

Electrical Properties of Nanostructured Interpenetrating Polymer Networks Based on Natural Rubber (NR)/Polystyrene (PS)

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ABSTRACT: The electrical properties of nanostructured sequential interpenetrating polymer networks from natural rubber (NR) and polystyrene (PS) have been studied in the frequency range of 10^2 – 10^7 Hz. The permittivity, volume resistivity, dielectric loss factor, and dissipation factor were analyzed as a function of frequency, blend composition, crosslinking level, and initiating system. It was found that the volume resistivity and dissipation factor first increase, reach a maximum around 10^3 – 10^5 Hz, and then decrease gradually with the increase of frequency. As the NR content is increased from 30 to 70%, the dissipation factor ($\tan \delta$) increases. On increasing the extent of the PS phase crosslink-

ing, the permittivity increases. However, at higher levels of PS crosslinking, the permittivity values decrease due to the agglomeration of PS phase arising from excessive crosslinking. The morphology studies using a scanning electron microscope confirmed the agglomeration of PS phase at high crosslinking level. The permittivity values are maximum at 4% of crosslinking content. The influence of initiating system on the dielectric properties was not very significant. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2017–2026, 2005

Key words: interpenetrating networks; dielectric properties; polystyrene; natural rubber; nanostructure

INTRODUCTION

Interpenetrating polymer networks are used as insulating and jacketing materials in electrical wire and cables. These systems usually have low temperature flexibility, good insulating characteristics, and moisture resistance. However, the final use of the systems depends on the nature of polymer used, the blend ratio, and the morphology of the system. The electrical properties of various blend systems were reported by different researchers.^{1,2} The available literature suggest that the dielectric properties of blend system in general depend on structure, crystallinity, morphology, and presence of filler or other additives.^{3–5} The measurement of dielectric properties as a function of temperature was used as a way of monitoring the miscibility of two phase polymeric systems.^{6,7} In heterogeneous polymer blends, the dielectric properties depend on interfacial polarization arising from the difference in conductivity of the two phases. The study of the dielectric properties is important as it provides a measure of the amorphous fraction of the material and is sensitive to orientation effects, mobility, and interaction between the participating dipoles.

The dielectric properties of nitrile rubber based blends were studied by George et al.⁸ Electrical properties of polyethylene based composites have been reported by Thomas and coworkers.^{9,10} IPN based on polybutadiene was developed by Kang and coworkers, and was used as an electrical insulator.¹¹ The electrical properties of only a few IPNs have been reported in the literature. In some recent studies, IPNs were made conductive by doping with a third minor component. Electrical conductivity of iodine doped pseudo-IPNs of polycarbonate-urethane and natural rubber (NR) was reported by Frisch et al.¹² In this case, the conductivity occurs through linear NR and was dependent on temperature, iodine molality, and weight fraction of NR. However, at high temperature the material became an insulator. Frisch and coworkers also reported conductivity studies of linear poly(carbonate) urethane and crosslinked polychloroprene doped with iodine.¹³ Yin et al. developed conducting IPN based on polyaniline and crosslinked cellulose.¹⁴ The conductivity of such systems depends strongly on the synthesis condition and concentration of doping material.

Careful scanning of the literature shows that only limited studies have been reported on the electrical properties of undoped IPNs. In this laboratory systematic investigations on the mechanical properties, morphology, viscoelastic behavior, thermal properties, and swelling behavior of NR/PS IPNs have been

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TABLE I
Nomenclature of IPNs

Sample code	Initiator	NR/PS ratio	DVB content
A ₀ N ₃₀ , A ₀ N ₅₀ , A ₀ N ₇₀	0.5% (AIBN)	30/70, 50/50, 70/30	0%
A ₁ N ₃₀ , A ₁ N ₅₀ , A ₁ N ₇₀	0.5% (AIBN)	30/70, 50/50, 70/30	2%
A ₂ N ₃₀ , A ₂ N ₅₀ , A ₂ N ₇₀	0.5% (AIBN)	30/70, 50/50, 70/30	4%
A ₃ N ₃₀ , A ₃ N ₅₀ , A ₃ N ₇₀	0.5% (AIBN)	30/70, 50/50, 70/30	6%
B ₀ N ₃₀ , B ₀ N ₅₀ , B ₀ N ₇₀	1% (BPO)	30/70, 50/50, 70/30	0%
B ₁ N ₃₀ , B ₁ N ₅₀ , B ₁ N ₇₀	1% (BPO)	30/70, 50/50, 70/30	2%
B ₂ N ₃₀ , B ₂ N ₅₀ , B ₂ N ₇₀	1% (BPO)	30/70, 50/50, 70/30	4%
B ₃ N ₃₀ , B ₃ N ₅₀ , B ₃ N ₇₀	1% (BPO)	30/70, 50/50, 70/30	6%
D ₀ N ₃₀ , D ₀ N ₅₀ , D ₀ N ₇₀	1% (DCP)	30/70, 50/50, 70/30	0%
D ₁ N ₃₀ , D ₁ N ₅₀ , D ₁ N ₇₀	1% (DCP)	30/70, 50/50, 70/30	2%
D ₂ N ₃₀ , D ₂ N ₅₀ , D ₂ N ₇₀	1% (DCP)	30/70, 50/50, 70/30	4%
D ₃ N ₃₀ , D ₃ N ₅₀ , D ₃ N ₇₀	1% (DCP)	30/70, 50/50, 70/30	6%

conducted.^{15–18} In the present study, the dielectric properties of sequential IPNs from NR and PS were measured as a function of frequency, initiating system, blend ratio, and crosslinking density. More specifically the permittivity, dissipation factor, dielectric loss factor, volume resistivity, and conductivity of the IPNs were analyzed with special reference to blend ratio and crosslinking of the PS phase. Attempts have been made to correlate the dielectric properties with the morphology of the system. This study is aimed at evaluating the possibility of the use of NR/PS IPNs as insulating materials.

