Effect of Adding Feldspar on Free Volume Properties of Crosslinked Polyester Studied by Positron Annihilation Lifetime Spectroscopy

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ABSTRACT: Positron annihilation lifetime spectroscopy (PAL) was applied to study the feldspar effect on the free volume properties of crosslinked polyester based on neopentyl glycol, succinic acid, phthalic anhydride, and maleic anhydride. The measurements have been carried on the polyester resin samples cured with three crosslinking agents namely styrene (SS) or styrene/methyl methacrylate (SM) or styrene/acrylonitrile (SA) comonomers mixtures in the ratios of 2 : 1 and loaded with different concentrations of feldspar in the range from 0 to 80 wt %. The free volume parameters (size and fractions of holes) depend on type of the crosslinking agent as well as the feldspar content added to the polyester. The results are supported by a significant variation in the nanoscale free volume hole size distributions. Moreover, the correlation between positron annihilation parameters and electrical parameters was discussed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3142–3146, 2012

Key words: polyester; positron annihilation; feldspar; free-volume; crosslinking agents

INTRODUCTION

Polyester composites are of great industrial importance because of their excellent electrical, mechanical, and chemical properties.[1] The main effect of the introduction of filler, such as feldspar, into polyester is to reduce the cost, cracking, shrinkage, and to modify the physical properties and appearance of the polymers. Feldspar is an abundant group of rock-forming minerals that constitutes 60% of the earth's crust and it is a very useful industrial mineral.[2]

Mansour et al.[1] have studied the effect of feldspar content and type of crosslinking monomer on the electrical and mechanical properties of polyester composites. The authors found that the addition of feldspar to polyester led to better electrical and mechanical properties, when compared with the cured polyester. They also used IR and ^{1}H-NMR spectroscopy to characterize the chemical structure of the prepared polyester.

There exist many physical probes for characterizing the structure and properties of polymer composites. 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.

Positron annihilation lifetime spectroscopy (PALS) has been successfully applied to measure the free volume holes in polymers.[3–6]

The objective of this work is to study the relation between the changes in the nanofree volume properties with the electrical and mechanical properties of polyester composites. At this stage, we are especially interested in how the properties of the free volume change when feldspar is added to the polyester matrix.

EXPERIMENTAL

Materials

An unsaturated polyester resin was synthesized with a 2.2 : 0.5 : 0.5 : 1 molar ratio of neopentyl glycol, succinic acid, phthalic anhydride, and maleic anhydride, respectively, with a one-step melt condensation technique. The details of the used polyester and their composites can be found elsewhere.[1]

The polyester resin was crosslinked with 30 wt % styrene monomer (SS) or styrene/ methyl methacrylate (SM) or styrene/acrylonitrile (SA) comonomers mixtures in the ratios of 2 : 1. Curing occurred after the mixtures were left at room temperature overnight followed by 2 h at 80°C in a thermostated oven. Different ratios of feldspar filler (fine-grade 0.1 mm, 100 mesh, obtained from El Nasr Phosphate

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Company, Cairo, Egypt), were used at concentrations 60, 70, and 80 wt % in the preparation of different polymer composites.

PAL measurements

The PALS measurements were performed in air at room temperature using a fast–fast coincidence system with a time resolution of 260 ps full width at half maximum (FWHM). A 20 μCi ^{22}Na positron source was deposited on Kapton foil (7 μm thick) and then sandwiched between two similar samples of the particulate composite.

