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Effect of metal type and content on mechanical, electrical and free-volume properties of styrenated polyesters

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Abstract This work is concerned with the preparation and characterization of composite materials prepared by molding a mixture of filler and styrenated polyesters. Positron annihilation spectroscopy (PAS) coupled with electrical and mechanical measurements have been used to investigate the effect of different fillers such as Cu, Al and Zn on some properties of styrenated polyesters. It has been found that, the permittivity (ε'), dielectric loss (ε'') and the conductivity (σ) increase by increasing the Cu and Al content in the two styrenated polyesters (PE1and PE2) while no significant effect is noticed in case of Zn content. On the other hand, the 10% as well as 20% of filler content is found to be an onset point at which a change in the variation trend of tensile strength and hardness occurs. Furthermore, the free-volume hole size (V_h) and its concentration (f) showed a decrease with increasing the amount of filler, except at 10% filler V_h showed an increase. These variations were interpreted in terms of the free-volume distributions and the correlation of free-volume parameters with conductivity (σ) and hardness.

Introduction

Metal–polymer composites have drawn considerable attention, due to the ease with which the polymer properties can be modified to achieve properties of both metals and polymers [1–5]. The physical and mechanical properties of the composite materials depend on the type and the volume fraction of the fillers and additives, such as metal or ceramic, as well as on the interfacial compatibility between the metal particles and the matrix [6, 7]. Some fillers and additives are introduced to the polymer to improve thermal and electrical conductivity, and to stiffen the matrix [8].

Various kinds of polymers and polymer matrix composites reinforced with metal particles have a wide range of industrial applications, because of their low density, high corrosion resistance, ease of fabrication, and low cost [9–11].

Polymeric thermosets are important class of materials from both academic and technological points of view. Unsaturated polyester cured with styrene monomer is a typical widely used resin in coating and composite technologies [12–14].

The free-volume concept plays an important role in polymer research and is widely used to describe and explain the behavior of physical properties [15]. The influence of the type of polymer matrix and filler on the electrical characteristics and free-volume properties of the composite has been studied in many works [16, 17].

Positron annihilation spectroscopy (PAS) has a high sensitivity for probing nanoscale size and concentration of the free-volume holes as well as electronic structure of materials through measurements of positron lifetime and momentum distribution of annihilation positron–electron pairs [18]. The positron annihilation lifetime (PAL) technique provides information about electron densities and the Doppler broadening of annihilation radiation (DBAR)

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measurement gives only qualitative information about the momentum density for materials under study [19]. In polymers, a fraction of positrons forms the positron–electron bound state known as positronium (Ps). Singlet para-positronium (*p*-Ps) with antiparallel spin orientation and triplet orth-positronium (*o*-Ps) are formed at a ratio of 1:3. The lifetime of *o*-Ps and the momentum distribution of *p*-Ps give information on the free-volume. Therefore, PAS has been applied to probe the free-volume properties and its distribution in polymer composites.

In the present study, copper, zinc and aluminum powders with different concentrations were used as fillers. Two commercial styrenated polyester resins were used as matrices. The influence of metal type and content on the mechanical, electrical and free-volume properties of the composites was studied. The ultimate objective of this study is to characterize the correlation between changes in free-volume with electrical conductivity and hardness of the samples being studied.

Experimental

Materials

Two different unsaturated polyester resins [2121P-1(PE1) and 2504APT-S (PE2)] supplied by Eternal Chem. Co., Kachsiung, Taiwan were used. The resins supplied already dissolved in styrene.

The physical properties of the polyester resins PE1 and PE2 are listed in Table 1.

The fine grade of metals with average particle size varies between 60–75 nm for copper (Cu), 260–280 nm for zinc (Zn) and 100–120 nm for aluminum (Al) were obtained from BDH chemicals Ltd, Poole, England.

Preparation of polymeric composites

Polymer composites were prepared by mixing different ratios of each metal (10–40 wt%) with unsaturated polyester/styrene mixture as provided from Eternal Chemical Co. 1.5% by weight of methyl ethyl ketone peroxide (MEKP) as initiator and 0.25% by weight a solution of 8% cobalt naphthenate as promoter in all cases. The prepared composites were left at room temperature (25 °C ± 1) until curing occur.

