

Study of Poly(vinyl chloride) Interfaces Using Slow Positron Beams

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ABSTRACT: Elemental and X-ray fluorescence analyses were performed to determine the chemical compositions of insulator and jacket poly(vinyl chloride) (PVC) samples. In addition, differential scanning calorimetry (DSC) measurement was performed to determine their glass-transition temperatures (T_g) and melting points. The effect of additives on the two investigated samples, as well as on a pure PVC sample, was studied using Doppler-broadening energy spectra coupled with the slow positron beam technique. Significant variation in the S parameter as a function of positron implantation energy and depth from the surface to

the bulk was observed in all samples. The S parameter increased at a very low positron energy (< 1 keV), saturated to about 6 keV, and then decreased up to 27 keV. The S parameter (ΔS) changed to the extent of the change in the breadth of the distribution of free-volume defects, which was larger in the jacket PVC sample, which had more additives, than in the insulator PVC sample. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3789–3793, 2006

Key words: poly(vinyl chloride) (PVC); additives; interfaces; free-volume

INTRODUCTION

Poly(vinyl chloride) (PVC) is commonly used in cable manufacturing in the production of either cable insulators or cable jackets because of its high strength and good insulation resistance.¹ The chlorine in PVC makes it a halogenated fire retardant polymer and more resistant to outside influences.² Recently, some additives have been added to PVC to minimize fire damage in electrical equipment.³ Many physical and fire characteristics of electric power cables made of PVC have been examined.^{4,5} A simulation of fire growth and propagation through PVC, which is used as an insulator and jacket fire retardant in power reactor cables, was performed.⁶

Positron annihilation spectroscopy (PAS) is a special nanoprobe that has been developed to directly determine the local free properties of polymeric materials. In addition, PAS is capable of determining the holes and free volume in a polymer without significantly interference by the bulk. It has been proven to be a direct and nondestructive probe for polymeric morphology studies.⁷ Positron annihilation lifetime spectroscopy can be used to measure the electrical and thermal properties of the fire retardant PVC, as well as the role of free volume as a function of temperature.^{6,8}

During the last 10 years there has been a steady growth in the application of slow positron annihilation spectroscopy to the study of free volume in polymers.^{9,10} In the present work, Doppler broadening of energy spectra (DBES) coupled with a slow positron beam were used to examine the defect profiles near the surface as well as in the bulk of two materials, PVC used as the insulator and as jacket cables, compared with those of a pure PVC sample. In addition, the concept of correlating physical defects such as free volume, holes, interfaces, and surfaces with the molecular structure and chemical defects of PVC materials was studied.

When a positron with well-defined energy is injected from a vacuum into a polymer, it either reflects back to the surface or penetrates the polymer. The fraction of positrons penetrating the polymer substrates increases rapidly as a function of positron energy. The mean implantation depth of the positron as a result of inelastic interactions with polymer molecules is expressed by the formula¹¹

$$Z(E_+) = (40 \times 10^3 / \rho) E_+^{1.6} \quad (1)$$

where z is expressed in nanometers, ρ is the density in kilograms per cubic meter, and E_+ is the incident energy in kiloelectronvolts. For example, in PVC samples with a density of 1.4×10^3 kg/m³ at an energy $E_+ = 1$ keV, the positron penetrated 29 nm from the surface.

After losing their kinetic energy, the positrons penetrating from the vacuum may either directly annihili-

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TABLE I
Physical and Mechanical Properties of Insulator PVC and Jacket PVC Samples

| Property | Insulator PVC | Jacket PVC |
|--|--|---|
| Color | Natural | Black |
| Density | $1.4 \times 10^3 \text{ kg/m}^3$ | $1.4 \times 10^3 \text{ kg/cm}^3$ |
| Tensile strength | 15 N/mm ² | 15 N/mm ² |
| Elongation | 200% | 200% |
| Hardness (Shore A) | 75–80 | 75–80 |
| Volume resistivity (at 20°C) | $1.5 \times 10^3 \text{ } \Omega\text{cm}$ | $1.5 \times 10^{3c} \text{ } \Omega\text{cm}$ |
| Dielectric rigidity (at 20°C) | 15 KV/mm | 15 KV/mm |
| Glass-transition temperature (T_g) | 85°C | 92°C |
| Melting point | 271°C | 273°C |

