Microstructure and Miscibility of Acrylonitrile–Butadiene Rubber/Ethylene–Propylene–Diene Monomer Blends Studied by Positron Annihilation Spectroscopy

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ABSTRACT: The free-volume properties and miscibility of ethylene–propylene–diene monomer/acrylonitrile–butadiene rubber blends with poly(vinyl chloride) used for compatibilization were investigated with positron annihilation lifetime spectroscopy and Doppler broadening of annihilation radiation. The results showed that the *ortho*-positronium annihilation lifetimes and intensities as well as the *S* parameter had a linear relationship with a negative slope as a function of the weight percentage of acrylonitrile–butadiene rubber, which indicated the miscibility of the blend. The filling effect of silica on the free-volume properties of an ethylene–propylene–diene monomer/acrylonitrile–butadiene rubber (75/25) blend was also examined. On the other hand, a correlation between the size and concentration of the free-volume holes and the electrical and mechanical properties of the aforementioned blends was established. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2564–2570, 2007

Key words: blends; compatibility; fillers; miscibility

INTRODUCTION

Polymer blends are of great importance in industrial applications because blending is a relatively simple way of creating a material with significantly improved properties.[1,2] They can exhibit higher performance at a lower cost; therefore, they have been attracting increasing attention in recent years.[3]

To predicate and enhance the physical properties of blends, it is important to understand the atomic-scale microstructure and interactions between the two phases of blends. There exist many physical probes for characterizing the structure and properties of polymer blends.[4] However, only a limited number of probes are available for characterizing free-volume properties because of the small size.

Positron annihilation spectroscopy is a sensitive probe for detecting free-volume holes in polymeric materials at an atomic scale.[5] When a positron enters a polymer, it may be annihilated directly with an electron or may capture an electron from the surrounding molecules to form a bound state, a so-called positronium (Ps) atom. Ps has an atomic radius similar to that of hydrogen.[6]

Ps is known to exist in two ground states. *para*-Positronium (*p*-Ps), consisting of an electron-positron state with antiparallel spins (spin = 0), is annihilated after a mean lifetime (τ_1) of 125 ps and produces two 0.511-MeV γ rays. *ortho*-Positronium (*o*-Ps), in which the spins of the two particles are parallel (spin = 1), is annihilated with the emission of three γ rays. The mean lifetime of *o*-Ps (τ_3) in a vacuum is 142 ns. In a polymer, however, *o*-Ps can pick off an electron with an antiparallel spin, and this results in a mean lifetime of a few nanoseconds (1–5 ns), depending on the electron density of the material surrounding the *o*-Ps. The simple quantum model[6] for Ps confined in a spherical box assumes that the annihilation rate of *o*-Ps inside the electron layer is 2 ns^{-1}, which is the spin-averaged annihilation rate of *p*-Ps and *o*-Ps and is very close to the annihilation rate of Ps.[7] The *o*-Ps annihilation lifetime (τ_3) as a function of the free-volume radius (R) is then given by

$$\tau_3 = 0.5\left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + \Delta R}\right)\right]^{-1} \quad (1)$$

where $\Delta R = 0.166$ nm is an empirical parameter obtained by the fitting of experimental τ_3 values to data from molecular solids with well-known hole sizes (R).[8] According to this relationship, one can obtain the average size of the free-volume holes (V_f) probed by *o*-Ps:

$$V_f = \frac{4}{3}\pi R^3$$

The probability of *o*-Ps formation is called the *o*-Ps intensity (I_3), and it is proportional to the number of

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cavities in the system.[9] In this manner, the total free volume can be evaluated with the following equation:

$$f = AI_3V_f \tag{2}$$

where f is the concentration of free-volume holes and the value of constant A is taken to be 0.015.[7]