EXPERIMENTAL

Materials used

Natural rubber

The natural rubber used was of ISNR-5 grade. It was supplied by Rubber Research Institute of India (RRII), Kottayam, India. The physical characteristics of NR are given in Table I.

Styrene monomer

Styrene monomer for IPN synthesis was supplied by Merck, Mumbai, India. The monomer was made inhibitor free by washing it with 1% NaOH and was dried before use.

Dicumyl peroxide

Dicumyl peroxide (40% active) was used as the vulcanizing agent for rubber and as the initiator for the polymerization of styrene. It was supplied by Kishore Rubber Products Pvt. Ltd., Pune, India.

Benzoyl peroxide

Benzoyl peroxide was obtained from BDH, Mumbai, India, and was used as initiator for styrene.

Azobis-iso-butyro nitrile

It was obtained from Sigma, Mumbai, India, and was used as the initiator.

Divinyl benzene (DVB)

Divinyl benzene was used as crosslinking agent for styrene. It was supplied by E. Merck, Germany.

IPN preparation

The IPN was prepared by the sequential technique. The NR is crosslinked first using DCP followed by the polymerization and crosslinking of the PS phase.

Crosslinking of NR phase

NR was masticated in a two roll mixing mill at room temperature. Dicumyl peroxide (4 phr) was added and mixed well with the rubber. The rheograph of the mix was taken on a Monsanto Rheometer and the optimum cure time was determined. The mix was vulcanized at 160°C on a hydraulic press to get crosslinked NR sheet. The following different series of IPNs were prepared using different initiators.

Crosslinking of PS phase

Series b. The vulcanized NR sheets were weighed and kept immersed in inhibitor free styrene monomer containing 1% benzoyl peroxide as initiator and 0, 2, 4, and 6% of DVB, which acts as a crosslinker for the PS

phase. The NR sheets were swollen for different time intervals to obtain varying weight percentages of PS. The swollen samples were kept at 0°C for a few h to achieve equilibrium distribution of styrene monomer in the matrix. The swollen networks were heated at 80°C for 6 h and at 100°C for 2 h to complete the polymerization and crosslinking of the styrene monomer. The hardened sheets were then kept in a vacuum air oven to remove the unreacted styrene. The final weight of the IPN was taken and the composition of the sample was determined.

Series d. In this method, 1% DCP and 0, 2, 4, and 6% of DVB, which acts as crosslinker for the PS phase, was added to the monomer and the rubber samples were allowed to swell in it as mentioned earlier. The swollen sheets were heated at 80°C for 6 h and at 100°C for 2 h to complete the polymerization and crosslinking. *Series a.* In this method, 0.5% AIBN and 0, 2, 4, or 6% of DVB, which acts as crosslinker for PS phase, was added to the monomer and the rubber samples were swollen in it as mentioned earlier. The swollen sheets were polymerized and crosslinked at 80°C for 6 h and at 100°C for 2 h in styrene atmosphere.

The hardened sheets, in all cases, were then kept in a vacuum air oven to make it free of unreacted styrene. The final weight of the sample was taken and the composition of the sample was determined. In all the three series, NR/PS semi- and full-IPNs with PS content up to 70% were prepared.

The IPNs are coded based on composition, initiating system of PS, and crosslinker content. The BPO, DCP, and AIBN initiated system are denoted by B, D, and A series, respectively. The DVB content was varied in order to have varying level of crosslinking. The blend composition is denoted as N₃₀, N₅₀, and N₇₀, where the subscripts indicate the weight percentage of rubber. The codings are given in Table I. The schematic representation of the synthesis of semi- and full-IPNs is given in our earlier publications.^{17,18}

Transmission electron microscopy

The morphology of IPNs was studied using JOEL-JEM 2010 Model transmission electron microscope. The samples were microtomed and the NR phase was stained using OsO₄. This was viewed under the microscope.

Scanning electron microscopy

The phase morphology of cryogenically fractured IPN specimens was examined using a scanning electron microscope. The fractured specimen is coated with gold before examining under the microscope.

Dielectric property measurement

The capacitance, resistance, and dissipation factors of NR/PS interpenetrating polymer networks were mea-

sured directly using a 4192 LF. Impedance Analyser (Hewlett Packard Co., Palo Alto, CA, USA) in the frequency range of 10²–10⁷ Hz, at room temperature. The test samples used were of disc shape with 2 mm thickness and 10 mm diameter. The samples were coated with conductive silver paint on either side and copper wires were fixed on the samples as electrodes.

The volume resistivity (ρ) was calculated using equation

$$\rho = \frac{RA}{t} \quad (1)$$

where ρ is the volume resistivity; R , the resistance; A , the area of cross-section; and t , the thickness of the sample.

The electrical conductivity (σ) is calculated as follows.

$$\sigma = 1/\rho \quad (2)$$

The permittivity (dielectric constant) (ϵ') was calculated from capacitance using the equation

$$\epsilon' = Ct/\epsilon_0 A \quad (3)$$

where ϵ' is the permittivity of the matrices, ϵ_0 is the permittivity of air ($8.85 \times 10^{-12} \text{ Fm}^{-1}$), C is the capacitance, A is the area of cross-section, and t is the thickness of the sample.