late surrounding electrons into two γ -rays or combine with an electron to form a positronium (Ps) atom.⁷ Ps formation is particularly important in polymeric and molecular materials. Ps atoms can be formed on most surfaces. There are two states of Ps: the singlet spin state, called para-positronium (p-Ps), and the triplet spin state, called ortho-positronium (o-Ps). The probability of the formation of these two states is 1:3. When p-Ps is localized in a defect with a dimension (Δx), the momentum (Δp) has a dispersion according to the Heisenberg uncertainty principle:

$$\Delta x \Delta p \geq h/4\pi \quad (2)$$

The S parameter from DBES spectra is a direct measure of the quantity of momentum dispersion. Although o-Ps has a longer lifetime in molecular substrates, neither its three-photon nor its two-photon pickoff annihilation contribute much to the current S parameter of DBES.⁹ Therefore, only the p-Ps part of Ps annihilation contributes to the S parameter of the DBES spectra. In addition, in a system with defects, the S parameter is a qualitative measurement of the free-volume defect size and concentration. The value of the S parameter also depends on the momentum of the valance electrons that annihilate the positron. On the other hand, the S parameter is also directly affected by Ps and positron diffusion behavior near the surface. Although both positrons and Ps atoms are known to localize in any defects, such as holes and free volume, a certain fraction may diffuse back to the surface and escape to the vacuum. Complete interpretation of the S parameter versus E_+ depends on the behavior and physical properties, mainly free-volume

defects, of both the positrons and the Ps atoms of a polymer.

EXPERIMENTAL

Two materials, insulator PVC and jacket PVC, were obtained from the Egyptian Electrical Cable Company (EECC; Cairo, Egypt). Some physical and mechanical properties of the two samples were tested in the EECC laboratory according to the American Society for Testing and Materials (ASTM) standards and are listed in Table I.

X-ray fluorescence analysis of the two materials was performed using DX4/RF/USR-type detector with an STD resolution of 157.9. Organic elemental analysis of the materials using a Schoniger flask was performed at the National Center for Radiation Research and Technology, Atomic Energy Authority (Cairo, Egypt). The results showing the weight percents of the different elements of the samples are listed in Table II. In addition, the T_g and melting point values of the investigated samples were measured using a Shimadzu-50, DSC-50 (made in Japan) in the temperature range of 0°C–400°C and are listed in Table I.

For the DBES experiments, a slow positron beam at University of Missouri, Kansas City (UMKC; Kansas City, MO), was used. The vacuum in the sample chamber was approximately 10^{-6} and 10^{-8} torr at high and low temperatures, respectively. The DBES spectra were recorded at room temperature (23°C) as a function of positron energy from 0 to 27 keV. The slow positrons were generated with a 15 mCi of ²²Na, moderated by the use of tungsten (W) foils, and electro-

TABLE II
Chemical Composition of Insulator PVC and Jacket PVC Samples

| Sample | Chlorine (%) | Calcium (%) | Lead (%) | Antimony (%) | Carbon Black (%) |
|---------------|--------------|-------------|----------|--------------|------------------|
| Insulator PVC | 1.85 | 1.16 | 4.57 | 0.00 | 0.00 |
| Jacket PVC | 1.84 | 0.71 | 13.89 | 2.45 | 42.5 |

magnetically transported to polymer samples. The DBES spectra were recorded using an HPGe detector (EG & G Ortec; with 35% efficiency and energy resolution of 1.5 keV at the 511-keV peak) at a counting rate of approximately 1500 cps. The total number of counts for each DBES spectrum was 0.3–1.0 million.

The insulator and jacket PVC samples, as well as the pure PVC sample, were measured by DBES. The DBES spectra obtained were characterized by an S parameter defined as the ratio of the integrated count between $E_1 = 509.45$ keV and $E_2 = 512.59$ keV (the central part) to the total count after the background was properly subtracted and is expressed as follows⁹:

$$S = \frac{\sum_{E_1}^{E_2} N(E_i)}{\sum_{E_i=0}^{\infty} N(E_i)} \quad (3)$$

Because the S parameter represents the relative value of the low momentum part of positron–electron annihilation radiation, it is sensitive to the change in positron and positronium states because of changes to its microstructure. When the positrons and Ps atoms were localized in a hole or in free volume with a finite size, the observed S parameter was a measure of the momentum broadening according to the uncertainty principle: a larger hole results in a larger S parameter.⁹

In addition, the change in the S parameter, ΔS , for both the insulator and the jacket PVC samples is calculated as follows:

$$\Delta S = S_0 - S_n \quad (4)$$

where S_0 is the S parameter of the pure PVC sample and S_n is the S parameter of the insulator and jacket PVC samples.

