STUDY OF THE NANOSTRUCTURE CHANGES IN RUBBER /POLY (VINYL CHLORIDE) BLENDS BY POSITRON LIFETIME AND ELECTRICAL MEASUREMENTS

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Abstract: *During the last few decades many positron annihilation lifetime spectroscopy (PALS) measurements have been carried out for characterization of the microstructure of various polymeric materials. Characterization of free volume for nanostructure is important for the development of polymers with improved physical and electrical properties. In the present study the PALS technique was employed for studying the free volume content in the polymer blend system of poly vinyl choloride (PVC)and rubber. Positron annihilation lifetime spectra are usually resolved into three lifetime components. The longest lifetime component* τ_3 *and its intensity* I_3 *were used to determine the free volume parameters. The correlations between PVC content and each mean free volume hole size* V_f *and fractional free volume* f_v *were obtained by PALS measurements. In addition, the electrical measurements such as tracking time and resistivity of the blend system were discussed. Results of PALS measurements shows a slight decrease in the* V_f *parameter with rubber content in PVC, while the fraction* f_v *showed linear decrease. A correlation between the PALS and electrical measurements (tracking time) was found. Thus, this correlation could be used as a calibration curve for determination of the free volume parameters in a simple way.*

Keywords: Positron lifetime, PVC/rubber blends, Free-volume size, Free-volume fraction, Surface resistivity, Tracking time.

1. Introduction

In molecular materials such as polymers, the study of free-volume parameters plays a major role in investigations of various physical, mechanical and transport properties due to their sizes, distribution and number density. Polymer blends provide many useful properties which combine the properties of the individual components. Polyvinyl chloride (PVC) is one of the most valuable products of the chemical industry. It is a widely used building material and extensively used in pipe systems. It is used in magnetic stripe cards, plumbing fixtures and insulation on electric wires.(1) Due to the combination of reasonable mechanical, dielectric properties, and good chemical resistance rubber/PVC blends are becoming increasingly interesting for many electrical applications, including cable insulation and jacketing construction. (2-4)

Various nanostructures in materials, and particularly the free volume, can be effectively investigated by using the PALS techniques because of the high affinity to trap positrons. After injection of positrons from, e.g., ^{22}Na radioactive source into a condensed medium, they rapidly thermalize in the solid matrix. In molecular substances, thermalized positrons may then annihilate as free positrons in the molecular matrix with electrons into 2γ-photons. The mean lifetime of this free annihilation is <0.5 ns. Furthermore, a significant fraction of the injected positrons form positronium (Ps) with an electron (2-10), either in the matrix, at the matrix/free volumes interface, or within the free volumes prior to annihilation. This fraction of Ps is very sensitive to the structure of the material and, in particular, to the size and number of open volumes in the sample, since Ps can only form where there is a sufficiently large open volume to accommodate the Ps state. Ps can exist in two spin states: The singlet state called para-positronium (p-Ps), with anti-parallel spins and total spin zero, and the triplet state called ortho-positronium (o-Ps), with parallel spins and total spin 1. In a vacuum**,** the o-Ps decays via the emission of 3γ-photons and has a relatively long lifetime of ~140 ns. The p-Ps has a considerably shorter lifetime of ~0.125 ns and annihilates into 2γ-photons. In small holes, the o-Ps lifetime is reduced due to collision of thermalized o-Ps with an electron from the surrounding walls (pick off annihilation) and emits 2γ instead of 3γ-photons. These γ-rays carry information about the electron densities at the annihilation trapping sites (free volumes).

Tracking, a peculiar phenomenon of polymeric materials containing carbon atoms in their molecular structure, occurs on the surface because of the creepage discharge resulting from surface contamination. The materials therefore, lose its function as an insulator. It varies with surface field intensity, surface current magnitude and the state of discharges, all of which are due to the surface wetting and the degree of contamination.[9-10] Surface resistivity is the resistance to current leakage along the surface of an insulator. It is very sensitive to humidity, surface cleaning and surface contour.

We report here results on the use of the PALS technique in the study of the correlations between composition and positron lifetime parameters (lifetime, intensity, free volume size and fractional free volume) for rubber/PVC blends. Moreover, we present the influence of the changes in free volume properties (sizes and fractions) on the electrical properties such as tracking time and surface resistivity.

2. Experimental Procedures

Materials

All materials used were commercial products which were utilized in the experiment without further treatment. Blending of rubber/PVC with compositions of 100/0, 75/ 25, 50/50, 25/ 75 and 0/100 by weight were done in a laboratory at room temperature. The blended compounds were vulcanized in a hydraulically operated press at 160 ˚C and 100 minutes as the usual procedure. The samples were of thickness 2 mm and made of different shapes according to the test requirement.