When a positron is injected into polymers, it interacts with molecules by an inelastic collision process leading to their ionization and excitation and it quickly reaches thermal energies.[3,7] During thermalization, the positron may annihilate with an electron from the material in free state or it may form, with the electron, a bound state called positronium (Ps) and then annihilation from the bound state takes place. Ps has two ground states called para-positronium (p-Ps), in which the positron and electron spins are antiparallel and decays with a lifetime of 125 ps, and the second form ortho-positronium (o-Ps), where the particles have parallel spins and have a mean lifetime of 142 ns in vacuum. In polymer this long o-Ps lifetime is shortened to 1–5 ns due to the pick-off of the positron by an electron of antiparallel spin in the surrounding medium.[8] o-Ps is preferentially trapped or formed in free volume holes or cavities where electron density is low. Since the o-Ps annihilation rate is proportional to the overlap of the positron and pick-off electron wave functions, it is logic to expect that the o-Ps lifetime (τ_3) is strongly dependent on the size of the free volume holes (V_f). Accordingly, the free volume hole radius, R, can be calculated from the value of τ_3 using a semiempirical equation given by Eldrup et al.[9] and Toa[10]:

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

Where $\Delta R = 1.656$ Å is the electron layer thickness around the hole.[8] Using the values obtained for the radii from Eq. (1) the size of the free volume holes can be calculated from: $V_f = (4/3)\,\pi R^3$. On the other hand, the intensity of o-Ps is directly related to the number of free volume holes.[4]

Therefore, pick-off annihilation of o-Ps in polymers can be interpreted as an indication of the change in average size and the number of free volume holes.[11]

Mechanical and electrical measurements

Compressive measurements were carried out according to ASTM D 695 with an Instron universal testing instrument (model 1178) (Norwood, MA) on cylindrical rods 2.5 cm long and 1.3 cm in diameter.

Dielectric measurements were carried out in the frequency range 100 Hz to 100 kHz with an LCR meter type AG-411 B (Ando Electric, Tokyo, Japan). The capacitance, loss tangent, and resistance were obtained directly from the bridge from which the permittivity (ε'), the dielectric loss (ε''), and direct current conductivity (σ) were calculated. A guard ring capacitor type NFM/5T (Wiss Tech Werkstatten GMBH, Weilheim, Germany) was used as a measuring cell. The cell was calibrated with standard materials, and the experimental error in $\varepsilon'$and ε'' was ± 3 and ± 5%, respectively.

Since, the compressive strength, the permittivity (ε'), the dielectric loss (ε''), and electrical conductivity (σ) data for crosslinked polyester and its composites have been published already[1] only some results will be given here to establish a correlation with PALS data.

RESULTS AND DISCUSSION

PAL measurements of the crosslinked polyester and its composites samples were analyzed into three lifetime components using LT9.0 program.[12] These three lifetimes are generally attributed to different states of positron annihilation as follows: the shortest lifetime component (τ_1) with intensity I_1 is corresponds to p-Ps. The intermediate component τ_2 with intensity I_2 is due to the positrons trapped in the defects present in the crystalline regions or in the crystalline-amorphous interface regions of the polymer composites. The longest lifetime component τ_3 with the intensity I_3 is assigned to the pick-off annihilation of o-Ps in the free volumes holes available mostly in the amorphous regions of the polymer matrix.

Figure 1(a,b) shows the variation of o-Ps lifetime components (τ_3 and I_3) and the free positron annihilation components (τ_2 and I_2) for the cured polyester with different crosslinking agents (SS, SM, and SA) and its composites with different concentrations of feldspar which provides information on the microstructural changes in amorphous and crystalline-amorphous interface regions of polymer, respectively. By comparing the three crosslinked polyester (SS, SM, and SA), one can find that, the values of τ_3 and I_3 in SS cured sample is higher than the corresponding values of SM and SA. This means that free volume hole size and its fraction in SS are higher than the other ones. However, addition of styrene/methacrylate (SM) or styrene/acrylonitrile (SA) mixture to the polyester increases the crosslinking density of it which appears as a decrease in free volume holes size and its fractions in SM and SA cured samples. In addition high polarity for the SM and SA