The dielectric loss (ϵ''), permittivity (ϵ'), and dissipation factor are related by the equation

$$\tan \delta = \epsilon''/\epsilon' \quad (4)$$

The dielectric loss is calculated using the equation

$$\epsilon'' = \tan \delta \epsilon' \quad (5)$$

RESULTS AND DISCUSSION

Morphology of IPNs

The morphology was studied using transmission electron microscopy (TEM). The TEM of D0N30, D1N30, and D2N50 samples are given in Figure 1. From the TEM it was observed that the phase domains of IPN system were nanostructured. In D0N30, the average dimension of the phase is 45 nm. In the D1N30 sample, the phase size is 22 nm; and in the D2N50 sample, the size is 12 nm. This leads to the conclusion that the morphology is dependent upon blend ratio and crosslinker level. Also, it was clearly noted that the systems are nano-structured where the two phases are intimately mixed. We have also examined the morphology of other initiating systems. In all three cases, the phase dimensions were nano-structured.

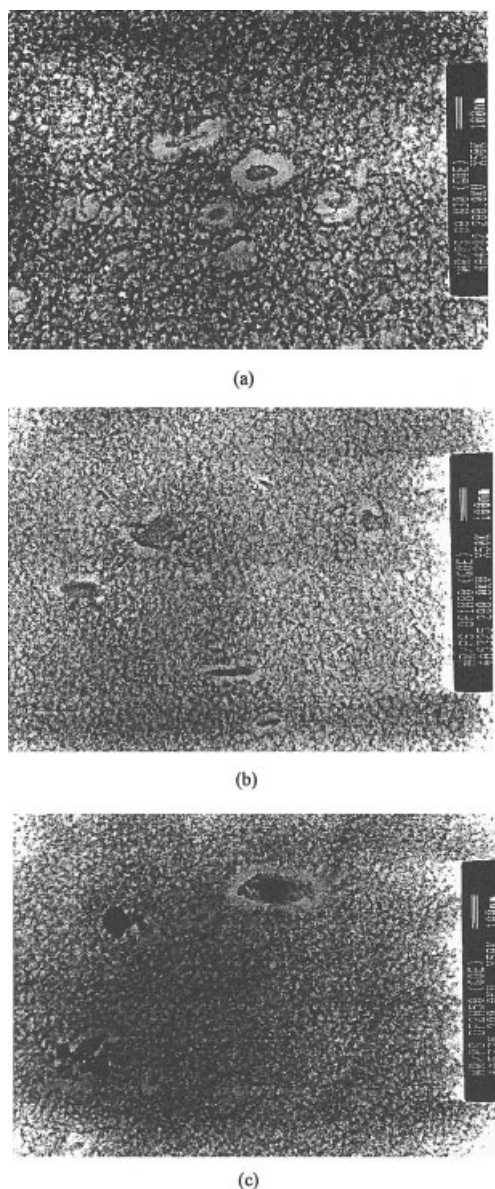


Figure 1 Transmission electron micrographs of (a) D0N30, (b) D1N30, and (c) D2N50 samples showing the nanostructured morphology.

Volume resistivity and conductivity

Resistivity study is important for insulating materials, since the ability to resist the leakage of electric current is essential in insulators. The effect of blend ratio on resistivity for the B₂ series is shown in Figure 2. The resistivity curves show three distinct regions as the frequency changes from 10²–10⁸ Hz. In the initial portion (up to 10³ Hz), the resistivity gradually increases with frequency. In the region between 10³–10⁴ Hz, the resistivity reaches a maximum and after that the resistivity falls rapidly with frequency. The behavior at low frequency is dependent upon the interfacial polarization arising due to the heterogeneity of the system. Beyond 10⁵ Hz, the resistivity is very low and

remains unaffected by frequency and blend composition. The effect of blend ratio is most prominent in the frequency region of 10²–10⁴ Hz for all the IPNs considered. This indicates that the dielectric property of NR/PS IPN is due to interfacial polarization, arising from the conductivity differences between the phases. This is further supported by the fact that these systems show nanostructured morphology where the interfacial area is highly increased, favoring interfacial polarization. As the rubber content increases from 30–70%, the resistivity decreases at a given frequency. This is due to the introduction of low resistivity rubber phase. Variation of volume resistivity with crosslink level is given in Figure 3. Here also three distinct regions of variation of volume resistivity with frequency could be seen. The resistivity decreases slightly with increasing the crosslinker content to 4%. However, at 6% DVB, an increase in resistivity is observed. This can be explained based on the morphology of D₀N₃₀, D₁N₃₀, D₂N₃₀, and D₃N₃₀ samples shown in Figure 4. The semi-IPNs have the lowest number of crosslinks, and for the full-IPNs the number of crosslinks increases with crosslinker level. In Figure 4 the effect of crosslinking of PS phase on the morphology is given. In D₀N₃₀ (Fig. 4a), D₁N₃₀ (Fig. 4b), and D₂N₃₀ (Fig. 4c), the two phases are distributed evenly showing good phase mixing. However, in D₃N₃₀ (Fig. 4d), the PS phase shows some agglomeration due to excessive crosslinking. Due to agglomeration the co-continuity of the system is lost. This makes the system resistant to electric conductance and therefore the volume resistivity is high.

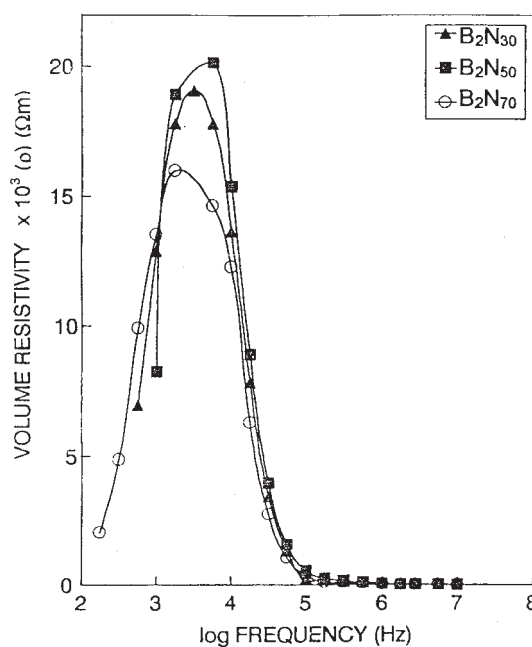


Figure 2 Effect of blend ratio on volume resistivity (B₂ series).