RESULTS AND DISCUSSION

From the organic elemental and X-ray fluorescence analyses (Table II), it is clear that the chlorine (Cl) concentrations of the insulator and jacket PVC samples were 1.85%, and 1.84%, respectively. Chlorine at these concentrations may be present as an additive or as a constitutive part of the polymer itself; this makes PVC a halogenated fire retardant polymer and more resistant to outside influence. That is because the chlorine atoms increase the attraction between chains of the polymer because of C=Cl dipolar,⁸ leading to a polymer of good mechanical and physical properties, as shown in Table I. Also, calcium (Ca) was added to both samples as filler, which gave the polymer a smooth surface.¹² A stabilizer such as lead (Pb) was added to PVC as an acid scavenger to prevent corro-

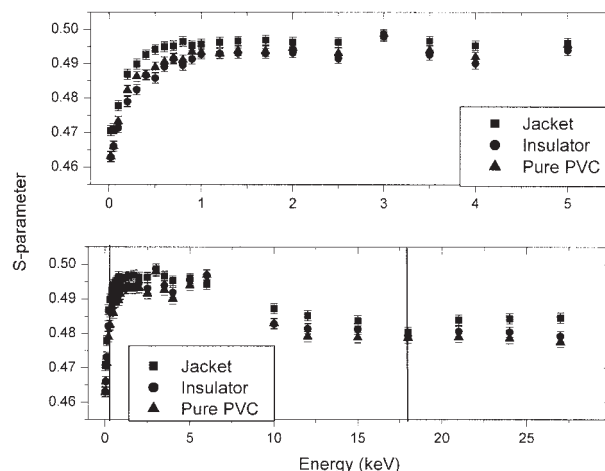


Figure 1 S parameter value versus positron incident energy for PVC samples.

sion of the metal conductor and further degradation of the polymer.³

In addition, the combination of antimony (Sb) with the jacket PVC sample is an important synergist that made the PVC more fire retardant.³ On the other hand, the addition of carbon black (CB) to the jacket PVC introduced an additional physical and chemical crosslinking, serving as an obstacle to segmental motion. It is used for reinforcement to give UV resistance as it absorbs UV radiation and inhibits decomposition of the polymer by sunlight.⁸ These two additives, in addition to the higher percentage of Pb (13.89%) additive in the jacket PVC, made its T_g and melting point shift higher than those of the insulator PVC, as listed in Table I. Accordingly, the T_g and melting point of both insulator and jacket PVC were higher than those of pure PVC, reported previously as $T_g = 80^\circ\text{C}$ and 185°C , respectively.¹³

The DBES experiment was performed on insulator and jacket PVC samples as well as on a pure PVC sample as a function of positron incident energy from 0 to 27 keV. Figures 1 and 2 show the S parameter results versus positron incident energy and mean depth of penetration for the three samples. The S parameter of the polymers depended on the fraction of positron stopped, the Ps formed in the holes, and the hole size.¹⁴ More Ps produces a larger S parameter. A decrease in free volume may reduce formation of Ps and hence reduce the S parameter. As shown in Figures 1 and 2, the jacket PVC sample had the highest S parameter. This illustrates that the highest concentration of free-volume hole size was in the jacket PVC sample. On the other hand, the distribution of free-volume defects was broader in the jacket PVC sample, which had more additives than the insulator PVC sample.