Table 1 Physical properties of PE1 and PE2

Property	PE1	PE2
Appearance	Faint blue—clear	Pink turbid
Specific gravity at 25 °C	1.11	–
Viscosity–Brook field at 25 °C	300–400	350–450
Acid value mg KOH/g	11–21	–
Styrene monomer content in resin (by weight)	36–39%	37.5–41.5%

Tensile measurements

Kinston 5500R universal testing machine was used for determining the tensile strength of the samples according to ASTM D 638 (2000). In our measurements the extension rate used was 12 mm/min. The accuracy of elongation measurements amounts to about ±1%.

Hardness measurements

Hardness was measured by the Universal testing machine (HPO 3000), Japan, using the average multiple readings for each specimen.

Dielectric measurements

Dielectric measurements were carried at frequency 100 Hz and at room temperature by using an LCR meter type AG-411 B (Ando electric Ltd. Tokyo, Japan). The capacitance (C), the loss tangent ($\tan \delta$) and the resistance R obtained directly from the bridge from which the permittivity (ε'), dielectric loss (ε'') and the dc conductivity σ were calculated. A guard ring capacitor type NFM/5T Wiss Tech. Werkstatten (WTW) GMBH, Weilheim, Germany was used as a measuring cell. The cell was calibrated using standard samples with known permittivity [20].

Positron annihilation lifetime (PAL) measurements

The PAL measurements were performed in air at room temperature using a fast–fast coincidence spectrometer having a time resolution of 266 ps full width at half maximum (FWHM). This lifetime spectrometer employed two plastic scintillation detectors mounted on photomultipler tubes, one with an energy window set for the 1.27 MeV γ-rays from ^{22}Na to provide a start signal and the other with an energy window set for 0.511 MeV annihilation γ-rays from the sample to provide a stop signal. The positron lifetime is the time difference between the birth γ-ray and one of the annihilation γ-ray of energy 0.511 MeV. A 20 μCi ^{22}Na positron emitter source was deposited on Kapton foil and then sandwiched between two identical pieces of the sample. All of the PAL spectra were analyzed by using the computer program LT 9.0 [21] which allows both discrete and long normal distribution of annihilation rate $\lambda = 1/\tau$.

In discrete lifetime analysis, three lifetime results were obtained. The shortest component (τ_1 & I_1) is related to *p*-Ps annihilation, the intermediate (τ_2 & I_2) is the one indicating annihilation of free positron in the polymer matrix as well as amorphous–crystalline interfaces, and the longest one (τ_3 & I_3) represents pick-off annihilation of the ortho-positronium (*o*-Ps) in free volumes. Since *o*-Ps annihilates from holes of free-volume which have a size and shape distribution the *o*-Ps lifetime will also show a distribution. From the distribution of the *o*-Ps annihilation rate $\lambda_3 = 1/\tau_3$ the mean size and the size distribution of free volume holes can be calculated.

It is well known that some free-volume fractions exist in polymers with the size of 0.106 nm; Ps has sufficient chance to be trapped in such holes. It is assumed that [22] the free-volume consists of a spherical hole with radius *R*, such that $V_h = \frac{4}{3}\pi R^3$.

The assumption is also made a theoretical model in which the Ps resides in a spherical potential well of radius $R_o = R + \Delta R$, where $\Delta R = 0.1656$ nm is the electron layer thickness around the hole.

The overlap integral between the *o*-Ps and the electron density has been calculated [23] and the annihilation rate λ_3 deduced according to the following semi-empirical rule:

$$\frac{1}{\lambda_3} = \tau_3 = 0.5\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1} \tag{1}$$

By fitting the above equation with the measured τ_3 values, *R* and V_h can be evaluated. The relative intensity of the longest component, I_3, is generally correlated to the concentration of holes which can be considered as trapping centers for Ps. A semi-empirical relation may be used to determine the fraction of free-volume (*f*) in polymers as:

$$f = CV_hI_3 \tag{2}$$

where *C* is the normalization constant. In common polymers, the value of *C* ranges from 0.001 to 0.002. The *C* value has not been measured in this work but as it is constant the *f* value must be proportional to the product V_hI_3.