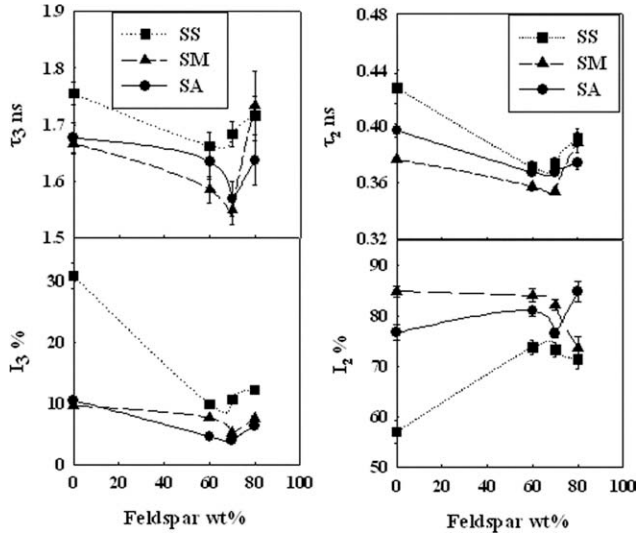

Figure 1 The variation of τ_3, I_3, τ_2, and I_2, with feldspar wt % for polyester composites (SS, SM, and SA).

system and high reactivity of the polar crosslinking agents increasing the crosslink density which inhibits o-Ps formation (I_3) in amorphous regions and increases probability of free positron annihilation (I_2) in crystalline-amorphous interface regions as shown in Figure 1(b).

On the other hand, the values of positron annihilation parameters (τ_3, I_3, τ_2, and I_2) are higher in plain crosslinked polyester than in polyester samples containing feldspar [Fig. 1(a,b)]. That is because when a filler is added into the polyester, more trapping potentials are created that decrease the probability of o-Ps formation (I_3) and result in more annihilation with free positrons (I_2).[13,14] Therefore, I_2 shows the opposite trend of I_3. In addition, low values of I_3 suggest low probability of o-Ps formation because of the strong polarity of crosslinked polyester molecules and due to the presence of polar groups in that filler which acts as Ps quencher. Furthermore, the variation in τ_2 shows the same trend of τ_3 which indicates small open volumes in this region which are affected by the addition of feldspar to the polyester. Consequently, the interaction between the matrix and the randomly distributed filler particles can restrict the main-chain segmental motion and reduce mobilization in polyester matrix, which can reduce the free volume hole size and its fraction.[6] Therefore, Ps formation occurs only at these free volume sites at the end of major chains and at side chain, where the electron density is relatively low.[15]

Also, it can be observed that both τ_3 and I_3 decrease sharply for feldspar concentrations less than 70 wt % while they increase for higher concentrations. This fact indicates that the feldspar mainly diffuses into the amorphous region and the concentration at 70 wt % is an inflection point. Also Mansour et al.[1] showed that the best physical and chemical properties are obtained for polyester composites containing 70 wt % feldspar. Generally, all the polyester samples containing feldspar sequences exhibit low values of o-Ps lifetime (τ_3) and Ps fraction (I_3) which can be explained by the improvement of chain packing due to the presence of feldspar in the polymer matrix.[15]

The probability density distribution V_f pdf in the three crosslinked polyester (SS, SM, and SA) as a function of V_f is shown in Figure 2(a). From this figure, it can be noticed that the average free volume hole size of SS ($\sim$ 74.5 Å) is higher than SM ($\sim$ 66.9 Å) and SA ($\sim$ 67.8 Å). This is due to the higher crosslinking density and the polarity of SM and SA systems which reduce the free volume size and inhibit o-Ps formation. The free volume distribution functions with feldspar content from 0 to 80 wt % are plotted in Figure 2(b–d). As shown in this figure, there exists a decrease in the size of the free volume holes to 66.6, 60.2, and 64.3 Å at 60 wt % of filler content in SS, SM, and SA composites, respectively,