It was found for the S parameter of the three samples as a function of positron incident energy (E_+)

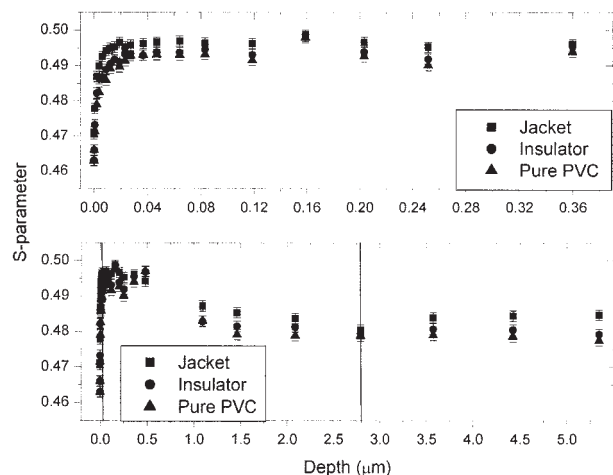


Figure 2 S parameter value versus mean depth of positron penetration for PVC samples.

that: (1) at very low energy, the S parameter increased, reaching its maximum at approximately 1 keV (≈ 27 nm); (2) after $E_+ = 1$ keV, the S parameter remained nearly constant up to about 6 keV ($\approx 0.481 \mu\text{m}$); (3) the S parameter then decreased, reaching a pure PVC value below 18 keV ($\approx 2.8 \mu\text{m}$); (4) the S parameter remained nearly constant below 18 keV in both pure and insulator PVCs, although it tended to increase in the jacket PVC sample.

Although the insulator and jacket PVC samples contained some additives, the increase in the S parameter versus E_+ near the surface can be attributed to the existence of a thin polymer layer, because their variation was similar to that on the surface of a pure PVC sample. The S-parameter data near the surface below 400 eV for pure PVC coincide nicely with the insulator and jacket PVC data. This is strong evidence that the surface of PVC is a thin polymer layer. The same behavior was observed in a series of polymer coating systems in a previous study.⁹ Following 400 eV of incident energy, the effect of the additives could begin to be seen from a depth of approximately 6 nm, where the increase in the S parameter of the jacket PVC sample, which contained a larger fraction of sub-nanometer free-volume defects was greater than that in the insulator PVC sample. The largest increase in the S parameter between 400 and 1 keV occurred 6–27 nm from the surface in all samples because of the larger fraction of positrons stopped and Ps formed in the polymer, leading to an increase in free-volume defects.¹¹

At a positron energy of more than 1 keV, the S parameter remained constant in each sample up to 6 keV at a depth ranging from 27 nm to $0.481 \mu\text{m}$, indicating that each sample had a constant number of free-volume defects in that depth range. The decrease in the S parameter in all samples from 6 to 18 keV in the depth range of 0.481 – $2.793 \mu\text{m}$ indicated a slightly lower number of free-volume defects than that in the

bulk (>18 keV). It was observed that at $E_+ = 18$ keV, the S parameters of the insulator and jacket PVC samples reached the value of pure PVC, indicating that the three samples had the same concentrations of free-volume defects at this depth ($2.79 \mu\text{m}$).

As the positron penetrated further into the bulk, increased Ps formation also was expected, which mainly contributed to the S parameter from p-Ps annihilation in the polymers. This behavior was obvious in the jacket PVC sample, as the S parameter started to increase at an energy of more than 18 keV, reflecting its much higher quantity of free-volume defects because its concentration of additives was higher than that in the insulator and pure PVC samples. The results indicated that the S parameter in the bulk of the jacket PVC sample (0.484 at 27 keV) was higher than that in both the insulator PVC (0.479 at 27 keV) and the pure PVC (0.477 at 27 keV) samples. In contrast, for all samples, the value of the S parameter in bulk was lower than that on the surface because when the positron energy increased, the number of free positrons escaping from the surface decreased.⁹

From the data on the PVC samples, it can be concluded that: (1) there was approximately 6 nm of polymer skin from the surface of the PVC samples; (2) inside the polymer skin there was an intermediate transition layer, where the additives started to disperse with the polymers; and (3) inside the transition layer was the bulk layer of the PVC samples (all shown in Figs. 1 and 2, where solid vertical lines represent the two boundaries separating the three layers of the PVC samples).