Doppler broadening of annihilation radiation (DBAR) measurements

The DBAR measurements are measured using hyper pure germanium detector. The measured full-width at half-maximum (FWHM) is established to be 1.2 keV at 662 keV of ^{137}Cs which is comparable with the variation of electron momentum usually of the order of ~1.5 keV. The energy dispersion of the equipment is 0.049 keV per channel. The same positron source as mentioned before for PAL measurements is used and sandwiched between two identical pieces of the sample. The total number of counts in the measured spectrum is 5×10^6. The line shape, *S*-parameter represents the probability of annihilation of positrons with valence electrons which is given as the area of the central part (low-momentum) of the spectrum. *S*-parameter is measured as the number of counts lying within an energy interval of 1.3 keV centered at the peak of the annihilation line. The *W*-parameter represents the probability of annihilation of positrons with core electrons which is given as the area of tail region (high-momentum) far from the center in fixed interval. *W*-parameter is measured as the sum of counts laying within the energy interval 3.4–5.1 keV from the peak center on either side of the peak.

Results and discussion

Mechanical properties

It is well known that the tensile strength of a composite is strongly related with the interfacial adhesion developed between reinforcement and matrix. Figure 1 shows the effect of fillers (Cu, Al, Zn) loading on the tensile strength and Vickers hardness of polyesters composites (PE1 & PE2). The results showed that at 10% of filler (for all fillers) sharp decrease in the tensile strength is observed for both polyester composites (PE1 and PE2). Beyond this value (>10%), the decrease in the tensile strength is small. In addition, the tensile strength of the composites containing Cu was found to be higher than those containing Al and Zn. No significant difference was observed between PE1 and PE2 composites. This is in agreement with the conclusion of Bigg [24] that at higher metal concentrations, the interaction between fillers impeded in the polymer matrix resulting in lower strength of the respective composites. The reduction in tensile strength is most likely due to the presence of metal particles that may act as stress raiser, and due to weak interfacial adhesion between the fillers and matrix.

From this figure it is notable that, the hardness of the composites increased with increasing filler content up to a 20% filler loading, and then decreased with further loading. This could be attributed to the poor surface contact of the filler with polymer matrix. On the other hand, the hardness of PE2 is found to be higher than PE1 composites. This is due to the presence of some additive in PE2.

Electrical properties

The permittivity ε' and dielectric loss ε'' were measured at constant frequency ($f = 100$ Hz) and at room temperature, 25 °C ± 1 for the two styrenated polyesters (PE1 & PE2) loaded with Cu, Al and Zn at different concentrations (10–40%).