PAL measurements

The PALS measurements were performed in air at room temperature (RT) using a conventional fast–fast coincidence system with a lifetime resolution of 255 ps. A 10 μ Ci positron source of $^{22}NaCl$ deposited on a thin Kapton foil (7.5 μm), was sandwiched between two identical polymer samples. The value of τ_1 was constrained at 0.175 ns. The PAL spectra were analyzed with LT-9 program. [11] More than 2×10^6 counts for each spectrum were satisfactorily and analyzed as three lifetime components as follows. The shortest lifetime component (τ_1, I_1) is ascribed to the p-Ps decay. In addition, the intermediate-lived (τ_2, I_2) and the long-lived (τ_3, I_3) components are attributed to free positron annihilation and o-Ps annihilation in the polymer matrix, respectively. Figure 1 shows the lifetime spectra for virgin PVC and rubber and rubber/ PVC blend samples.

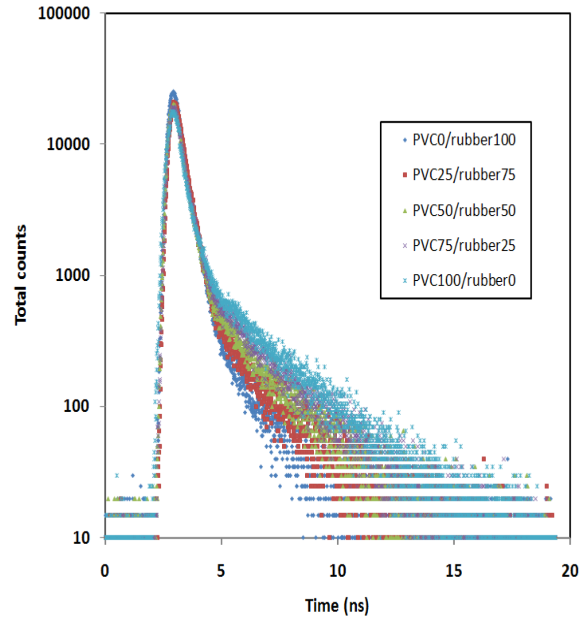

Fig.1. Typical PAL spectra for rubber/PVC polymer samples.

The o-Ps lifetime is determined by an overlap integral between the positron and the electron densities in the free volumes. The annihilation of o-Ps in a spherical free volume cavities can be described by a simple quantum mechanical model [12,13] which assumes the Ps atom to be localized in a spherical potential well having an infinite potential barrier of radius R with an electron layer of thickness ΔR,(R_o=R+ΔR). This model provides the relationship between the radius *R* of the free-volume hole and the *o*-Ps lifetime as

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \quad (1)$$

where ΔR (=1.656 Å) is an empirical parameter, which is determined by fitting the experimental values of τ_3 obtained for the materials with known hole size. [14-17] Since, the real volumes are not spherical but irregular shaped[18]. The rough estimation of the actual free volume size, V_f, is given by $\frac{4}{3}\pi R^3$

Furthermore, the fractional free-volume, f_v, can be used to understand the changes in the free volume fraction (free volume content) with the help of PAL measurements as follows: (7-8)

$$f_v = AV_f I_3 \quad (2)$$

where I_3 is the o-Ps intensity, which depends on the probability of o-Ps formation and the number density of free-volume holes. A is an empirical constant and its value ranges from 0.001 to 0.002 in common polymers. (7, 8, 15,16)

Electrical Measurements

According to the test method for evaluating resistance to tracking, IEC standard No. 587 test method, the tracking time (min) was determined at RT by using an AC supply voltage at 4.5 kV and frequency 50 Hz. The contamination condition was 0.1 % solution of ammonium chloride with a rate of flow of 0.6 ml/min whereas the length of the sample surface is 80 mm and its width is 40 mm. The conductivity of the contaminant was 2500 µS/cm. while the surface resistivity $\rho(\Omega.cm^2)$ was determined for different blends according to Standard Test Methods for DC Resistance of Insulating materials "ASTM D257-61".

