JMEPEG (2004) 13:583-587
DOI: 10.1361/10599490420593

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1059-9495/$19.00

Correlation Between Free-Volume Parameters and Physical Properties of Polyethylene-Nitrile Rubber Blend

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(Submitted December 17, 2003)

Positron annihilation lifetime spectroscopy (PALS) was used to study the immiscibility of a polar nitrile rubber (NBR) that had been blended with pure and waste, low- and high-density polyethylene (PE). The effect of the weight percent of the rubber added to the PE was also investigated. It was found that a complicated variation (positive and negative) in both free-volume parameters (τ_3 and I_3) from the values of the initial polymers forms an immiscible blend. These results are supported by a significant broadening in the free-volume hole size distributions. This has been interpreted in terms of interfacial spaces created between the boundaries of the two phases. Furthermore, a correlation was established between the free-volume parameters (τ_3 and I_3) and the electrical and mechanical properties of the before mentioned polymer blends as a function of the weight percent of waste PE.

Keywords free-volume distribution, nitrile rubber, polyethylene, positron annihilation

1. Introduction

Recently, the use of recycled polymers, such as waste polyethylene (PE), has become one of the most important aspects of production that the industry must overcome concerning the problem of environmental pollution. This polymer can be consumed by blending it with other polymers to form new products with a wide variety of properties, and it has an economic impact.[1]

Polymer blends are of great industrial importance because they have different electrical and mechanical properties compared with their individual components.[2,3] On a molecular scale, different high-molecular-weight polymers have proven to be immiscible when mixed together, and they tend to separate into phases containing predominantly their own kind of polymers. Several researchers have expanded greatly on this subject.[4-6]

Mohammed et al.[1] have studied the immiscibility of nitrile rubber (NBR) as a polar polymer blended with pure and waste low-density PE (LDPE) and high-density PE (HDPE) by dielectric methods and by calculating the heat of mixing. They found that the addition of waste PE to NBR leads to better electrical and mechanical properties when compared with those for the blends having one pure component.

There exist many physical probes for characterizing the structures and properties of polymer blends.[5] However, only a limited number of probes are available for characterizing the free-volume properties due to the very small size and dynamic nature of the free volume.

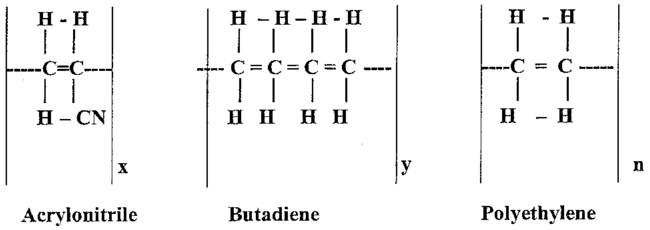

Fig. 1 Chemical structure of initial polymers in this study

Positron annihilation lifetime spectroscopy (PALS) is a unique probe for characterizing the free-volume properties of polymers.[7,8] In PALS, one employs the positron (i.e., an antiparticle of the electron) as a nuclear probe. Due to its positively charged nature, the positron is repelled by the ion cores that are localized in the atomic size, free-volume holes of the polymer. Therefore, the positron and positronium (Ps) (i.e., a bound atom that consists of a positron and an electron) annihilation signals are mainly generated from the free-volume holes in the polymer.

In the present work, PALS has been used to investigate the immiscibility of pure and waste LDPE and HDPE when blended with different volume percentages of NBR. The research also aimed to establish the correlations between the electrical and mechanical properties of the polymer blends with the microstructure free-volume properties as a function of the wt.% of the polymer blend.

2. Experiment

The materials used in this study were supplied by Petrochemical Department, Egyptian Petroleum Research Institute, Nasser City, Cairo, Egypt. The rubber used was NBR (68% butadiene acrylonitrile copolymer with 32% acrylonitrile). The blend preparation has been described elsewhere.[1] The chemical structures of the initial polymers used in this investigation (i.e., the NBR and the PE) are shown in Fig. 1.