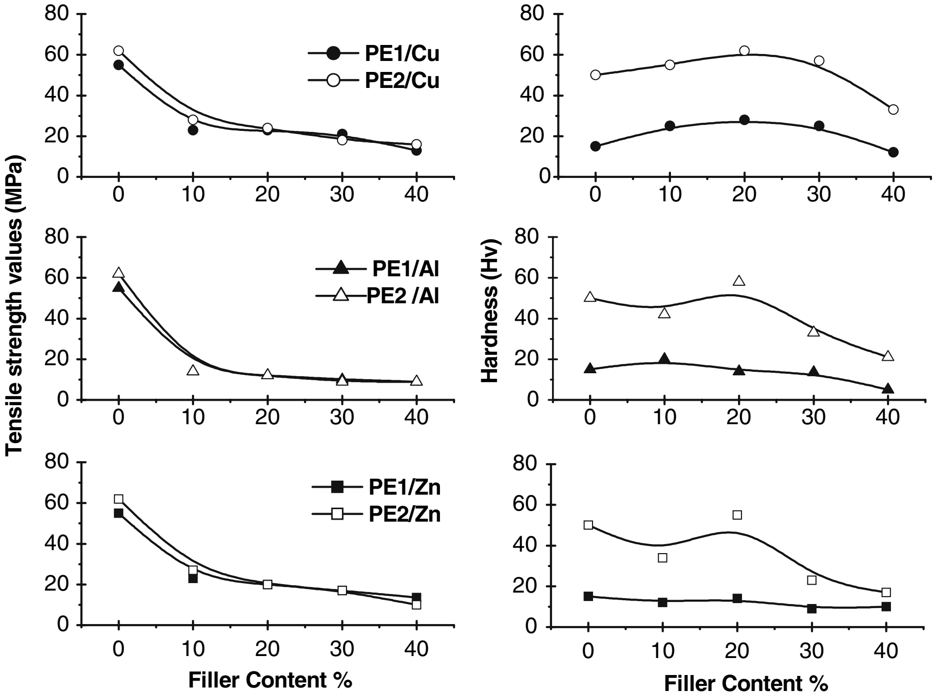


Fig. 1 Effect of filler content on the tensile strength and hardness of PE1 and PE2 composites

Figure 2 represents the variation of ε' and ε'' as well as σ versus filler content. From this figure, it is clear that the values of ε' and ε'' increase by increasing the Cu and Al content while no significant effect is observed in case of Zn content. It is also seen from the figure that the values of ε' and ε'' for PE2 composite samples are slightly higher than those of PE1 but no detectable change in case of Zn composites in both. The lowest values of ε'' given for both polyester composite samples containing zinc in comparable with those containing Cu and Al indicate that these samples are characterized by good dielectric properties.

It was noticed that, σ increases by increasing filler content and follows the same trends of ε' and ε'' but still lies in the insulating range [25]. These results could lead to

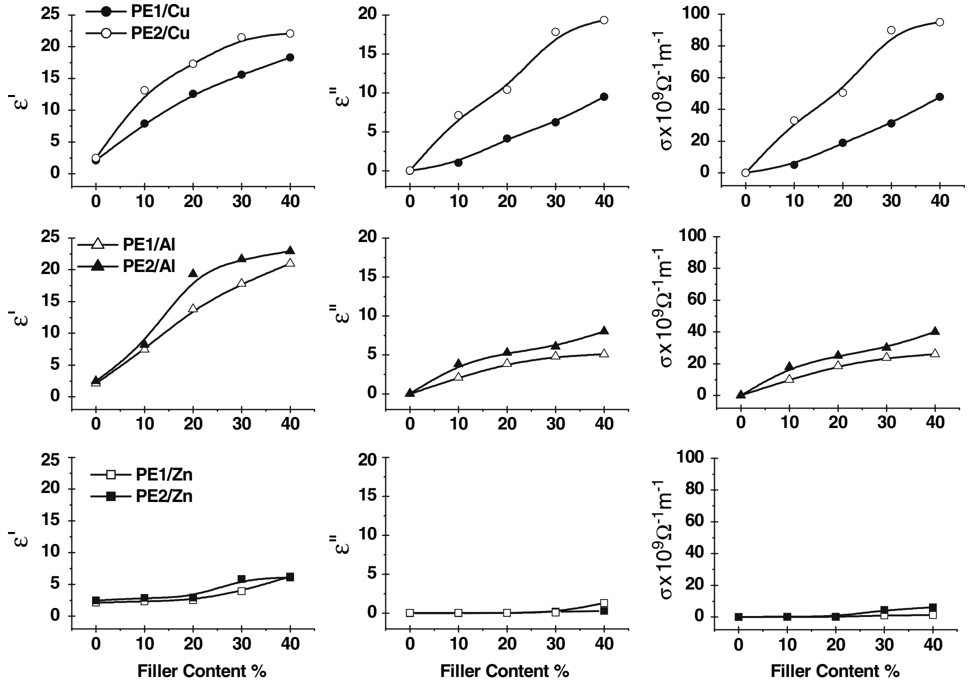


Fig. 2 Variation of the permittivity ε', dielectric loss ε'' and electrical conductivity σ versus filler content for PE1 and PE2 composites

a conclusion that, σ values decrease when the metal embedded in the polyester/styrene matrix due to the change from metal to metal oxide by the effect of heat released from the curing of the polyester.