3. Results and Discussion

Five different sets of samples having various weight percentages (0, 25, 50, 75 and 100) of rubber blended with PVC were subjected to PAL and electrical measurements. In polymers three positron lifetimes, τ_1, τ_2 and τ_3, are often obtained with values from 0.1 to 5 ns. (1-8)

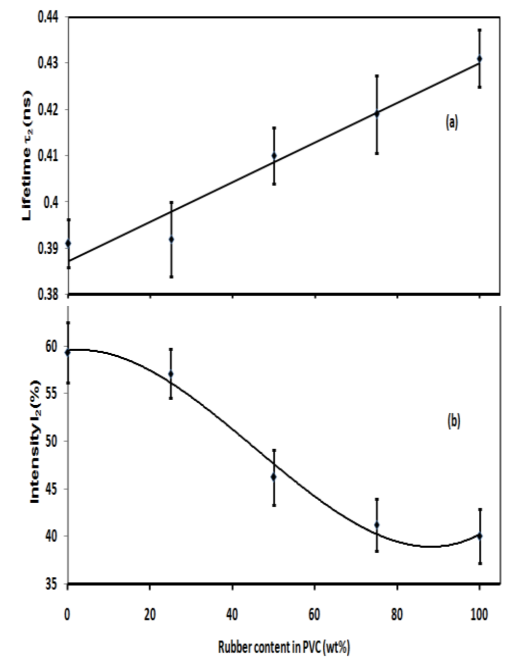

Fig. 2. Variations of second lifetime τ_2 and its intensity I_2 with rubber content in PVC polymer.

Figures 2a and b show the effect of the rubber content on the intermediate lifetime components τ_2 and I_2. The values of τ_2 linearly increased from 390 to 430 ps with the increase in rubber content (Figure 2a). Simultaneously, the intensity I_2 slightly decreased at 25 wt.% of rubber content and then significantly decreased to 75 wt.%. Beyond this rubber content, the intensity was saturated (Fig. 2b). The intensity I_2 is usually ascribed to the concentration of the annihilated free positrons in the crystalline regions or at the crystalline-amorphous interface boundaries; therefore, the component I_2 needs to be given special attention here because the values of I_2 are related to the defects density. Accordingly, the increase in τ_2 is related to an increase in large defects size by a decrease in the number of smaller defects. Hence, this leads to a decrease in the concentration of free positron annihilations I_2 with the increase in rubber content as shown in Fig. 2b.

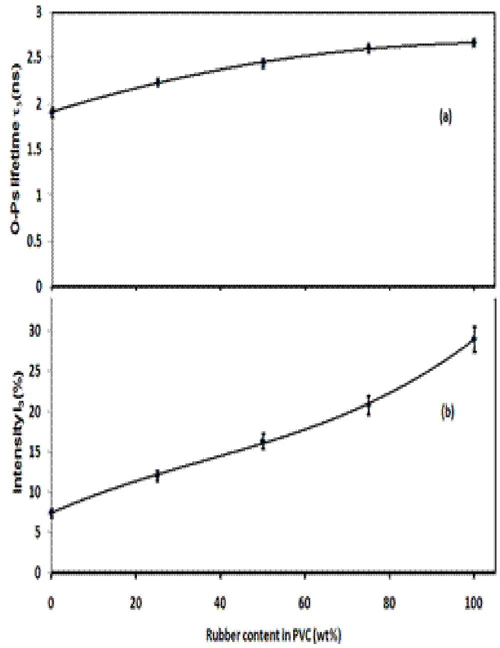

Fig. 3. Variations of o-Ps lifetime component τ_3 and its intensity I_3 with rubber content in PVC polymer.

Figure 3a and b show the variation of the o-Ps pick-off annihilation parameters (τ_3 and I_3) with the increase of rubber in the blends. It is observed from Figure 3a that a slight increase in pick-off lifetime τ_3 was observed from 1.91 to 2.67 ns. This long lived component which is ascribed to o-Ps annihilation occurs only within the amorphous regions. [2-8, 17-25] The dependence of the intensity I_3 on rubber content in PVC polymer is shown in Fig. 3b. The intensity I_3 is correlated to the probability of o-Ps annihilation and the number density (concentration) of free-volume holes.[2-6, 14-19] Figs. 4a and b display the variations of free volume size, V_f, and fractional free volume, f_v, with rubber content. The free volume size increased with the rubber content from 83 to 163 A^{o3}, as shown in Fig. 4a. Accordingly, a decrease in crosslinking for the polymer blend occurred. A similar result was obtained in an earlier work.[26,27] The lower crosslinking reduced rigidity of the PVC. From Fig. 4b one can observe a continuous increase in the calculated fractional free volume f_v with decrease in PVC content.