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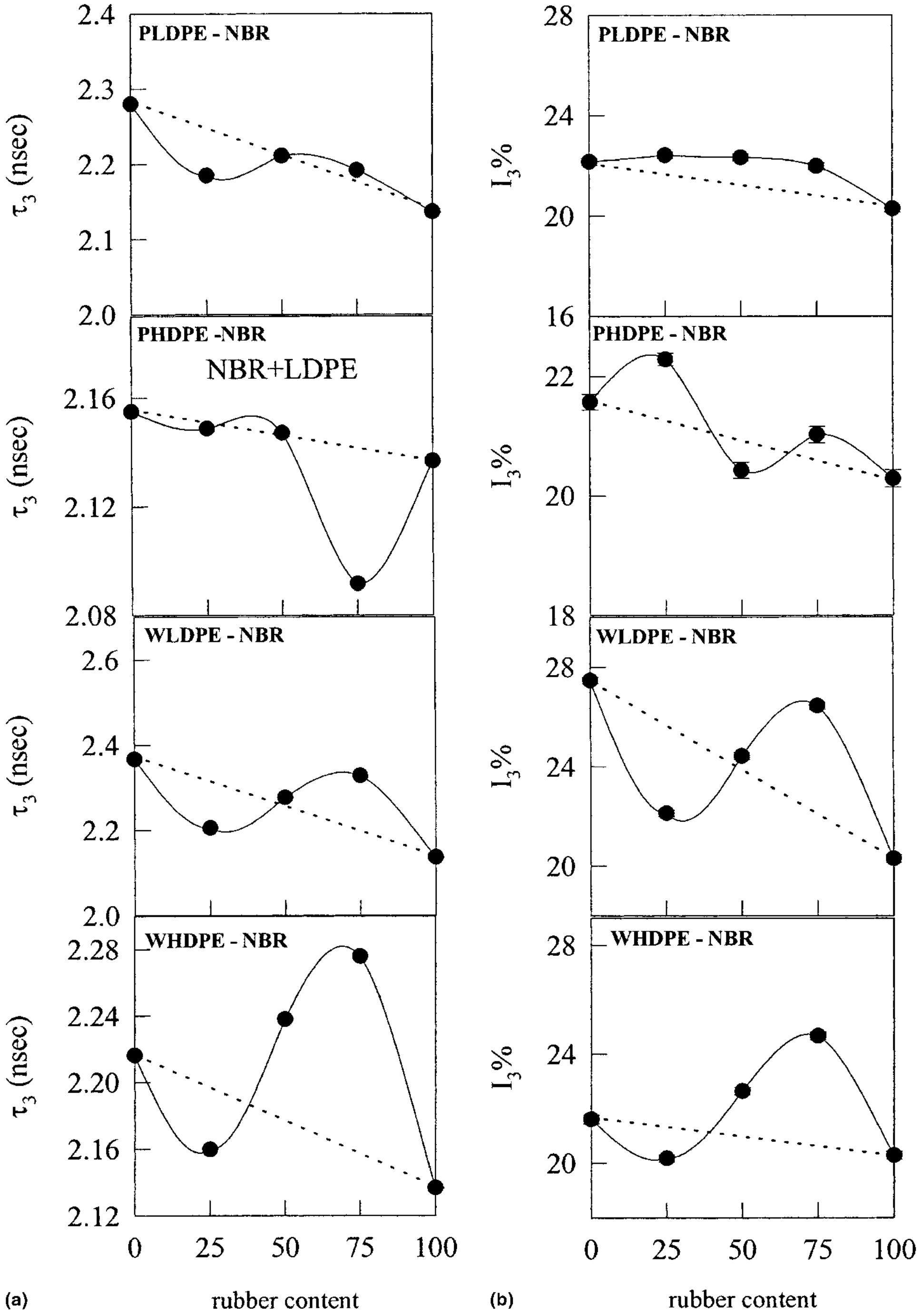

Fig. 2 (**a**) o-Ps lifetime τ_3 and (**b**) intensity I_3 of PE-NBR blends versus the wt.% of NBR. Solid and dashed lines are drawn through the points for clarity, and dashed lines represent the linear relationship.

Table 1 Positron and Ps lifetime results obtained by finite-term analysis in initial polymers

Polymer	τ_3, ns	I_3, %	R, Å	V, Å^3	f, %
LDPE (pure)	2.280 ± 0.011	22.159 ± 0.131	3.090 ± 0.08	124	4.9
LDPE (waste)	2.367 ± 0.009	27.465 ± 0.126	3.161 ± 0.08	132	6.5
HDPE (pure)	2.155 ± 0.010	21.570 ± 0.132	2.984 ± 0.09	111	4.3
HDPE (waste)	2.216 ± 0.019	21.613 ± 0.158	3.036 ± 0.08	117	4.6
NBR	2.136 ± 0.011	20.289 ± 0.145	2.968 ± 0.09	110	4.0