Ravikumar and Ranganathaiah[10] used positron annihilation lifetime spectroscopy (PALS) and differential scanning calorimetry to study microstructural changes in poly(trimethylene terephthalate) (PTT)/ethylene–propylene–diene monomer (EPDM) blends with and without the compatibilizer poly(EPM-*graft*-MA). The PALS results for the blends without the compatibilizer showed an increase in V_f and f with increasing EPDM content in the blend. However, poly(EPM-*graft*-MA)-compatibilized blends of PTT and EPDM showed a noticeable decrease in the free-volume parameters, which was clearly due to the compatibilizing effect through increased interactions between the blend components. Dai et al.[1] used the PALS technique to investigate the free-volume-hole properties of vulcanized EPDM/polypropylene (PP) blends. Their results showed that the free-volume-hole concentration (I_3) deviated positively from the linear additive when the weight percentage of EPDM was below 50%, but it deviated negatively when the weight percentage of EPDM was over 50%. These results demonstrated that the noncrystalline regions of PP and EPDM in the blend were partially miscible. Wang et al.[11] investigated the microstructure of carbon black (CB) filled high-density polyethylene (HDPE)/EPDM composites with PALS and Doppler broadening of annihilation radiation (DBAR). They found that τ_3 and I_3 showed a nonlinear relationship with the EPDM content, whereas the S parameter was very sensitive to the changes in the microstructure of HDPE (CB)/EPDM composites.

Eid and El-Nashar[12] studied the electrical and mechanical properties of EPDM/acrylonitrile–butadiene rubber (NBR) blends with and without poly(vinyl chloride) (PVC) for compatibilization. They found that a 75/25 EPDM/NBR blend possessed the most promising properties. For that reason, they chose this blend to be loaded with 30–90 phr silica to study its mechanical and electrical properties. Also, this group investigated the miscibility of these blends by using a dielectric method and by calculating the heat of mixing.[12]

As a continuation of Eid and El-Nashar's work,[12] this study was conducted to investigate the changes in the free-volume properties of EPDM/NBR blends with PVC for compatibilization as well as the effect of silica as a filler on the free-volume parameters of a 75/25 EPDM/NBR blend. This study was also aimed at establishing a correlation between the electrical and mechanical properties of the polymer blends with the microstructure free-volume properties as a function of the weight percentage of the polymer blend and at confirming the miscibility of the blend with PALS and DBAR.

EXPERIMENTAL

Materials

The materials used in this study were supplied by the Polymer and Pigments Department of the National Research Center (Dokki, Egypt):

- EPDM (Vistalon 6505), produced by Exxon Chemical Company (Koln, Germany), with a diene (ethylidene norbornene) content of 9%, an ethylidene content of 55%, and a density of 0.86 g/cm^3, was used.
- NBR from Bayer AG (Leverkusen, Germany), with an acrylonitrile content of 32%, was used.
- The PVC (10 phr) resin was used as a compatibilizer for the NBR/EPDM blends.
- Light reinforcing silica (82% precipitated silicon dioxide) was used as a filler (30–90 phr). The average size of the silica particles was 22 nm.
- 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 was 24 rpm with a gear ratio of 1:1.4. The compounded blends were left overnight before vulcanization.
- The vulcanization was carried out in a heated platinum press at 152 ± 1°C under a pressure of about 40 kg/cm^2, and the time of vulcanization was 10 min.
- More details about the mechanical (stress and strain at yield) and electrical measurements are described in ref. 12. These measurements were carried out at room temperature.