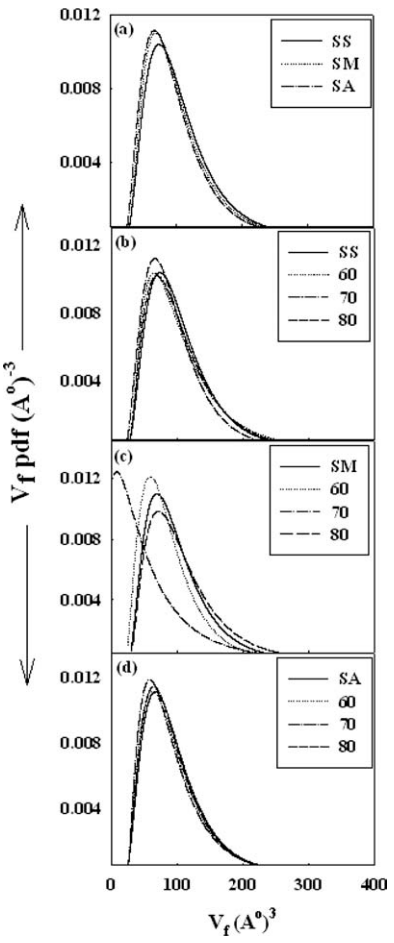

Figure 2 The probability density distribution V_f pdf for crosslinked polyester as a function of V_f.

from the corresponding values of unfilled polyester. After the feldspar atoms link to polymer chains and fix them together, mobility is decreased significantly. Because of this effect the average size of the free volume holes becomes smaller all over the polymer composites.

Figure 3 shows a negative correlation between free volume parameters (V_f and I_3%) and electrical parameters (ε′, ε″, and σ) of polyester composites (SM was chosen as a representative case). As shown in Figure 3 the values of electrical parameters are higher at low free volume hole size (V_f) and fraction (I_3%) which correspond to high concentration of feldspar content (70 wt %). This is due to the presence of polar group in feldspar which increased the values of electrical parameters and inhibited Ps formation leading to a decrease in values of free volume parameters.

Figure 4 represents the correlation between free volume parameters (V_f and f%) and the compressive strength values. The compressive strength has a strong correlation with V_f and f%. The compressive strength values of the crosslinked polyester were comparatively higher than that with feldspar filled polyester. This may be due to the incorporation of the feldspar which reduced the volume fraction of the matrix.

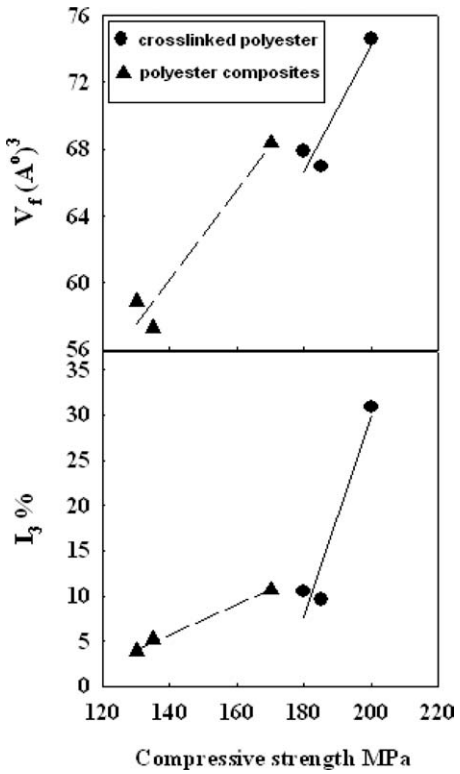

Figure 4 Correlation between compressive strength values and free volume parameters (V_f and I_3) for polyester composites (SS, SM, and SA).