The positron annihilation lifetimes of polymer blends were determined by detecting the prompt γ-ray (1.28 MeV) from the nuclear decay that accompanies the emission of a positron from the ^{22}Na radioisotope and the annihilation of γ-ray (0.511 MeV). The positron lifetime measurements were performed in air at room temperature using a fast-fast coincidence system with a time resolution of 230 ps full width at half maximum (FWHM). A 20 μCi ^{22}Na positron source, which was held between 7 μm thick Kapton foils, was sandwiched between two identical pieces of the sample. PALS spectra, containing 10^6-10^7 counts, were collected for each sample. All PALS spectra were analyzed using the PATFIT program,[9] which is a finite-term lifetime analysis and continuous lifetime analysis program that uses the Laplace inversion program CONTIN.[10]

In the finite-term lifetime analysis, the following three lifetimes were obtained: the shortest lifetime component (τ_1 and I_1) is the lifetime and intensity of the parapositronium (p-Ps); the intermediate lifetime component (τ_2 and I_2) is the lifetime and intensity of the free positrons; and the longest lifetime (τ_3 and I_3) is the lifetime attributed to the ortho-positronium (o-Ps). In the PAL method, the results of the o-Ps lifetime were used to obtain the mean free-volume hole size through the use of a semiempirical equation.[7]

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

$R_o = R + \Delta R$, where $\Delta R = 0.166$ nm is the thickness of the homogenous electron layer in which the positron annihilates. The average of the free-volume hole size ($V_f = 4\pi R_3$) and its fraction (f = A I_3 V_f, where A is a constant equal to 0.01) which are probed by the o-Ps lifetime (τ_3) and its intensity (I_3) could be calculated.

The CONTIN program[10] was employed using the measured reference spectrum in Al. The free-volume hole radius distributions are then obtained by converting the o-Ps lifetime into R according to Eq (1) and the free-volume distribution function are calculated. Finally, the free-volume probability density function (V_f pdf) versus the free volume size V_f is obtained.

2.1 O-Ps Mean Lifetimes and Intensities (Free-Volume Parameters) of the Initial Polymers

Table 1 presents the free-volume parameters of the initial polymers. The o-Ps lifetime τ_3 and its intensity I_3 are related to the free-volume size and fraction, which are highly dependent on the chemical structure, the composition, and crystallinity of the polymer.[5] Once a positronium (Ps) is formed, the o-Ps seeks intermolecular spaces that are formed in amorphous regions of the polymer blend or the crystal-amorphous interfaces.[11] The results show that NBR has a slightly smaller size of free volume (110 Å^3) than the corresponding free-volume PE. This is due to the polarity of the nitrile group (C = N) in rubber, which is known to be electron attracting, and thus, reduces o-Ps formation as well as the triple bond between C and N, which restricts the free rotation leading to the reduction of 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. Therefore, τ_3 and I_3 in NBR are considered to be reduced due to the packing structures, becoming smaller than the corresponding values of PE.

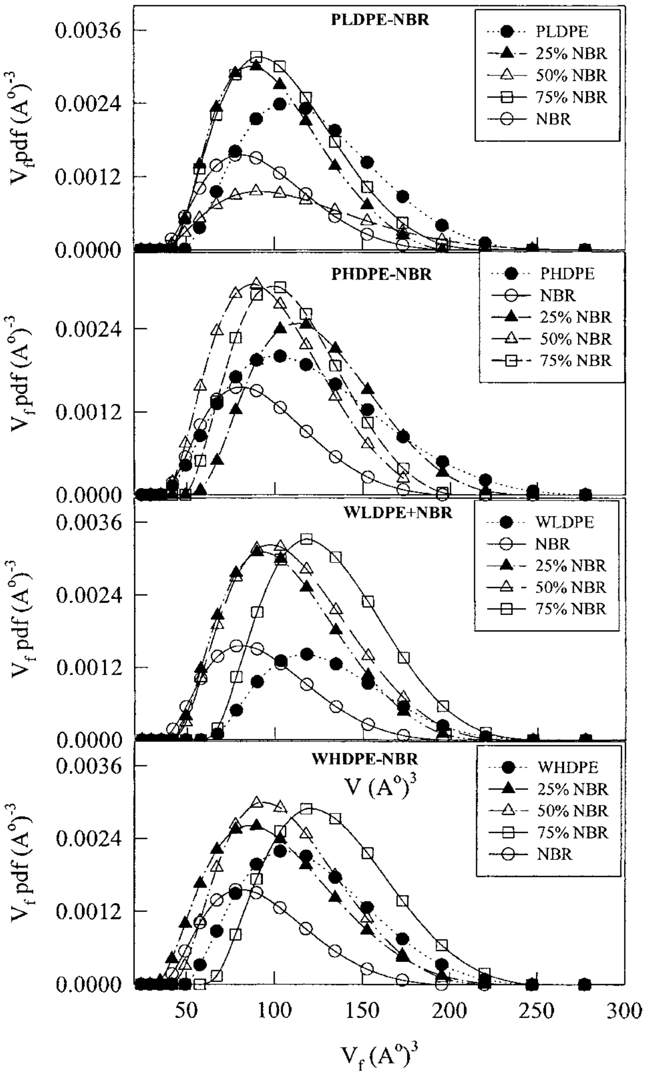

Fig. 3 Free-volume hole distributions of PE-NBR blends at different wt.% values of NBR.