Positron annihilation

Positron annihilation lifetime (PAL) and line shape *S*-parameter were measured at room temperature for styrenated polyester PE1 and PE2 filled with Cu, Al and Zn in the range from 10 to 40 wt%. The values of V_h, which is a measure of the nanoscale size of free-volume holes in unfilled PE1 and PE2, are 0.0686 nm^3 and 0.069 nm^3. The corresponding value of *f*, which is a measure of the concentration of free-volume holes are 2.3% and 2.2% ± 0.001, respectively. The *S*-parameter which is a measure of the Ps formation in the free-volume holes are 0.375 and 0.377 ± 0.0005, respectively. Figure 3 represents the variation of free-volume hole size (V_h) and its concentration (*f*) as a function of wt% of filler content.

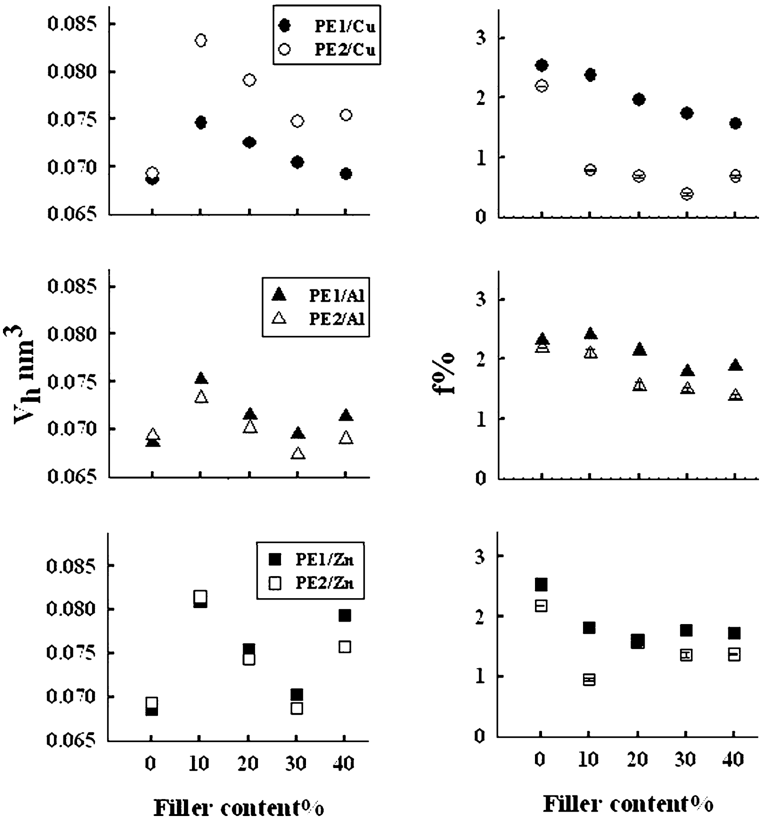
From the figure, one can observe that, 10 wt% of the filler causes a significant increase in V_h compared to that unfilled (PE1 & PE2) in all cases of metal composite samples. On the other hand, a decrease in *f* was observed in all cases. This initial trend can be explained as due to formation of polymer metal complexes resulting in rearrangement of the molecular structure as revealed by increase in free-volume size (V_h) and a decrease in its concentration (*f*) [26].

With increasing wt% (20–40%) of the filler, a gradual decrease in V_h, and *f* is observed in case of Cu and Al fillers while opposite trend in case of Zn (at 40%) is observed. This is due to the fact that, these fillers thus inhibit the *o*-Ps formation most probably by filling some of the free-volume holes in the polymer matrix and lead to a decrease in both V_h, and *f* in polymer composites. On the other hand, Zn filler leads to formation of free-volume holes with large size and low fractions; this is due to large average particle size of Zn. Therefore, positrons may annihilate in the filler added and thus the number of positron available to form Ps in the polymer is reduced with wt% of fillers.

Figure 4 shows the free-volume distributions obtained for the PE1 and PE2 samples without filler and after embedded with different wt% of different types of metals. The distribution of free-volume shifts from a small to larger size at 10 wt% of filler, then it becomes smaller with increasing wt% of filler. These results confirmed the above results in Fig. 3.

The probability of annihilation of free-positrons and *o*-Ps with low momentum valence electrons and the probability of positron annihilated with core electrons are represented by the *S*-parameter and *W*-parameter in Fig. 5.