To quantitatively interpret the results, the change in the S parameter (ΔS) of the pure PVC sample compared to that of both the insulator and the jacket PVC samples was calculated according to eq. (4). Figures 3 and 4 also show the plots of ΔS versus positron energy

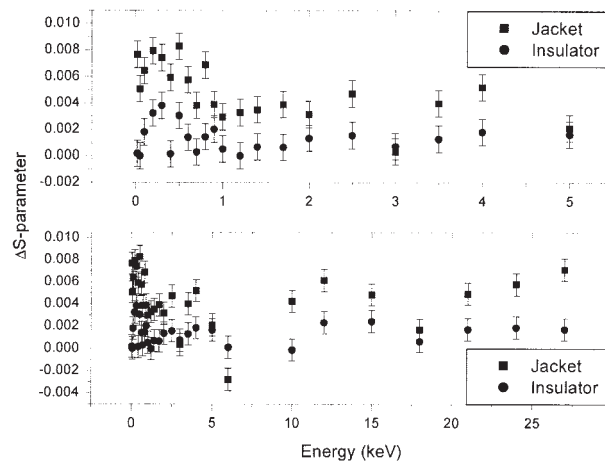


Figure 3 Differences in the S parameter value versus positron incident energy between the pure PVC sample and both the jacket and the insulator PVC samples.

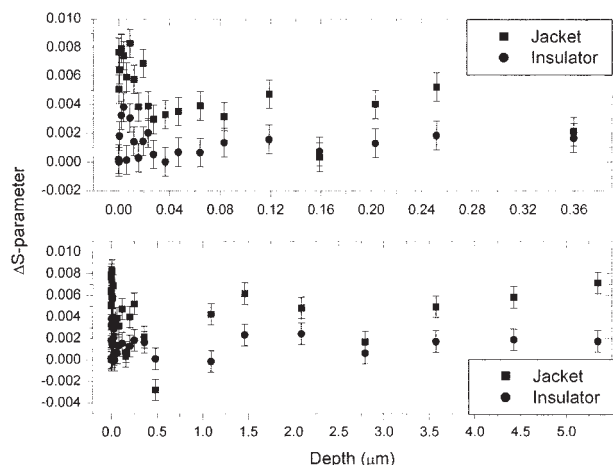


Figure 4 Differences in the S parameter versus mean depth of positron penetration between the pure PVC sample and both the jacket and the insulator PVC samples

at three depths: surface, near surface, and bulk. The ΔS parameter describes the change in the free volume of a polymeric material.¹⁴ In Figures 3 and 4, it can be observed that for the two samples, the ΔS value was small on the surface, increased below 1 keV, and saturated from 1 to 6 keV. As the positron penetrated the bulk, the values of ΔS for the two samples became coincident at $E_+ = 18$ keV and a depth of $2.8 \mu\text{m}$. After this, the ΔS of the insulator PVC saturated, whereas that of the jacket PVC increased significantly. It is obvious that the ΔS was affected by the additives, with the ΔS in the jacket PVC, doped with more fillers and stabilizers, higher than that in the insulator PVC in the positron energy and depth ranges studied. Additive molecules went between the tightly packed chains of PVC and dispersed in the polymer matrix, resulting in the formation of new bonds between the polymer chains. This changed the free volume of the polymer, leading to an increase in the ΔS that was larger for the jacket PVC than for the insulator PVC. On the other hand, there was a correlation between crosslinking and ΔS at different depths, as observed previously.¹⁴ This indicates that the change in the crosslinking density introduced by CB aggregates in the jacket PVC meant a change in the free volume. This led to a bigger increase in the ΔS of the jacket PVC than in that of the insulator PVC.

CONCLUSIONS

Doppler-broadening energy spectra coupled with the slow positron beam technique are capable of probing

free-volume defect profiles from the topmost layer (~ 6 nm) of a surface to the bulk layers ($\sim 5.3 \mu\text{m}$). The observed parallel variation in the S parameter in the pure, insulator, and jacket PVC samples was consistent with the view that this variation results from the change in the concentration of free-volume holes due to additives. Variation in the S parameter as an indicator of a PVC polymer skin layer and a transition layer ($2.8 \mu\text{m}$) entering the bulk of the PVC was interpreted. The results indicated that at 27 keV the S parameter in the bulk of the jacket PVC (which had high additives) and the insulator PVC was 0.484 and 0.479, respectively, whereas it was 0.477, the lowest value, in pure PVC. The higher level of additives introduced into the jacket PVC had a significant effect on the ΔS , especially in the bulk.

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