PALS measurements

The positron lifetime was measured by the detection of the time difference between the birth of γ rays of β$^+$ decay in the source and the annihilation of γ rays with an energy of 511 keV. The γ rays were converted by scintillator and photomultiplier detectors into analog electrical pluses. The pulses were processed by discriminators. Their output pulses started and stopped a time-to-amplitude converter. The amplitude of the output pulse was proportional to the time difference between the birth and annihilation of γ rays and thus represented a measure of the positron lifetime. The single annihilation event was stored after analog–digital conversion in the memory of a multichannel analyzer. The channel numbers represented the timescales. The lifetime measurements were performed in air at room temperature with a fast–fast coincidence system. The time resolution of the spectrometer, as measured with ^{60}Co, was 230 ps for the full width at
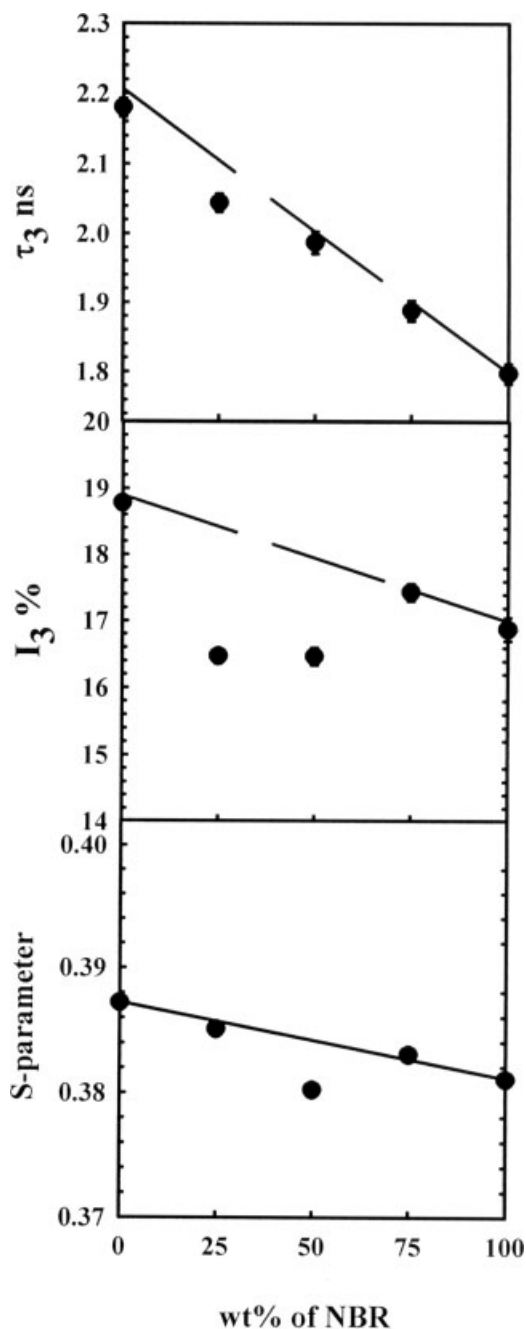
Figure 1 Variation of τ_3, I_3, and S with the weight percentage of NBR in the NBR/EPDM blends. The straight lines present additive predications.

half-maximum. A 20-μCi ^{22}Na positron source was used in this study, and it was deposited and sealed in 7-μm-thick Kapton foil. The positron source was placed between two similar pieces of the sample under study. For each spectrum, it contained 1 million total counts.

The measured lifetime spectra can be normally resolved into a number of exponentials, each representing an annihilation process with a mean lifetime (τ) and a relative intensity (I). All spectra were fitted with three lifetimes with the computer program PATFIT.[13]

The shortest component (τ_1 and I_1) is related to *p*-Ps annihilation, the intermediate component (τ_2 and I_2) is related to the annihilation of free positrons, and the longest one (τ_3 and I_3) is the *o*-Ps component.

