Study on the Microstructure of EPDM/NBR Blend by Positron Annihilation Spectroscopy

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ABSTRACT: Positron annihilation lifetime and Doppler broadening of annihilation radiation techniques were employed to investigate the relationship between free-volume hole properties and miscibility of ethylene propylene diene monomer (EPDM)/acrylonitrile butadiene rubber (NBR) blends. It has been found that there were positive and negative deviations in free-volume hole size (τ_3) and concentration (I_3) as well as *S*-parameter from linear relationship of initial polymers indicating the immiscibility of the blend. The broadening in free-volume hole distribution by increasing NBR content in EPDM/NBR blend confirm the results obtained by finite term analysis. From the fill-

ing effect of silica on free-volume properties of EPDM/NBR (75/25) blend, it has been found that the addition of silica up to 50 phr is the most promising concentration for electrical application. Furthermore, correlations were established between free-volume hole size and fraction combined with the results of electrical (dielectric constant and dielectric loss) and mechanical (stress at yield and strain at yield) properties. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3001–3008, 2008

Key words: blends; poly(propylene) (PP); rubber; mechanical properties

INTRODUCTION

Polymer blends are the combinations of at least two polymer components which are miscible on a molecular scale or form immiscible or phase-separated heterogeneous multiphase systems.[1,2]

Complete knowledge of the microstructural change at the molecular level is necessary to understand the mechanism of miscibility of blends. Nondestructive techniques that can be used to study the microstructural properties, as well as contribute to understanding the behavior of blends in polymers are positron annihilation lifetime spectroscopy (PALS), and Doppler broadening of annihilation radiation (DBAR) measurements.[3–6]

In PALS, by introducing positrons from a radioactive source (^{22}Na) into a polymer sample and measuring the lifetime of the positrons, conclusions can be drawn about the microstructure properties in the polymer. There are three different ways for the positron to annihilate with an electron in the sample. Therefore, three lifetimes are generally attributed to different states of positron annihilation in the following way: τ_1, which is the short-lived component with intensity I_1, is attributed to *para*-positronium (*p*-Ps) and free annihilations; τ_2, the intermediate component with intensity I_2 is mainly due to the positrons trapped in defects present in the crystalline regions

or trapped in crystalline-amorphous interface regions.[7] The longest lifetime component, which is the *ortho*-positronium (*o*-Ps) lifetime, τ_3 with intensity I_3, has a long lifetime of about 142 ns in vacuum and annihilation occurs with the emission of three gamma-rays. However, in polymeric materials, Ps is trapped in the potential well of free-volume holes. In this case, the annihilation of *o*-Ps occurs through the so-called pick-off reaction in which the positron annihilates with an electron of opposite spin at the internal surface of the free-volume hole. This process reduces to a lifetime of *o*-Ps from 140 ns to typically a few nanoseconds (1–5 ns).

Theoretical models[8] relate the *o*-Ps lifetime to the free-volume hole size in which the *o*-Ps annihilates. According to this, positronium is assumed to be localized in a spherical potential well having an infinite potential barrier of radius R_0 with an electron layer in the region $R < R_0$, and predicts the connection between τ_3 and the free-volume hole size R (spherical). By using this model R, the average radius of the free-volume holes can be determined from the relation,

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R_o} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_o}\right)\right]^{-1}$$

where $R_o = R + \Delta R$, ΔR being the thickness of the electron layer (=0.1656 nm).

The fractional free-volume (*f*) can be determined from the lifetime measurements. The relative intensity of *o*-Ps lifetime component, I_3 is assumed to be

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proportional to the number of free-volume holes because it gives the information on the *o*-Ps formation probability. The fractional free-volume (%) is expressed as an empirically fitted equation as[9]:

$$f = AV_f I_3$$

where V_f (in Å^3) is the volume of free-volume holes calculated by using the spherical radius as $V = 4/3\pi R^3$, and A is empirically determined to be 0.0018 from the specific volume data.[10]