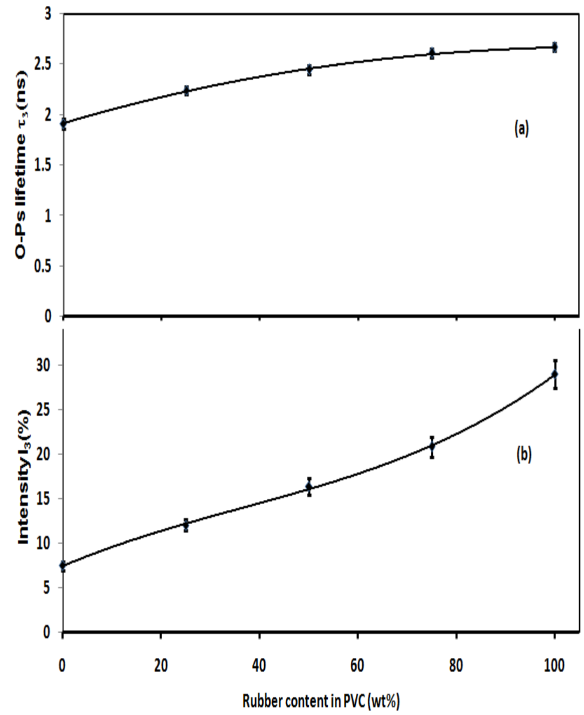

Fig. 4. Variations of free volume and fractional free volume with rubber content in PVC polymer.

Tracking is a process of formation of permanent conducting path across the surface of insulation due to surface erosion under voltage application. The tracking and erosion resistance is dependent on the chemical composition of polymers. The influence of the free volume size V_f on the electrical parameters, tracking time (T_t) and surface resistivity ρ of the present samples are shown in Figs 5a and b. It is observed from Fig.5a that, there is a positive correlation (r=0.99) between free volume size V_f and the track time for the rubber/ PVC blend samples. Accordingly, three times change in the track time (42 min) for the pure rubber corresponding to one time change (14 min) in case of the pure PVC samples. The insulation resistance which is the ratio of voltage applied to a sample to the current flowing in the sample that is made up of surface resistivity. A significant jumping in the resistivity is observed above rubber 75/ PVC 25 blend as in Fig. 5b.

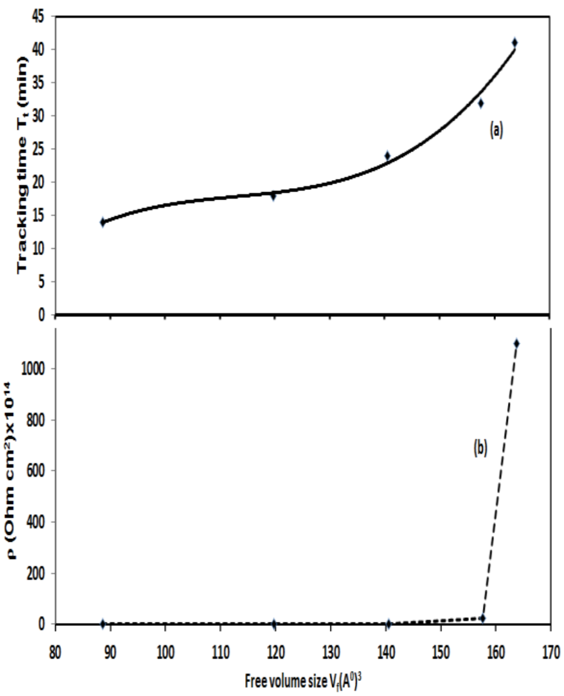

Fig. 5. Variations of tracking time, T_t, and surface resistivity, ρ, with free volume size for rubber content in PVC polymer.

The increase of free volume size with tracking time resulted in a increasing the scattering centers for the surface electrons. This reflected in jumping surface resistivity from the value of 23 X 10^{14} $\Omega.cm^2$ at 75% rubber content to 1100 X 10^{14} $\Omega.cm^2$ at pure rubber. The above correlation can be established as a calibration curve to determine the free volume size from the T_t measurements.

4. CONCLUSIONS

The PALS is a non-destructive technique provides information about nanostructure change of rubber/PVC blend through free volume measurements. The measurements showed that the free volume size for the blend decreased with increase the rubber content. Accordingly, the pure rubber has the highest free volume value (163$A^{\circ 3}$) compared to the lowest one (83$A^{\circ 3}$) which was found for pure PVC polymer. The fractional free volume gave the same behavior as the free volume size for the polymer blend. The electrical measurements for the blend show that existence of correlation between the tracking time and the free volume size measurements. This correlation can be used a calibration curve for determination the free volume parameters in simple way from electrical measurements.

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