DBAR measurements

The DBAR measurements were taken with a hyperpure germanium detector. The measured full width at half-maximum was established to be 1.2 keV at 662 keV of ^{137}Cs. The energy dispersion of the equip-
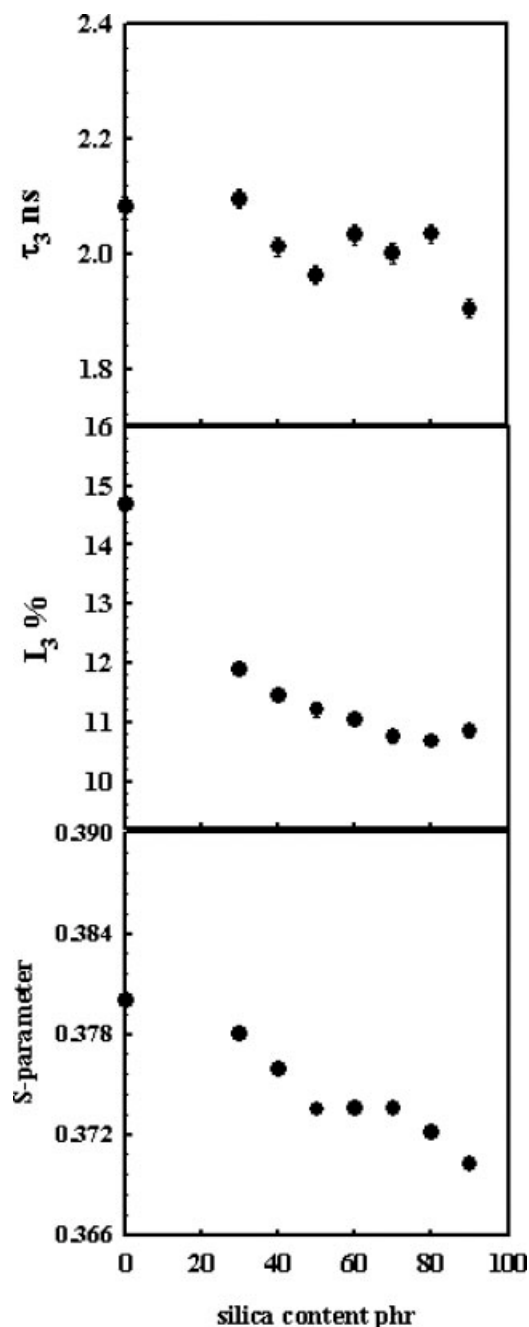
Figure 2 Variation of τ_3, I_3, and S with the silica content (phr) in the 75/25 EPDM/NBR blend.
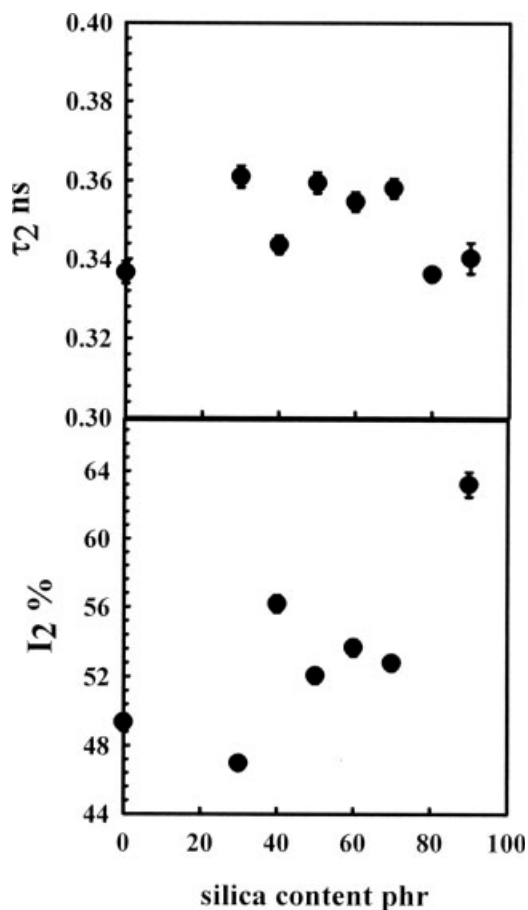
Figure 3 Variation of τ_2 and I_2 with the silica content (phr) in the 75/25 EPDM/NBR blend.

ment was 0.049 keV per channel. The positron source was 15 μCi of ^{22}NaCl deposited on Kapton foil and sandwiched between two identical pieces of the sample. The total number of counts in the measured spectrum was ~5 × 10^6. The S parameter was defined as the ratio of the central area to the total area of the 511-keV annihilation peak after the background was properly subtracted. As the line shape, the S parameter represented the probability of the annihilation of positrons with the valence electrons, and it was given as the area of the central (low-momentum) part of the spectrum.