Weng et al.[11] investigated the microstructure of CB filled HDPE/ethylene propylene diene monomer (EPDM) composites with positron annihilation spectroscopy (PAS). They found that lifetime parameters (τ_3, I_3) show nonlinear relation with EPDM content, while *S*-Parameter was very sensitive to the microstructure change in the composites. Gomaa et al.[12] used PALS to investigate the effect of weight percent of a polar nitrile rubber (NBR) blended with pure and waste, low- and high-density polyethylene. They found that the broadening in free-volume hole distributions indicated the immiscibility in the blend and confirmed the results obtained by finite term analysis. They concluded that the addition of waste PE in the blend leads to improvement in mechanical and electrical properties of the polymer. Felix et al.[13] applied PALS to study a set of PMMA (polymethyl-methacrylate) + MMA (methyl-methacrylate) + TEGDMA (triethyleneglycol-dimethacrylate) blends. They investigate the correlation between free-volume and miscibility of the components in the blends. They concluded that it is possible to produce a PMMA + TEGDMA blend with the presence of a low fraction of MMA/TEGDMA copolymer situated at interface between the PMMA and TEGDMA regions allowing a higher degree of compatibility of the components. Debowska et al.[14] studied the influence of morphology on *ortho*-positronium annihilation characteristics in polyamide 6 with the use of PALS technique. The determined *ortho*-positronium characteristics reflect variations in morphology and particularly the presence of defects at the interface between the crystalline and amorphous region in the polyamide samples.

Systematic electrical and mechanical study was carried out on EPDM blended with NBR and have been performed by Eid et al.[15] They investigated the immiscibility of these blends using dielectric method as well as by calculating the heat of mixing. They have chosen the blend EPDM/NBR (75/25), which possesses the most promising electrical and mechanical properties to be loaded with silica in increasing quantities (30 up to 90 phr) and studied their electrical and mechanical properties.

As an extension of Eid et al. work, the purpose of this study is to confirm and investigate the immiscibility of EPDM/NBR blends with different ratio 25, 50, and 75 phr using PALS and DBAR measurements. Also, the effect of silica on microstructure of EPDM/NBR (75/25) blend have been studied. In addition, a correlation between electrical (dielectric constant and dielectric loss) and mechanical (stress at yield and strain at yield) as macroscopic properties and the free-volume size and fraction as microscopic properties as a function of polymer blends and silica contents are established.

EXPERIMENTAL DETAILS

Materials

The investigated materials were supplied by Polymer and Pigments Department, National Research Center, Dokki, Cairo, Egypt. Ethylene propylene diene (EPDM) Vistalon 6505 produced by Esso Chem., Germany, with diene (ethyl nonbornene) content 9% as well as ethylene content 55% and density of 0.86 was used. Butadiene acrylate copolymer (NBR) from Bayer AG, Germany, with acrylonitrile content of about 32%, and specific gravity of 1.17 ± 0.005 was used.

Light reinforcing silica 82% precipitated silicon dioxide with specific gravity 1.95 was used as filler and loaded with 30–90 phr. Zinc oxide and stearic acid from Aldrich were used as activator with specific gravity at 15°C, 5.55–5.61, and 0.9–0.97, respectively. The accelerator used was *N*-cyclohexyl-2-benzothiazole sulphonamide (CBS), a pale-gray, nonhygroscopic powder having a melting point of 95–100°C and a specific gravity of 1.27. The antioxidant used was the phenyl β-naphthylamine (PβN) with specific gravity of 1.18–1.24 and melting point of 105–106°C. Peroxide as curing agent (IPBP), 1,3 bis (isopropyl) benzene peroxide on calcium carbonate, trade name "Perkadox 14140," density 1.5 g/mL from Aldrich, was used. Curing system used was sulfur, a pale-yellow powder of sulfur element having specific gravity of 2.04–2.06.

The mixing was carried out on a Laboratory two-roll mill (470 mm diameter and 300 mm working distance). The speed of the slow roll is 24 rpm with a gear ratio of 1 : 1.4. The compounded blends were left over night before vulcanization. The vulcanization was carried out in a heated platinum press under a pressure of about 40 kg/cm^2 and temperature of 152°C ± 1°C.