On the other hand, the values of the o-Ps parameters (τ_3 and I_3) of waste PE are higher than those containing pure PE. This may be due to the difference in the degree of crystallinity which was found to be 60% for LDPE and 87% for HDPE, respectively.[1]

2.2 O-Ps Mean Lifetimes and Intensities (Free-Volume Parameters) of Blends

The results of o-Ps, lifetime τ_3, and intensity I_3, as a function of the wt.% of pure and waste PE-NBR in the polymer blend are shown in Fig. 2(a and b). In this case, τ_3 and I_3 changed (with respect to the linear relationship of the two initial polymers) from a negative deviation at a low wt.% in the NBR to a positive deviation for the high wt.% in the NBR-

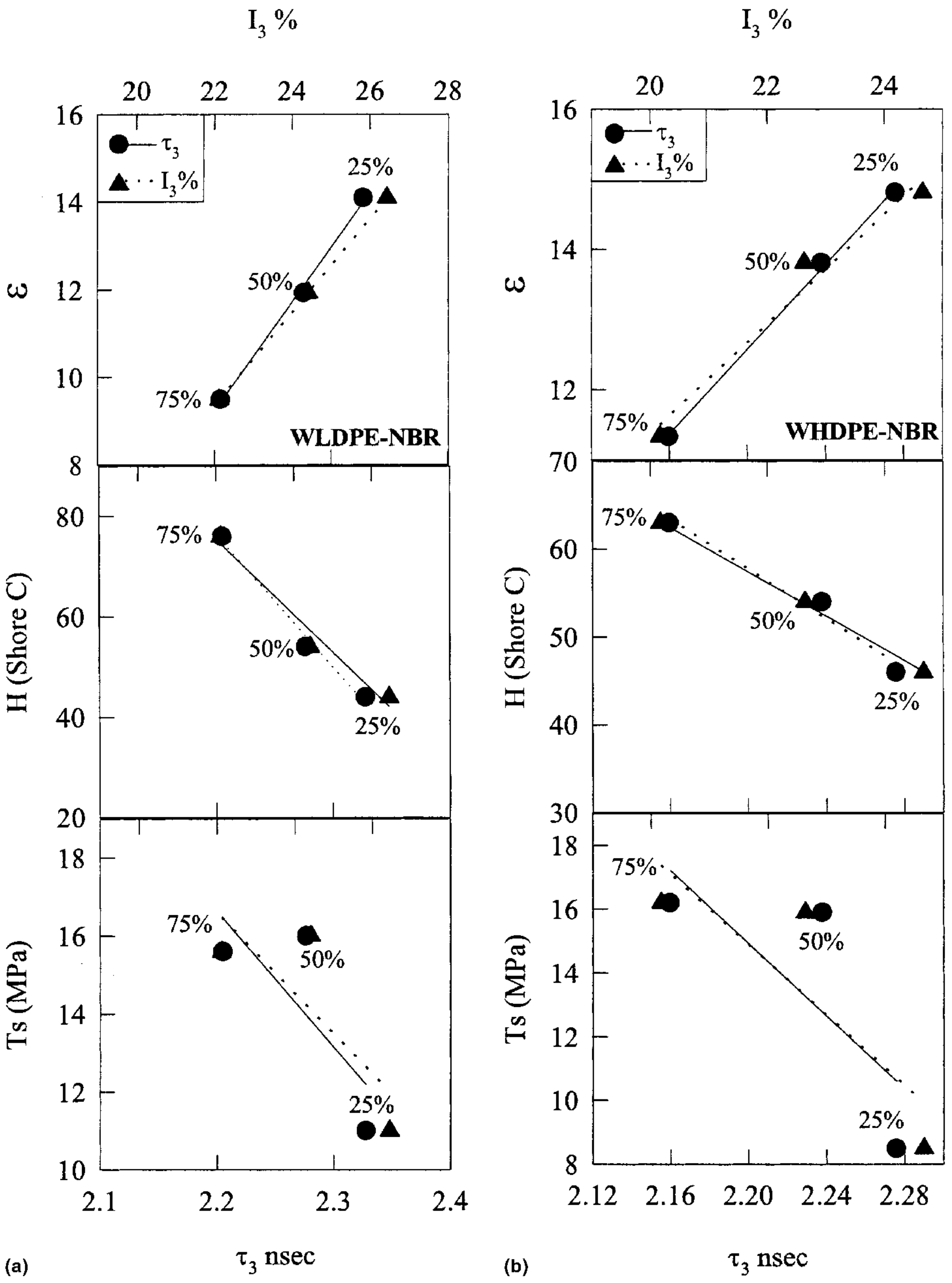

Fig. 4 Correlation between τ_3 and I_3, and ε, H, and Ts as a function of the wt.% of waste PE-NBR blends. Solid and dashed lines are drawn to guide the eye. (**a**) WLDPE-NBR, waste low density PE; (**b**) WHDPE-NBR, waste high density PE

waste PE blends. A maximum in o-Ps lifetime and intensity was observed at 75/25 NBR-waste PE blend, and a minimum at 25/75 NBR-waste PE blend.

The complicated behavior of the free-volume parameters (τ_3 and I_3) in NBR-PE blends results from the trapping and detrapping of positrons between free-volume holes and interfaces,[5] indicating that these blends are immiscible. In addition, phase separation has a stronger effect on the o-Ps formation. These results indicated the high sensitivity of the positron and o-Ps atom to interfacial spaces, created between the boundaries of the two phases.

2.3 Free-Volume Distributions in Blends

Figure 3 shows the results of the free-volume size distributions [V_f (pdf)] of pure and waste PE-NBR blends, including the initial polymers as a function of wt.%. The results showed the following:

- The free-volume hole sizes in blends are distributed between the higher and lower values of the corresponding values of the initial polymers.
- The free-volume distributions in the NBR-PE blend are broader than those of the initial polymer, which can be

attributed to the formation of interfacial regions between immiscible polymers, confirming the results obtained from the PATFIT analysis.

These distributions are expected to occur as a consequence of the different phases and interfaces present in the blend. This leads to the conclusion that studies of free-volume hole size distributions can give an indication of blend immiscibility on a molecular scale.