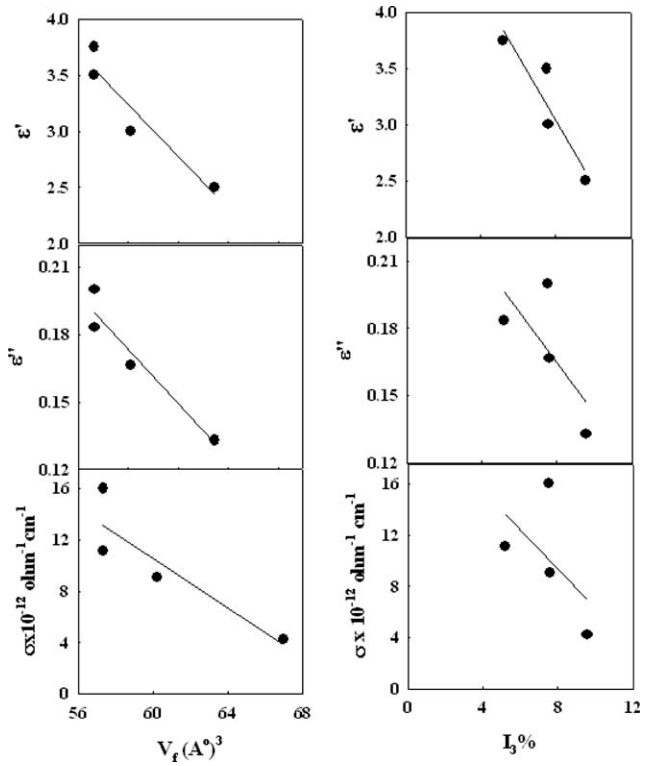

Figure 3 Correlation between electrical parameters (ε′, ε″, σ) and free volume parameters (V_f and I_3) for polyester composites (SS, SM, and SA).

CONCLUSION

The free volume, the electrical and mechanical properties of the studied polyester composites are influenced first of all by the type of crosslinking agents and content of the filler. Correlation between the free volume parameters and the electrical and mechanical properties showed that, the polyester composites exhibited good electrical properties at small free volume hole size and low fraction while the reverse correlation is observed for mechanical properties. Furthermore, PALS data support the results obtained in the previous study which showed that the best results were obtained for polyester composites containing 70 wt % feldspar.

References

1. Mansour, S. H.; Asaad, J. N.; Abd-El-Messieh, S. L. J Appl Polym Sci 2006, 102, 1356.
2. Kauffman, R. A.; Van Dyk, D. Industrial Minerals and Rocks, 6th ed.; Society for Mining, Metallurgy and Exploration: Littleton, CO 1994; p 473.
3. Jean, Y. C. In Positron Spectroscopy of Solid; Dupasquier, A.; Mills, A. P., Jr., Eds.; IOS Pub: Amsterdam, 1995; p 563.
4. Jean, Y. C. Microchem J 1990, 42, 72.
5. Mohsen, M.; Aly, E., Gomaa, E.; Hegazy, A.; Mahmmoud, G. A. J Mater Sci Eng 2010, 4, 75.

6. Mansour, S. H.; Gomaa, E.; Bishay, I. K. J Mater Sci 2007, 42, 8473.
7. Zengeni, E.; Hartmann, P. C.; Sanderson, R. D.; Mallon, P. E. App Poly Sci 2011, 119, 1060.
8. Scharder, D. M.; Jean, Y. C. Positron and Positronium Chemisitry; Elsevier: Amsterdam, 1988.
9. Eldrup, M.; Lightbody, D.; Sherwood, J. N. Chem Phys 1981, 63, 51.
10. Tao, S. J. J Chem Phys 1972, 56, 5499.
11. Ashalatha, M. B.; Sathyanarayana, P. M.; Shariff, G.; Thimmegowda, M. C.; Ramani, R.; Ranganathaiah, C. Appl Phys 2003, A76, 1.
12. Kansy, J. Nucl Instrum Methods Phys Res 1996, A374, 235.
13. Danch, A.; Osaba, W. Desalination 2004, 163, 143.
14. Wang, J.; Vincent, J.; Quarles, C. A. Nucl Instr Meth 2005, B241, 271.
15. Gomaa, E.; Hassan Aly, E.; Mohsen, M. J Polym Sci Part B: Polym Phys 2009, 47, 227.