Mechanical measurements

Both stress and strain at yield were carried at room temperature on a tensile testing machine, Zwick 1425, according to ASTM-D412-98a, 1998.

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TABLE I
Positron and Positronium Parameters in Initial Polymers

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Polymer	τ_3 (ns)	I_3 (%)	R (Å)	V (Å^3)	f (%)	S-parameter
NBR	1.781 ± 0.011	15.809 ± 0.134	2.63 ± 0.0009	76.8 ± 0.5	2.18 ± 0.04	0.3550 ± 0.0005
EPDM	2.083 ± 0.022	21.165 ± 0.122	2.92 ± 0.6	104.4 ± 0.6	3.98 ± 0.08	0.4032 ± 0.0004

Dielectric measurements

LCR meter type AG-411B (Ando Electric Ltd., Japan) was used. The capacitance C and the loss tangent, tan δ, were obtained directly from the bridge from which the permittivity ε was calculated. A guard ring capacitor type NFM/5T (Wiss Tech. Werkstatten [WTW] GMBH, Germany) was used as a measuring cell. The cell was calibrated using standard materials and the experimental error in ε was found to be ±3%.

Positron annihilation lifetime measurements

The positron annihilation lifetimes (PAL) in polymer blends were determined by detecting the coincidences between the prompt γ-ray (1.28 MeV) from the nuclear decay that accompanies the emission of a positron from ^{22}Na radioisotope and the annihilation γ-ray (0.511 MeV) inside the material using a conventional fast–fast coincident lifetime spectrometer. A 20 μCi of ^{22}NaCl positron source, held between 7 μm thick Kapton foils, was sandwiched between two identical pieces of each sample. The time resolution of the system is found to be 230 ps (FWHM). All of the PAL spectra obtained were analyzed using the PATFIT program.[16]

Doppler broadening of annihilation radiation measurements

The Doppler broadening measurements are performed using hyper-pure germanium detector. The measured FWHM is established to be 1.2 at 662 keV of ^{137}Cs. The energy dispersion of the equipment is 0.049 keV per channel. The number of channels included in the annihilation peak area is 300. The used positron source is 15 μCi of ^{22}Na deposited on Kapton foil and sandwiched between two identical pieces of the sample. The total number of counts in the measured spectrum is ~ 10^7. From Doppler broadening spectra, S-parameter is measured as the number of counts lying within an energy interval of 1.3 keV centered as the peak of the annihilation line. The line-shape S-parameter represents the probability of annihilation of positron and positronium with valance electrons. S-parameter is given as the ratio of the area of the central (low-momentum) part of the spectrum to the total area of the 511 keV annihilation peak after the background is subtracted.

RESULTS AND DISCUSSION

Free-volume hole size and concentration in initial polymers

The o-Ps lifetime τ_3 and intensity I_3 are the parameters, which vary as functions of the chemical structure and the composition of polymers.[3] They are used to evaluate the free-volume hole properties such as mean free-volume size (V) and fraction (f). On the other hand, the measured Doppler broadening S-parameter is mainly determined by the concentration of free-volume holes in polymers, which are very effective positron trapping centers.[10]

The free-volume hole parameters of initial polymers are represented in Table I. The results show that NBR has a smaller hole size of free-volume with low concentration than the corresponding free-volume values of EPDM. The smaller values of free volume in NBR could be interpreted in terms of molecular structure and its packing in the polymer. The triple bond between C and N in NBR restricts the free rotation leading to a reduction in free-volume size. This means that the main chains of NBR are tightly packed so as to reduce the intermolecular spaces in the amorphous regions.[17] On the other hand, the polarity of nitrile group (C≡N) in NBR polymer is known to be electron-attracting and thus reduces o-Ps formation.[12] In addition, the measured S-parameter, which is a measure of Ps formation, has a strong correlation with the free-volume concentration. The lower free-volume concentration in NBR leads to a lower concentration of low-momentum part of the positron–electron annihilation radiation in subnanometer defects such as free-volumes results in a decrease in S-parameter in NBR than the corresponding value in EPDM.