2.4 Correlation Between O-Ps Parameters (τ_3, I_3), and Electrical and Mechanical Properties in Waste PE-NBR Blends

The correlations among the permittivity (ε) at 1 KHz, the hardness (H), tensile strength (Ts), and free-volume parameters (τ_3 and I_3) of waste PE-NBR blends are shown in Fig. 4(a) and (b). The following observations were noted. 1) A negative correlation between ε and the free-volume parameters (τ_3 and I_3), in which the permittivity decreased as a function of the wt.% of waste PE, whether it is HDPE or LDPE. It is also clear that the values of ε for HDPE-NBR blends are slightly higher than those of LDPE-NBR blends, due to the higher degree of crystallinity of HDPE, which is responsible for the higher values of ε. Also, one can see that the waste HDPE-NBR blends are promising for electrical insulating purposes. 2) The increase in H and Ts was oppositely correlated with free-volume parameters (τ_3 and I_3) with the addition of NBR in the blends. Both H and Ts increase due to the addition of a large amount of waste PE, while τ_3 and I_3 decrease. This means that the mechanical properties (H and Ts) are improved by the replacement of NBR with about 75% waste PE, either LDPE or HDPE.

From these results, it is clear that the addition of waste PE in an NBR-PE blend leads to improvements in the mechanical and electrical properties of the polymers. There is no significant relationship for the case of pure PE-NBR blends.

3. Conclusion

In this study, it was reported that the free-volume parameters and the free-volume hole size distributions in NBR-PE blends are a function of blend composition. The results showed both positive and negative deviations for the free-volume parameters from the linear additive relationship in the blends with different rubber percentages. The broadening in free-volume hole distributions indicated the immiscibility in the blend and confirmed the validity of the results obtained by finite-term analysis.

The results also showed that the addition of waste PE in an NBR-PE blend leads to an improvement in the mechanical and electrical properties of the polymers.

PALS confirmed the conclusion that waste PE, which contributes a high risk of environmental pollution, can be consumed by blending it with rubber to form new industrial polymer blends that possess promising electrical and mechanical properties.

Acknowledgment

We are deeply grateful to IAEA Africa Section, Technical Support Department for providing the setup of positron annihilation techniques.

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