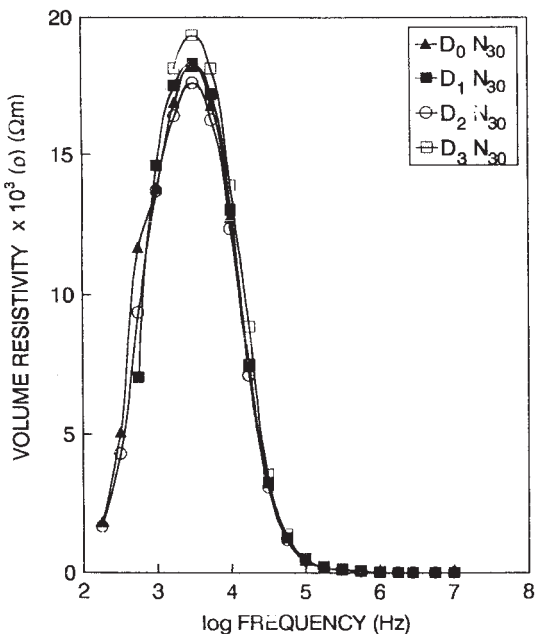


Figure 3 Effect of crosslinking level on volume resistivity (DCP series).

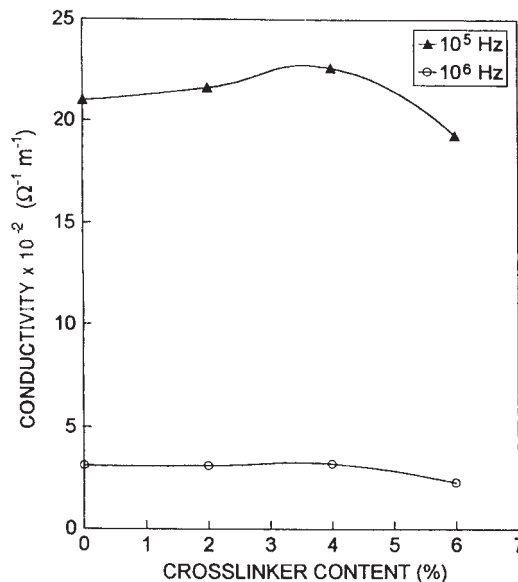


Figure 5 Effect of crosslinker content on conductivity (DCP series).

Figure 5 shows the effect of crosslinking level on conductivity (σ) at two different frequencies. The conductivity values increase up to 4% DVB and then decrease. In all cases the conductivity is lowest at 6% DVB content. It is important to notice that the magni-

tude of conductivity is very low at all frequencies. The low conductivity can be explained based on the chemical nature of the system. The NR and PS phases are both non-conducting due to the absence of any ionic particles. The impurities in small amounts and other ingredients added to the system during curing and

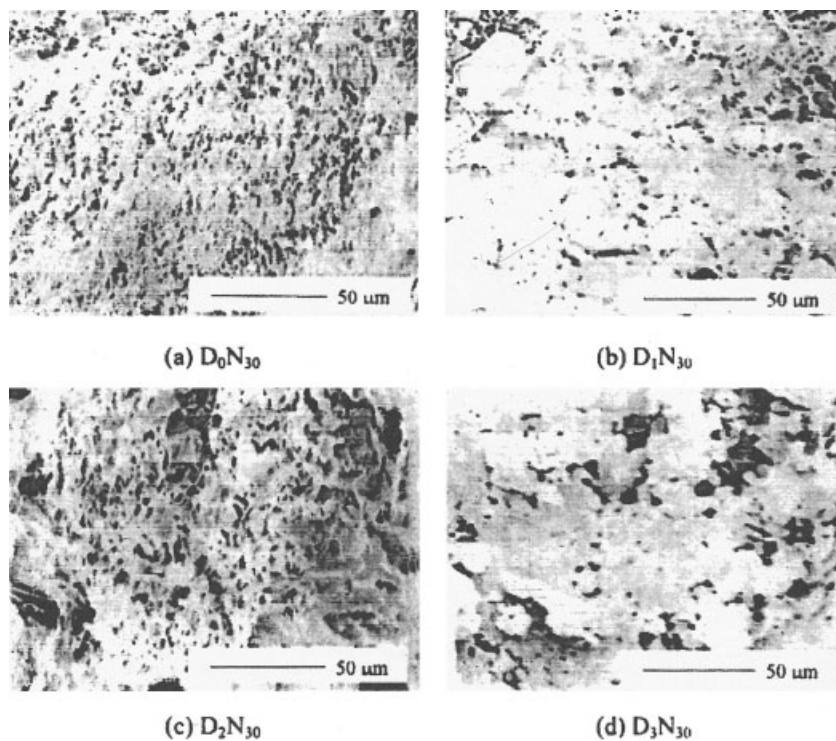


Figure 4 Scanning electron micrographs showing the effect of crosslinking level on morphology: (a) D_0N_{30} , (b) D_1N_{30} , (c) D_2N_{30} , and (d) D_3N_{30} .