Free-volume hole size and concentration in EPDM/NBR blends

The variation of τ_3, I_3, and S-parameter as a function of wt % of NBR in NBR/EPDM blend are shown in Figure 1. One can observe that, a decrease in τ_3 and its intensity I_3 which as a measure of free-volume hole size and concentration, as well as in S-parameter as a measure of Ps formation by decreasing the
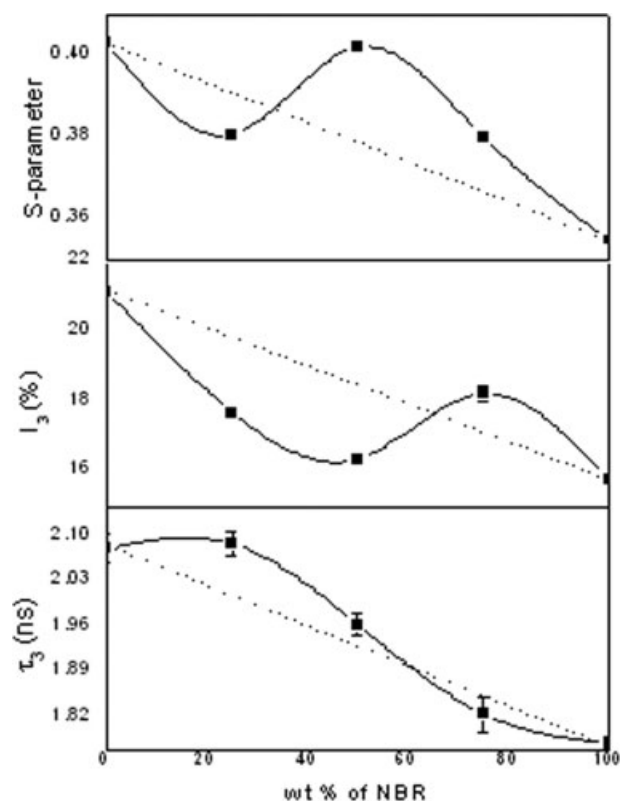
Figure 1 The variation of τ_3, I_3, and S-parameter with wt % of NBR in the EPDM/NBR blend.

wt % of EPDM, and by increasing wt % of NBR in blend is due to crosslinking of molecular chain after vulcanization. These results are agreement with the results obtained before on EPDM/poly (trimethylene terephthalate) incompatible blends,[18] where the free-volume values tend to decrease by reducing the wt % of EPDM in blend. On the other hand, τ_3 changes from positive deviation at low weight percent of NBR (25%) to a negative deviation at high percent (75%) of NBR, whereas I_3 and S-parameters show the reverse trend. The fluctuation of τ_3, I_3, and S-parameter, which is due to a fluctuate level of interfacial interactions results from the trapping and detrapping of positron and positronium between free-volume holes and interfaces.[3] The weak interaction between two dissimilar polymer molecules took place in the regions between two amorphous regions indicating that this EPDM/NBR blend is immiscible.[19]

The variation in EPDM/NBR blend can be interpreted as follows: two processes are probably present, namely, intermolecular and interstructural processes. The intermolecular process is predominant at low wt % of NBR where the EPDM molecules would interact with the active group of NBR leading to the breaking of molecular bundles and chains separated. As a result, an increase in size of free-volume holes with low concentration is observed. On the other

hand, the interstructural process is predominant at high wt % of NBR where NBR molecules are distributed in the intermolecular spaces leading to a decrease in the free-volume hole size by high concentration.

To observe the variation of any interfacial spaces, the second positron lifetime components (τ_2, I_2) are plotted as a function of wt % of NBR in EPDM/NBR blend as shown in Figure 2, showing positive deviations of τ_2 with different intensities I_2.

