. In silane-treated silica-filled blends, the dielectric constant increased up to 20 wt % loading, whereas at 30 wt % loading, the ϵ' value decreased; in cork-filled blends, the ϵ' value increased by the addition of 10 wt % cork, whereas further loading decreased the ϵ' values. The increase in ϵ' value upon the addition of fillers was correlated with the presence of polar groups in the filler and interfacial polarization. The loss factor increased upon the addition of carbon black and silica, whereas the addition of cork decreased the ϵ' values. Dynamic vulcanization leads to an increase in ϵ' values. Among the different vulcanizing systems used, the sulfur system showed the lowest value, and the DCP-vulcanized system

showed the highest ϵ' value. The mixed-vulcanized system showed an intermediate value. The dissipation factor and loss factor values also increased due to vulcanization.

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