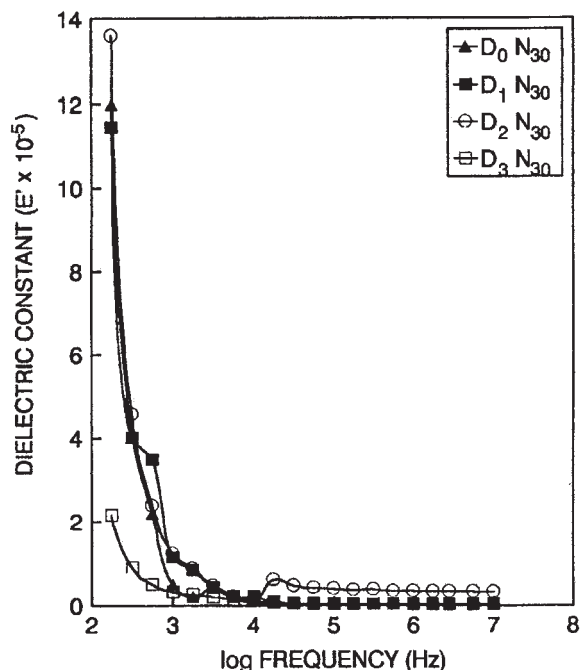


Figure 6 Effect of crosslinking level on permittivity (DCP series).

polymerization are the only factors that contribute to the conductivity. The crosslinker DVB also does not carry any charges. All the bonds in the systems are —C—C linkages, which are incapable of having any permanent charge separation. The initiators like the DCP, BPO, and AIBN used, may act as impurities and hence increase the conductivity of the system. This may give rise to the orientation of electronic or atomic polarization at medium and high frequencies.

Dielectric constant, loss factor, and dissipation factor

The variation of permittivity, loss factor, and loss tangent has been evaluated as a function of frequency. In Figure 6, the effect of frequency and crosslinking level on permittivity for the D₁ series is shown. The permittivity values decrease with increase in frequency at lower frequency ($<10^4$ Hz) followed by a leveling off at higher frequency ($>10^4$ Hz). Generally the permittivity of a material arises due to polarization of molecules and the permittivity increases with polarization. The different types of polarization possible in polymeric systems are electronic, atomic, dipole, and interfacial polarizations.^{19,20} In Figure 6, we can see that the permittivity values are higher at low frequency ($<10^4$ Hz) and are followed by a sharp decrease as the frequencies are increased. Generally, the behavior at low frequency can be explained by the interfacial polarization. The interfacial polarization decreases with increasing frequency. The interfacial polarization is due to differences in the conductivity of

the two phases. The orientation polarization requires more time compared to electronic and atomic polarization. The orientation polarization is prominent at low frequencies and decreases with increase in frequency. At high frequency the permittivity has contributions as from atomic and ionic polarizations. These contributions are small and so the permittivity value shows only a slight change with increase in frequency above 10^4 Hz.

The permittivity values increase when the crosslinker content increases from 0–4% and above that the permittivity value decreases. In D₀N₃₀, D₁N₃₀, and D₂N₃₀ samples, the increase in crosslinking of the PS phase increases the phase mixing of the system (Fig. 4). The enhanced phase mixing increases the possibility of interfacial polarization. So the permittivity values increase from D₀N₅₀ to D₂N₅₀ samples. As observed from the morphology studies at high crosslinking level (D₃N₃₀), the agglomeration of PS phase affects the phase distribution adversely. This reduces the interfacial polarization and hence the permittivity values are low.

Figure 7 shows the effect of frequency and crosslinker content of PS phase on the dissipation factor for the DCP series. There are two relaxation peaks observed between 10^3 – 10^4 Hz for D₀N₃₀, D₁N₃₀, D₂N₃₀, and D₃N₃₀ samples showing the presence of phase separation in the system. The smaller initial peak corresponds to PS transition and the second peak represents the NR transition. The numerical value of $\tan \delta$ is generally determined by both polarity and chain mobility. The polarity determines the nature of the relaxation and the relaxation time determines the numerical value of $\tan \delta$ at a specific frequency. At a

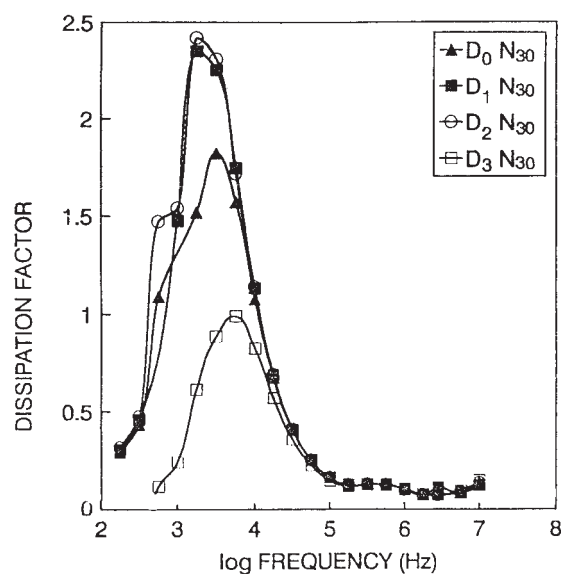


Figure 7 Effect of crosslinking level on dissipation factor (DCP series).

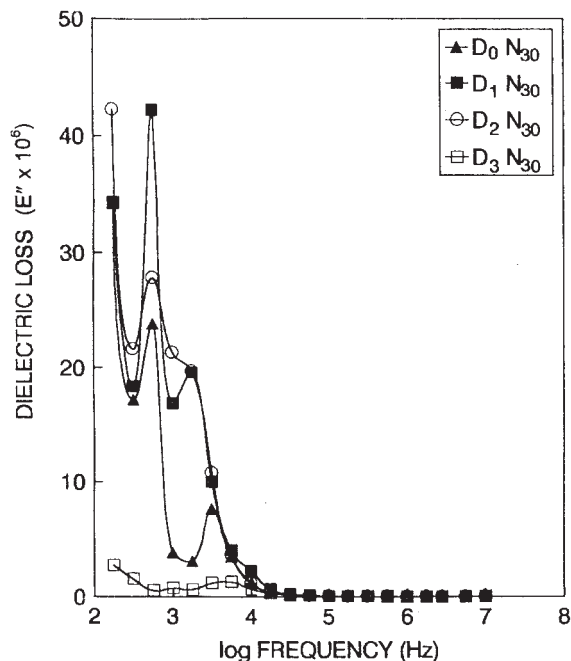


Figure 8 Effect of crosslinking level on dielectric loss factor (DCP series).

given frequency the magnitude of $\tan \delta$ increases with crosslinking level up to 4% DVB. But in D_3N_{30} sample (i.e., 6% DVB) the relaxation peak diminishes, though the relaxation mechanism is the same. Observation of the relaxation peak at low frequency indicates that the interfacial polarization is the major aspect governing the dielectric properties. The fall on relaxation magnitude in D_3N_{30} samples can be explained based on the morphology. The PS phase agglomeration adversely affects the phase mixing of the system and leads to the reduction in relaxation magnitude.