The difference in the free-volume due to the blending between the two polymers can be seen more clearly in the free volume hole size distributions, which are extracted from positron lifetime spectra, and gives us an indication of the blend miscibility on molecular scale.[20] The computer program LT 9.0[21] is used to allow long normal distribution of the long lifetime of annihilation rate ($\lambda = 1/\tau$) and the results of the free-volume probability density function, V (pdf) are shown in Figure 3. From the figure, it is observed that, there is the Gaussian-like distribution for 25%NBR in between those of the two original polymers. This is because the blend is homogeneous on the molecular level at this composition. While at 50%NBR and at 75%NBR the distributions are shifted to the right indicating the nonhomogenity at these compositions.[20] On the other hand, an immiscible blend is expected to exhibit a broader distribution as a consequence of the different interfaces present in the blend. This broadening is observed at 75%NBR. The immiscible blend of Ps-PC showed a similar broadening result.[3] The observed trends are consistent with the results obtained by the finite lifetime analysis [Fig. (1)].
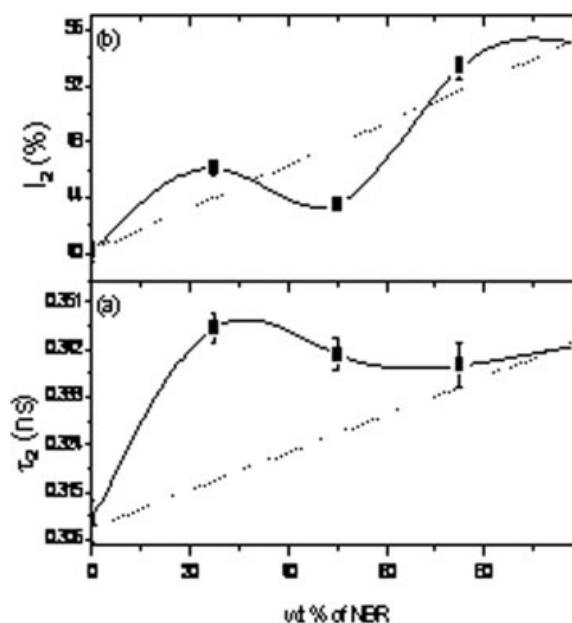
Figure 2 The variation of τ_2 (a), and I_2 (b) with wt % of NBR in EPDM/NBR blend.
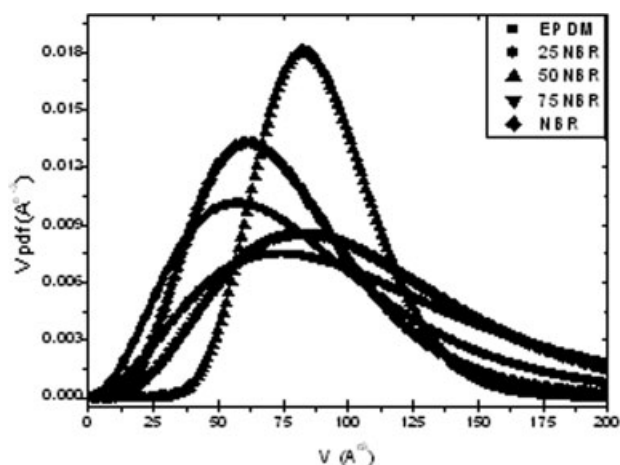
**Figure 3** Free-volume hole distributions V (pdf)(V) of EPDM/NBR blend at different wt % of NBR.

The effect of silica on free-volume properties in EPDM/NBR (75/25) blend

Filler such as silica has a high effect on free-volume properties.[22,23] The variation of τ_3, I_3, and S-parameter, as well as τ_2 and I_2 with silica contents from 30 phr up to 90 phr in EPDM/ NBR (75/25) blend are shown in Figures 4 and 5, respectively.