In polymeric materials, the S parameter represents the relative contribution of the low-momentum part of the positron–electron annihilation radiation in sub-nanometer defects such as free volumes.[14]

RESULTS AND DISCUSSION

Free-volume properties of the EPDM/NBR blends

The o-Ps lifetime (τ_3) and its intensity (I_3), used as measures of V_f and f, and the S parameter, used as a measure of Ps formation, are highly dependent on the

chemical structure and crystallinity of the polymers.[4] The positron annihilation results show that NBR has a smaller free-volume size (~77 Å^3) and fraction (~2.5%) than the corresponding free-volume size (~102 Å^3) and fraction (~3.6%) of EPDM. This is due to the polarity of the nitrile group (C≡N) in NBR, which is known to be electron-attracting and thus reduces o-Ps formation. In addition, the triple bond between C and N restricts the free-volume rotation, leading to a reduction in V_f and f as well as Ps formation. This means that the main chains of NBR are tightly packed to reduce the intermolecular spaces in the amorphous regions.[15,16] Therefore, τ_3, I_3, and S in NBR are considered to be reduced because of the packing structures and become smaller than the corresponding values of EPDM.

The variation of τ_3, I_3, and S with the weight percentage of NBR in the EPDM/NBR blends is shown in Figure 1. The decrease in the free-volume parameters and S for the EPDM/NBR blends is due to the increasing amount of NBR in the blend because NBR has a lower free-volume size.[10] In addition, the decrease in τ_3, I_3, and S with an increasing weight percentage of NBR is due to the crosslinking of the molecular chains
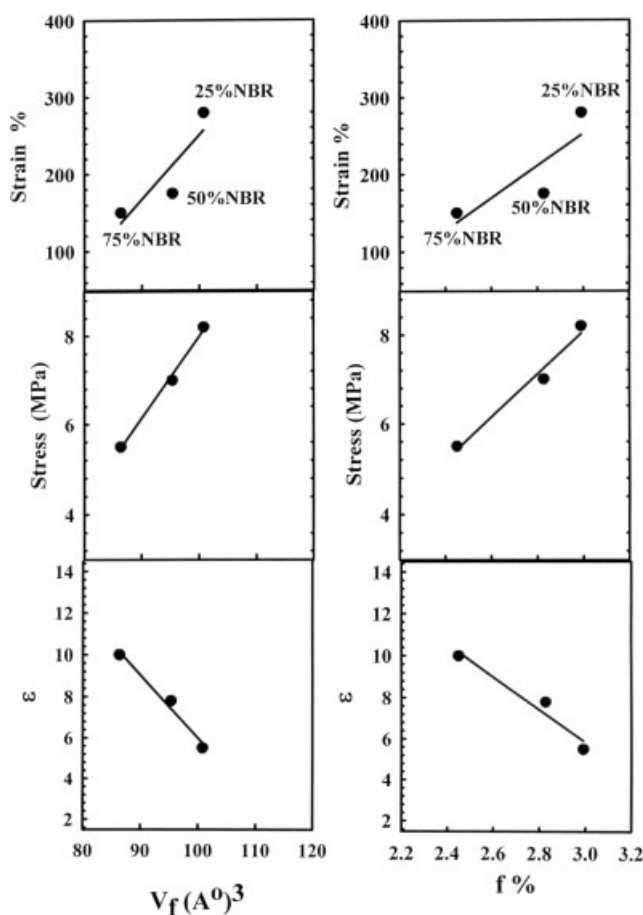
Figure 4 Correlation between the stress, strain, ε, and free-volume parameters (V_f and f) in the EPDM/NBR blends.
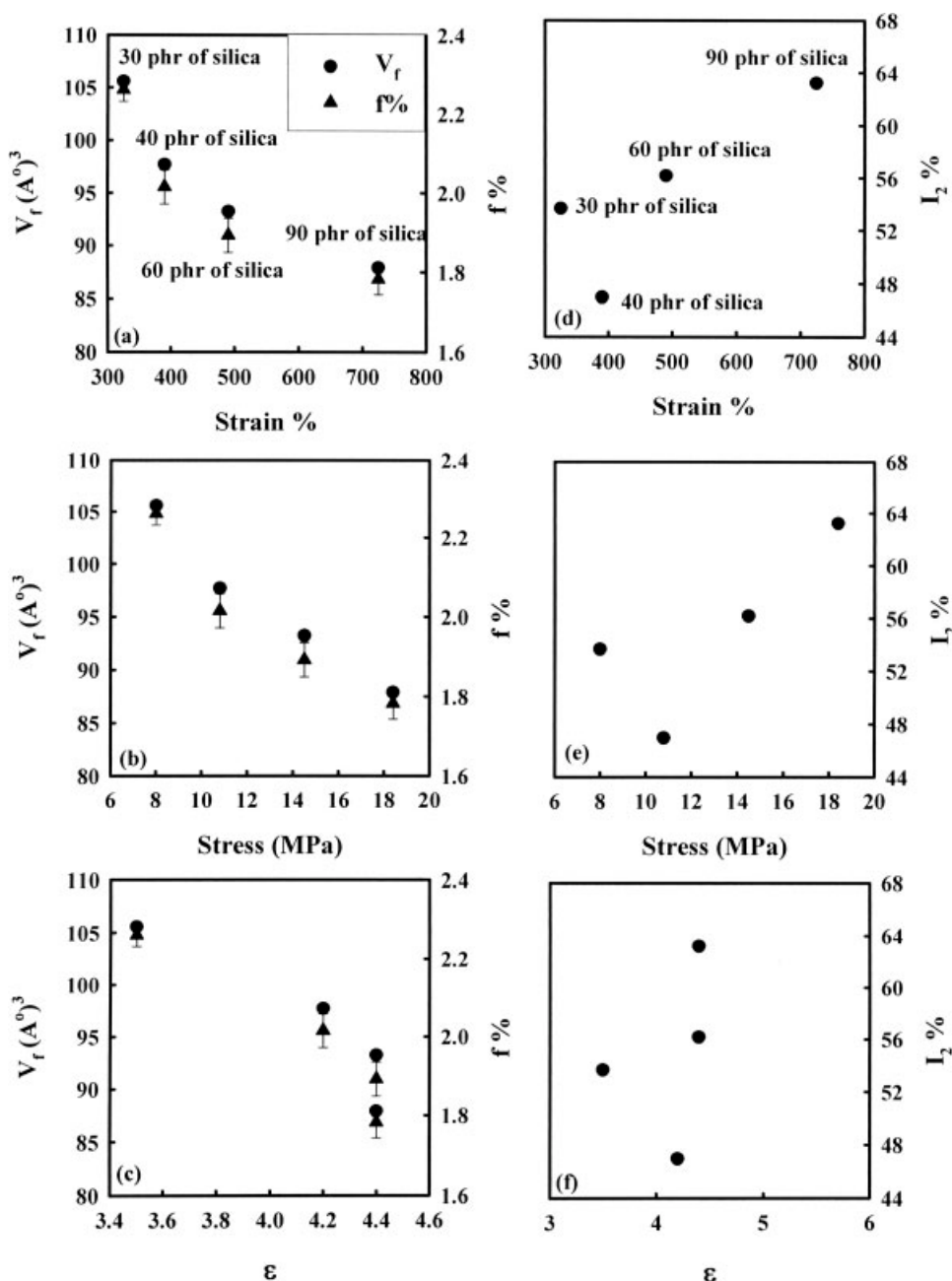
Figure 5 Correlation between the stress, strain, ε, and (a–c) free-volume parameters (V_f and f) and (d–f) probability of a free annihilation positron (I_2) in the 75/25 EPDM/NBR blend loaded with silica.

after vulcanization. On the other hand, the free-volume parameters (τ_3, I_3, and S, as shown in Fig. 1) of these blends exhibited a linear relationship with a negative slope as a function of the weight percentage of NBR, which indicates the miscibility of this blend.[4] This can be interpreted as increased interaction between the blend components.