Figure 8 illustrates the variation of dielectric loss factor with a crosslinking level at different frequencies. Here also two peaks due to PS and NR transitions are observed in the low frequency region (i.e., around 10^3 – 10^4 Hz). The relaxation trend is similar to that of the $\tan \delta$ values.

In Figure 9, the change of permittivity with blend ratio is given for the B_2 series. The ϵ' value drops with increasing frequency, as seen earlier. The contribution due to orientation, atomic, and ionic polarizations are small. So the permittivity value shows only a slight change with increase in frequency above 10^4 Hz; the blend ratio does not show any effect on ϵ' values. This again shows that the dielectric properties are due to interfacial polarization, rather than to orientation, electronic, or atomic polarization. In the low frequency region the effect of composition is clear. The N_{50} samples have the highest ϵ' and N_{30} and N_{70} have almost the same value.

The measurement of dissipation factor ($\tan \delta$) and loss factor (ϵ'') is important for the development of

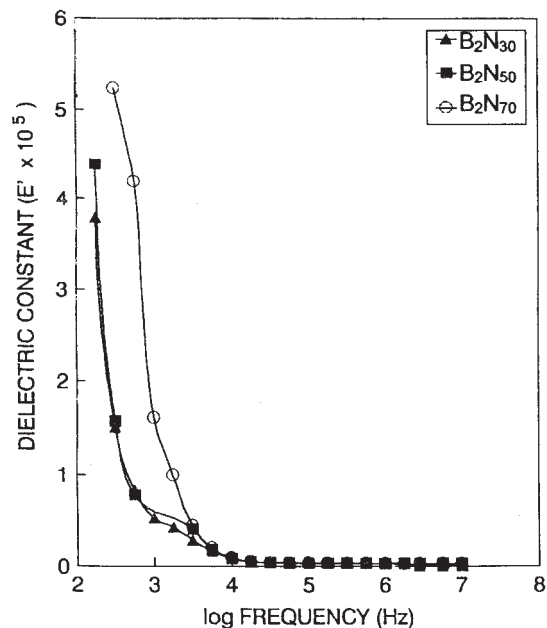


Figure 9 Effect of blend ratio on permittivity (B_2 series).

insulating materials. In Figure 10, the variation of dissipation factor with NR concentration is given for the B_2 series. In all these IPNs the relaxation region is observed in the frequency range of 5.62×10^2 – 10^4 Hz. Two peaks are observed in this frequency region corresponding to NR and PS transitions showing phase separation. The $\tan \delta$ values increase with NR content, that is, $B_2N_{30} < B_2N_{50} < B_2N_{70}$. In Figure 11 the change in dielectric loss factor with blend ratio is given. The variation of loss factor is prominent in the low frequency region, that is, in the frequency region

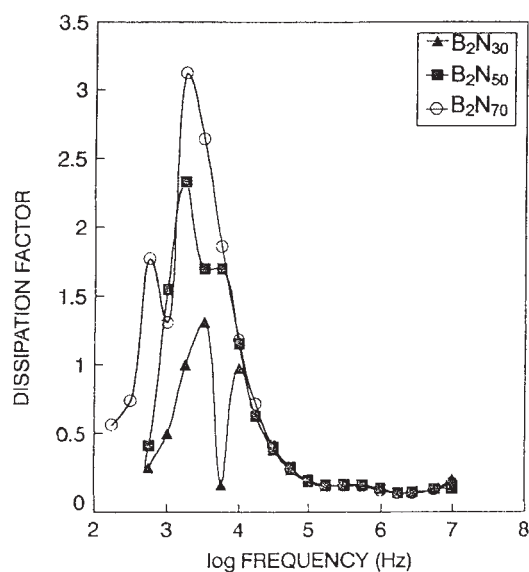


Figure 10 Effect of blend ratio on dissipation factor (B_2 series).

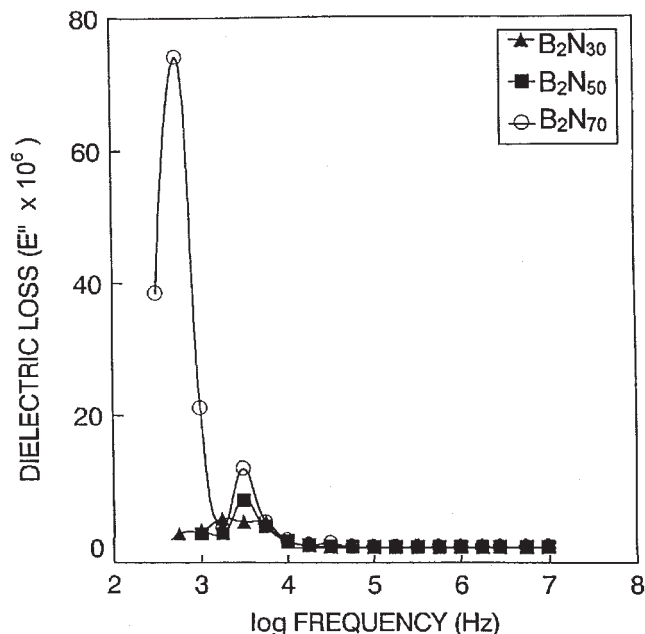


Figure 11 Effect of blend ratio on dielectric loss factor (B_2 series).

of 10^2 – 10^4 Hz. These loss peaks are attributed to the dielectric relaxation of NR and PS phases involving interfacial polarization. The relaxation peak is highest in the N_{70} samples and N_{30} and N_{50} samples have almost the same values. The addition of rubber does not affect the relaxation mechanism but enhances the relaxation magnitude.