One can observe from Figure 4 that τ_3 does not change by adding silica until 40 phr, this indicate that the addition of silica filler does not change the
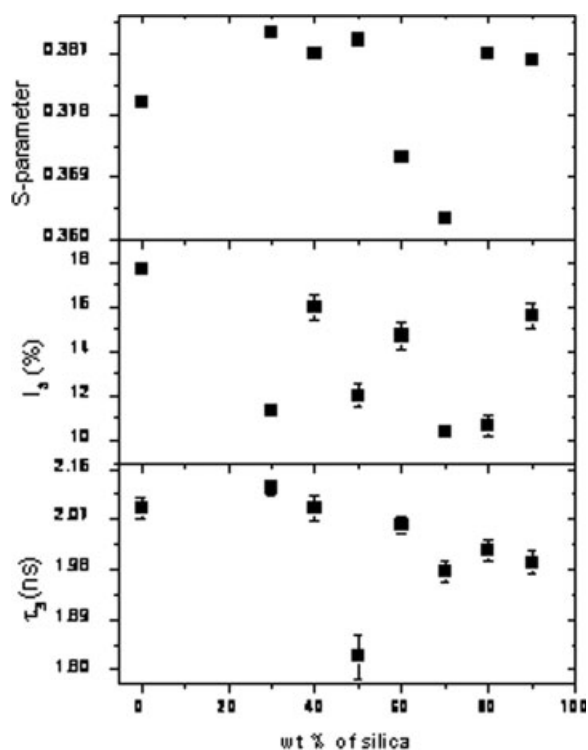
Figure 4 The variation of τ_3, I_3, and S-parameter with wt % of silica in EPDM/NBR (75/25) blend.
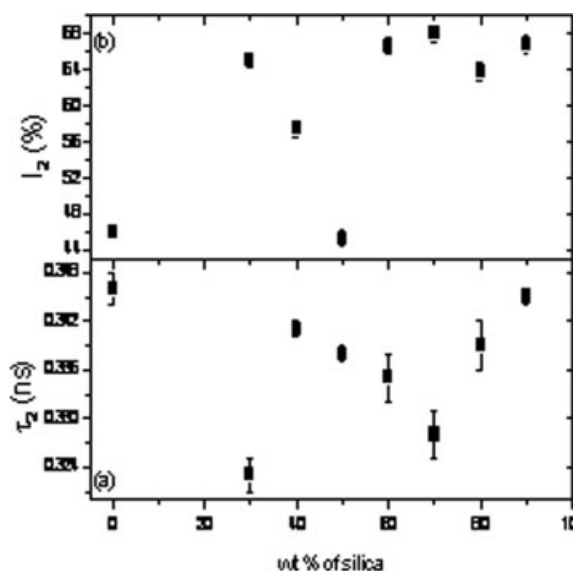
Figure 5 The variation of τ_2 (a), and I_2 (b) with wt % of silica in EPDM/NBR (75/25) blend.

radius of the free-volume in the blend, which determines the o-Ps pick-off lifetime.

In addition, by adding silica, positron may annihilate in the silica and thus the number of positrons available to form positronium in the blend is reduced. On the other hand, the addition of silica changes in the crosslinking density of the blend and inhibit the o-Ps formation by providing an additional positron interaction mechanism, which competes with positronium formation in the blend.[22] As a result, the values of o-Ps intensity (I_3) are affected showing fluctuate changes by adding silica up to 60 phr. The addition of more silica creates new positron trapping sites at both silica–polymer interfaces and at the matrix leading to an increase in all positron parameters as shown in the figures.

These suggestions are confirmed by an increase in the second components of the positron lifetime (τ_2, I_2) with increasing the amount of silica (Fig. 5), indicating that the addition of silica creates new positron trapping sites at silica–rubber interfaces.[23]

The high values of S-parameter due to the addition of silica particles up to 50 phr indicate that the chance of positron and positronium annihilation with low-momentum electron increases, which suggested high-electron momentum density distribution up to 50 phr. From these results, one can concluded that the most promising silica concentration for electrical application is up to 50 phr.

Correlation between free-volume parameters, electrical and mechanical properties in blends