Free-volume properties of EPDM/NBR (75/25) with silica contents

A filled polymer differs substantially from a virgin one over a wide range of properties. The presence of a

filler affects the electrical, mechanical,[12] and free-volume properties. The variations of τ_3, I_3, and S with the silica content (30–90 phr) loaded in the 75/25 EPDM/NBR blend are shown in Figure 2. τ_3, I_3, and S decrease with increasing silica content, and this means that the addition of silica changes the crosslinking density of the blend and inhibits o-Ps formation by providing an additional positron interaction mechanism, which competes with Ps formation in the blend.

In addition, the silica particles fill some of the holes in the blend matrix, leading to a decrease in both V_f and f.[17,18] However, positrons may be annihilated in the silica, and thus the number of positrons available

to form Ps in the blend is reduced with an increasing amount of silica.

This suggestion is confirmed by increases in both τ_2 and I_2 with an increasing amount of silica (Fig. 3), and this indicates that the addition of silica creates new positron trapping sites at silica–rubber interfaces.[19]

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

Because, the electrical and mechanical data for EPDM/NBR blends have been published already[12] only some results will be given here. The correlation between the permittivity (ε) at 1 kHz, stress, strain, V_f, and f as a function of the weight percentage of NBR in EPDM/NBR blends is shown in Figure 4.

Figure 4 shows a linear correlation with a positive slope between the free-volume parameters (V_f and f) and mechanical properties (stress and strain) of the blend. On the other hand, a linear correlation with a negative slope between the free-volume parameters (V_f and f) and ε can be observed. The mechanical properties decrease with an increasing weight percentage of NBR in the blend. This decrease of the stress and strain may be explained as follows: the large amount of NBR in the blend causes decreases in V_f and f of the blends. Therefore, probably two processes are present: intermolecular and interstructural processes. With a low amount of NBR, the intermolecular process predominates, and the EPDM molecules interact with the active group of NBR, leading to the breaking of molecular bundles and chain separation, which lead to increases in V_f and f. On the other hand, with a large amount of NBR, the interstructural process is predominating, and the NBR molecules are distributed in the intermolecular space; this leads to decreases in V_f and f. This means that, in the first process, the mechanical properties increase with a decrease in the NBR concentration in the blend, whereas in the second process, the opposite trend occurs. The increase in ε at a low value of V_f with the weight percentage of NBR is due to the increase in C≡N dipoles, which leads to an increase in the orientation polarization and the presence of interfacial polarization.[12]

The correlation between the stress, strain, ε at 1 kHz, and free-volume parameters (V_f and f) of an EPDM/NBR (75/25) blend loaded with silica is shown in Figure 5(a–c). The free-volume parameters are linearly correlated with the stress, strain, and ε with a negative slope. Both V_f and f decrease with increasing silica content (phr), which leads to increasing ε, stress, and stain. This is due to the redistribution process of the silica within the polymer matrix. However, the silica particles can be participating in filling more free-volume holes, and this decreases the size and concentration.

Figure 5(d–f) shows the correlation between the stress, strain, ε at 1 kHz, and I_2 (probability of a free annihilation positron) of EPDM/NBR (75/25) with the silica contents. I_2 increases with the stress and strain, and this indicates an increase in the silica–polymer interfaces corresponding to the separation of segments. The addition of silica to the polymer matrix provides traps for free positrons and confirms the results of Figure 5.

CONCLUSIONS

The variation of the o-Ps parameters (τ_3 and I_3) and S of the EPDM/NBR blends shows a linear relationship with a negative slope as a function of the weight percentage of NBR, and this confirms the miscibility of this blend.

The addition of silica causes a decrease in the free-volume size and its concentration as well as the S parameter and hence increases the direct annihilation of free positrons at the polymer–filler interfaces.

The free-volume parameters (V_f and f) show a linear correlation with the mechanical and electrical properties of the blend with a negative or positive slope, which depends on the addition of silica.

The addition of silica to an EPDM/NBR blend leads to the formation of new industrial polymer blends that possess promising mechanical and electrical properties.

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