In Figures 12 and 13, the loss factor (ϵ'') and dissipation factor ($\tan \delta$), respectively, are plotted as a function of initiating system at different frequencies.

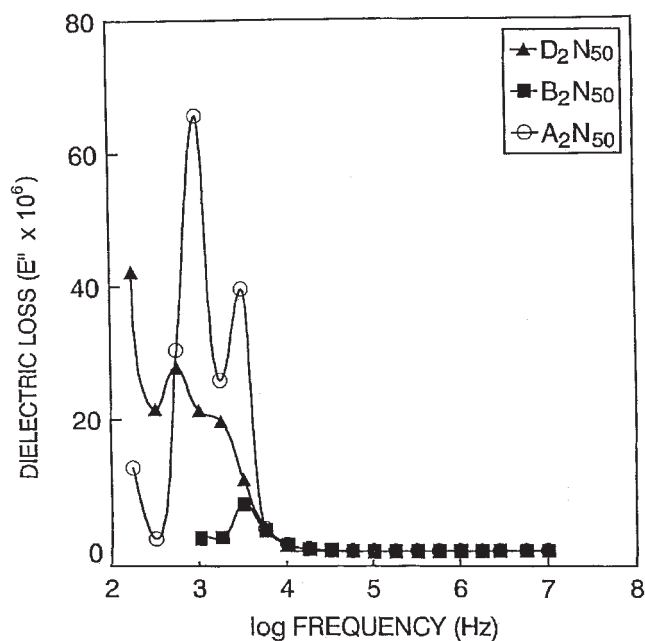


Figure 12 Effect of initiating system on dielectric loss (N_{50} series).

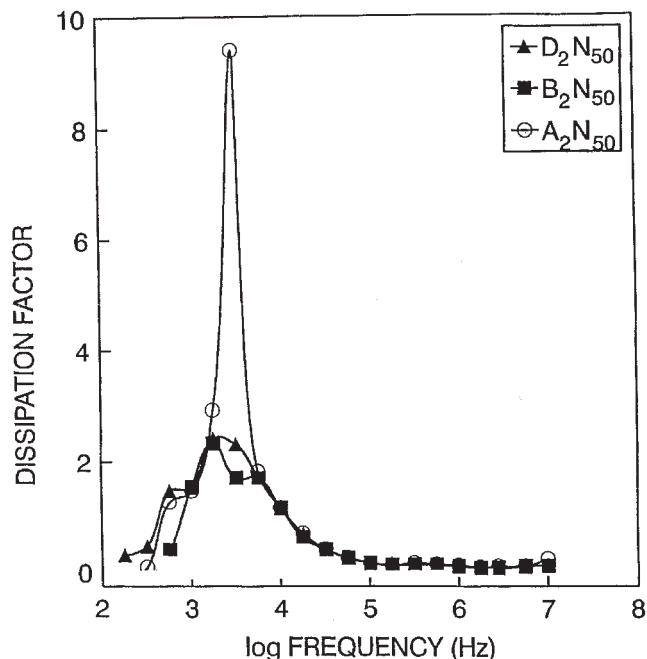


Figure 13 Effect of initiating system on dissipation factor (N_{50} series).

The loss factor peaks due to PS and NR transitions are observed around 10^3 – 10^4 Hz in the case of D_2N_{50} and A_2N_{50} samples. In the case of B_2N_{50} sample, only a single peak is visible. The dissipation factor exhibits two peaks corresponding to the plastic and rubbery phases. It is clear that initiating system does not affect the relaxation mechanism appreciably. The magnitude of the relaxation peak ($\tan \delta$) is almost the same for D_2N_{50} and B_2N_{50} samples. But in the case of A_2N_{50} sample, the magnitude of the peak corresponding to NR relaxation is increased and the peak is slightly shifted to higher frequency. This may be due to the polarization caused in the system due to the presence of azo-bis-isobutyro nitrile. The effect of orientation polarization of peroxide groups in BPO and DCP is small compared to that of $C\equiv N$ in AIBN. Therefore, in the A_2N_{50} sample, the $\tan \delta$ and E' are due to interfacial and orientation polarizations.

As noted above, the effect of blend ratio, crosslinker level, and initiating system on the dielectric parameters is most pronounced in the frequency region of 10^2 – 10^4 Hz. Above 10^4 Hz the dielectric properties remain constant with respect to frequency, blend ratio, crosslinker level, and initiating system. It has been shown by Ferry that at 25° , for materials with $\tan \delta \gg 1$, the relaxation occurs in the frequency region of 10^2 – 10^4 Hz.²¹ The NR/PS IPN system has $\tan \delta \gg 1$ in most cases and therefore the polymer relaxation occurs at 10^2 – 10^4 Hz.