Figure 6 shows the correlation between the permittivity (ε) at 1 kHz, stress at yield, strain at yield, and both free-volume hole size (V) and its fraction (f) as
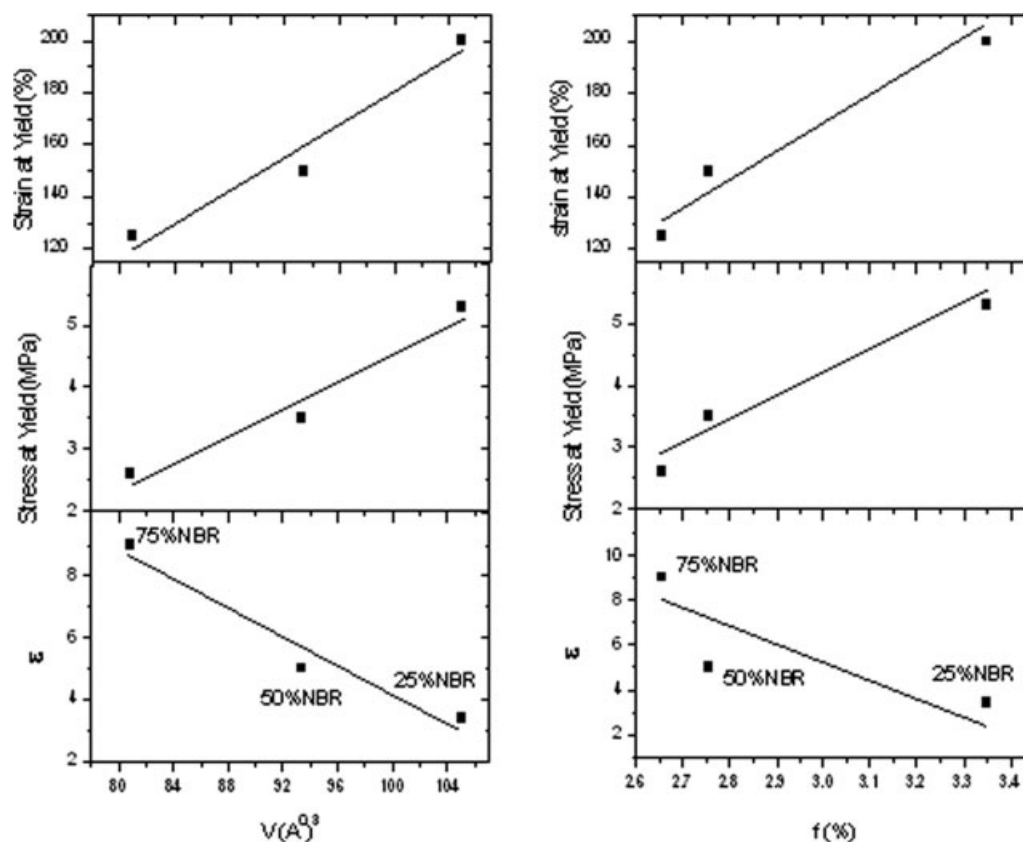
Figure 6 The variation of ε, stress, and strain as a function of free-volume size (V) and fraction (f) in EPDM/NBR blend.

a function of wt % of NBR in EPDM/NBR blend. It is observed that the stress and strain at yield decrease while ε increases by increasing wt % of NBR in EPDM/NBR blends. On the other hand, the free-volume hole size (V) and its fraction (f) are directly correlated with mechanical properties (stress and strain), and inversely correlated with the electrical properties (ε) by increasing wt % of NBR in the blend. The directly correlation between mechanical properties and both V and f is explained on the basis that by increasing wt % of NBR in the blend causes decrease in the size and concentration of free-volume holes of the blend due to the two intermolecular and interstructural processes in EPDM/NBR blend. The inversely correlation between ε and both V and f is due to the increase in C≡N dipoles which leads to an increase in the orientation polarization and the presence of interfacial polarization.[17]

It is observed that the stress, strain, and free-volume parameters have their highest values, while ε has its lowest value at EPDM/NBR (75/25) blend. This means that the optimum mechanical and electrical properties obtained for such blend can be reached when EPDM/NBR ratio is 75/25, which confirms the results obtained in reference,[15] where

the mechanical properties are increased by decreasing NBR content up to 25 phr, after which they decreased till it reached that of NBR itself.