Comparison with theory

The experimental data can be compared with theoretical models. The permittivity of a polymeric system containing two components can be expressed in the general form:²²

$$\varepsilon'_c = V_1\varepsilon'_1 + (1 - V_1)\varepsilon'_2 \quad (\text{Model I}) \quad (6)$$

where ε'_1 and ε'_2 are the permittivities of components 1 and 2; and V_1 and V_2 are the volume fractions of components 1 and 2, respectively. The Lichteneker-Rothers logarithmic equation is appropriate for layered structures that are neither parallel nor perpendicular to the electrical field. The logarithmic variation of permittivity was also expressed by the equation:²²

$$\log \varepsilon'_c = V_1 \log \varepsilon'_1 + (1 - V_1) \log \varepsilon'_2 \quad (\text{Model II}) \quad (7)$$

The permittivity of two phase mixtures based on spherical particles that consider all the possible interactions is given by Reynolds and Hough as²³

$$\varepsilon'_c = \frac{1}{4} [H + (H^2 + 8\varepsilon'_1\varepsilon'_2)]^{1/2} \quad (\text{Model III}) \quad (8)$$

where

$$H = (3V_1 - 1)\varepsilon'_1 + (2 - 3V_2)\varepsilon'_2 \quad (9)$$

The Maxwell-Wagner-Sillers equation can also be used to predict the ε' values; it is given as²²

$$\varepsilon'_c = \varepsilon'_2 \frac{2\varepsilon'_2 + \varepsilon'_1 + 2V_1(\varepsilon'_1 - \varepsilon'_2)}{2\varepsilon'_2 + \varepsilon'_1 + V_1(\varepsilon'_1 - \varepsilon'_2)} \quad (\text{Model IV}) \quad (10)$$

The applicability of the Clausius-Mossotti equation²²

$$\varepsilon'_c = \frac{(1 - V_1)2\varepsilon_2'^2 + 1 + (2V_1)\varepsilon_1'\varepsilon_2'}{(1 - V_1)\varepsilon_1' + (2 + V_1)\varepsilon_2'} \quad (\text{Model V}) \quad (11)$$

was also checked.

Figure 14 gives the experimental and the theoretical variation of permittivities with blend composition. The Clausius-Mossotti equation gives the best correlation of permittivities with experimental results.

CONCLUSION

The dielectric properties of NR/PS IPNs were studied with special reference to the effects of blend ratio, initiating system, crosslinking level, and frequency. As both the rubbery and plastic phases have no appreciable conductivity, the IPNs developed also have limited conductivity. The dielectric properties that are noticeable at low frequencies are primarily due to the

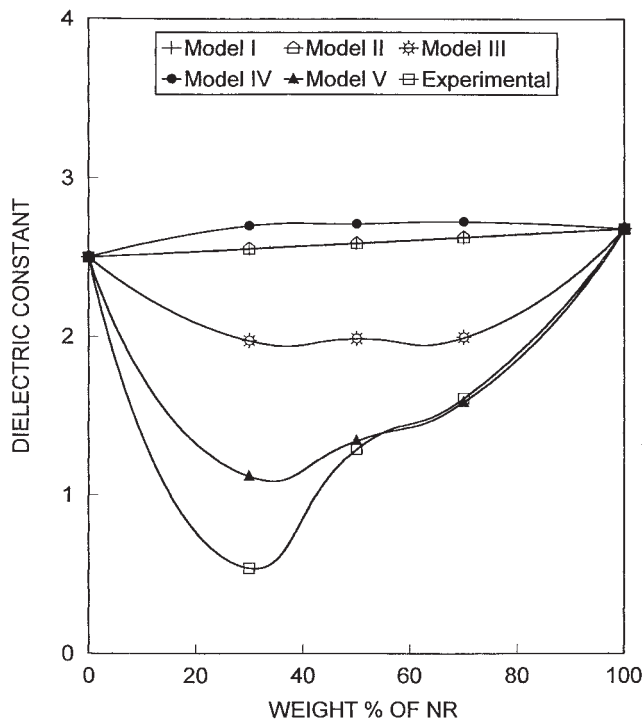


Figure 14 Comparison of theoretical models with experimental values of permittivity.

interfacial polarization. This is the result of the conductivity differences between the NR and PS phases. The presence of curing agents like BPO and DCP added during vulcanization and polymerization does not contribute to the conductivity of the system appreciably. In the AIBN series, the orientation of $C\equiv N$ contributes to the dielectric properties.

The effect of blend ratio on volume resistivity and conductivity was analyzed. It was found that volume resistance decreases with increase in rubber content and conductivity increases with increase in rubber content. The volume resistivity is also found to decrease with increase in PS crosslinking. But at high level of PS crosslinking (i.e., above 4% DVB), the resistivity increases due to PS phase agglomeration.

The permittivity values increase with increase in NR content. The increase in permittivity is most noticeable in the low frequency region. This shows that interfacial polarization is the key factor contributing to the dielectric properties. As the crosslinking level is increased, the permittivity values increase up to 4% DVB and above that the ε' values drop. The crosslinking of PS results in a uniform phase distribution, increasing the number of interfaces and conductivity up to 4% DVB. The nanostructured phase morphology where interfacial area is highly increased also favors the interfacial polarization. Above 4% the agglomeration of PS phase reduces the uniformity of the system and the permittivity decreases. The comparison of permittivity values with theoretical calculation

showed that the Claussius–Mossoti equation fits best with the experimental values.

The loss and dissipation factors exhibit two peaks around 10^3 – 10^4 Hz and after that the values decrease. In all cases two peaks were observed in this frequency region corresponding to PS and NR transition, indicating phase separation in the system. The relaxation mechanism is the same, irrespective of blend ratio or crosslinking level, but the relaxation magnitude varies with blend ratio and crosslinking level. The dielectric properties show appreciable effect with varying blend ratio, crosslinker level, and initiating system in the frequency region of 10^2 – 10^4 Hz. This is due to the fact that the polymer chain relaxation occurs as a result of interfacial polarization at this frequency range in the case of NR/PS IPNs.

The magnitude of electrical conductivity is very low in all cases. The resistivity values are found to decrease up to 4% DVB content and then increase at 6% DVB content. So highly crosslinked samples have the maximum insulating properties. However, the fabrication problems at high crosslinking would have to be overcome.

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