Figure 7 shows the correlation between ε at 1 kHz, stress at yield, strain at yield and V and f in EPDM/NBR (75/25) blend loaded with silica. It is observed that ε and stress at yield increase while strain at yield decreases by increasing wt % of silica in EPDM/NBR blend. On the other hand, the free-volume size V shows a gradual decrease while free-volume fraction (f %) shows fluctuate change by increasing silica contents in the blend. This is due to the redistribution process of the silica within the polymer matrix which leads to the orientation of chain segments in which the segments tend to align themselves in more ordered arrangements. These results confirm the above result that the addition of silica in the blend providing an additional positron interaction mechanism, which competes with positronium formation in the blend leading to a decrease in free-volume size with different concentrations.

CONCLUSION

- The microscopic free-volume hole size and concentration results as determined by PALS and
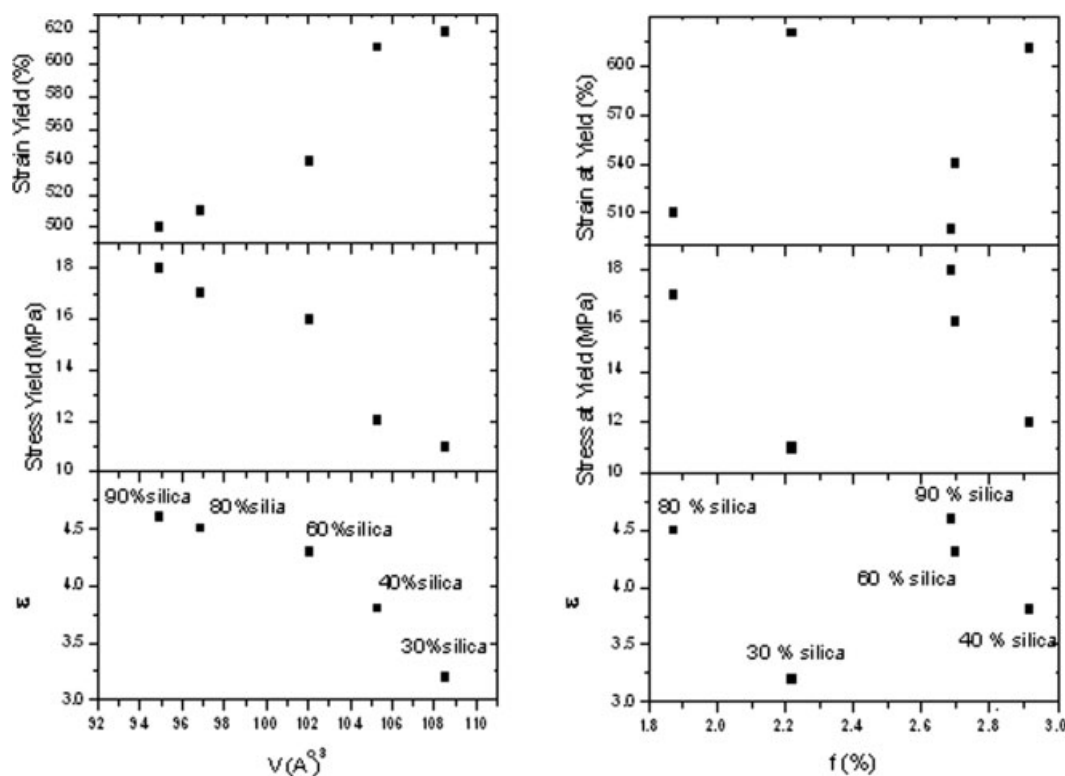
Figure 7 The variation of ε, stress, and strain as a function of free-volume size (V) and fraction (f) in EPDM/NBR (75/25) loaded with silica.

DBAR show a fluctuating positive and negative deviations from the linear relationship of initial polymers in EPDM/NBR blends with different NBR percentage which confirm the immiscibility of this blend.

- The observed trends of free volume probability density function are consistent with the results obtained by the finite lifetime analysis.
- The S-parameter results confirmed the conclusion that EPDM/NBR (75/25) blend loaded up to 50 phr of silica possess the most suitable electrical (dielectric constant and dielectric loss) and mechanical (stress at yield and strain at yield) properties.
- The complicated variation of free-volume hole size and concentration in the immiscible blends observed by PAS is a result of the high-sensitivity of the positron and positronium atom not only to free-volume holes but also to any interfacial spaces.

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