Fig. 3 Variation of free-volume hole size (V_h) and its concentration (*f*%) as a function of filler content



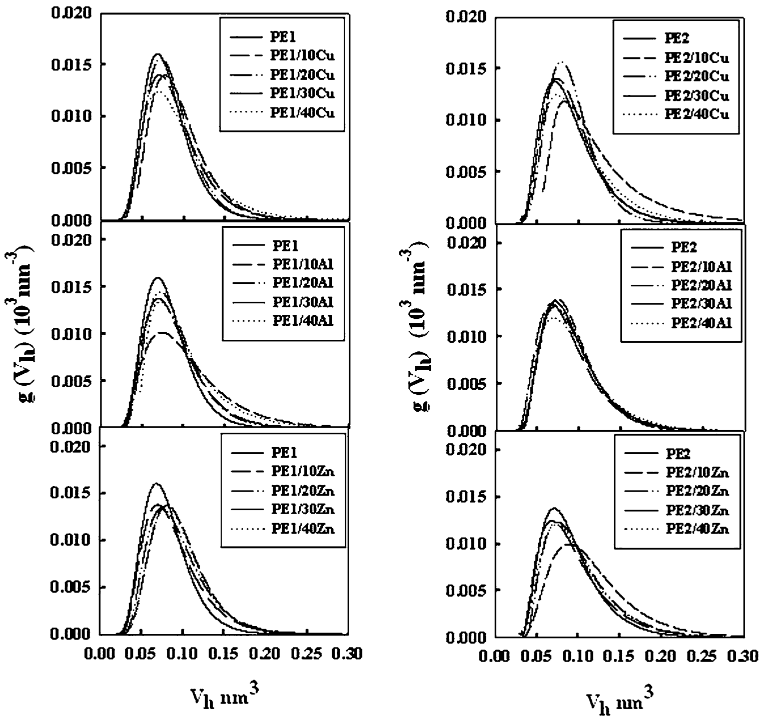


Fig. 4 Free-volume hole distributions of PE1 and PE2 composite samples

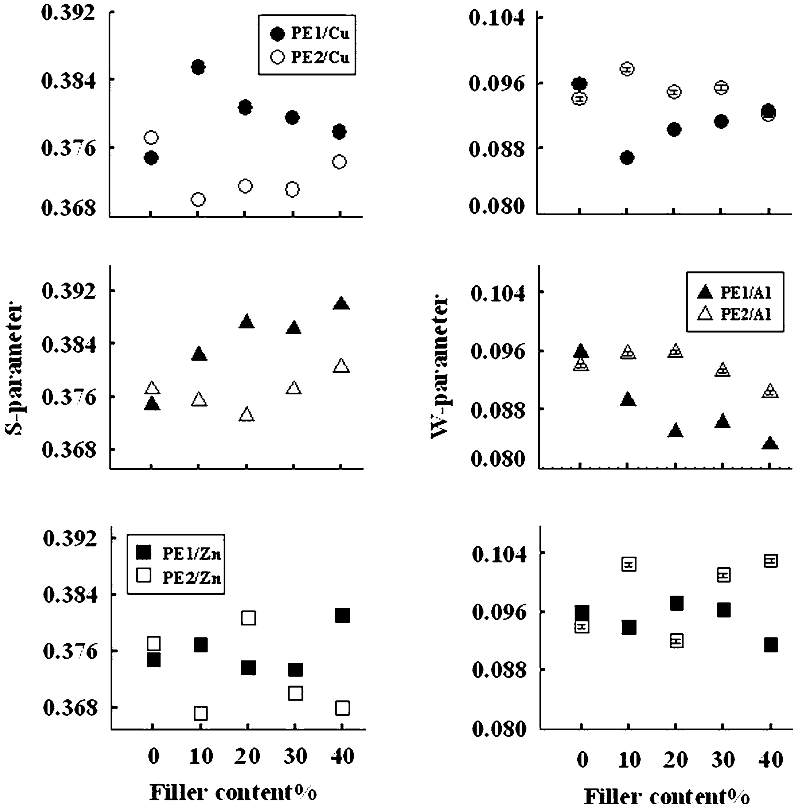
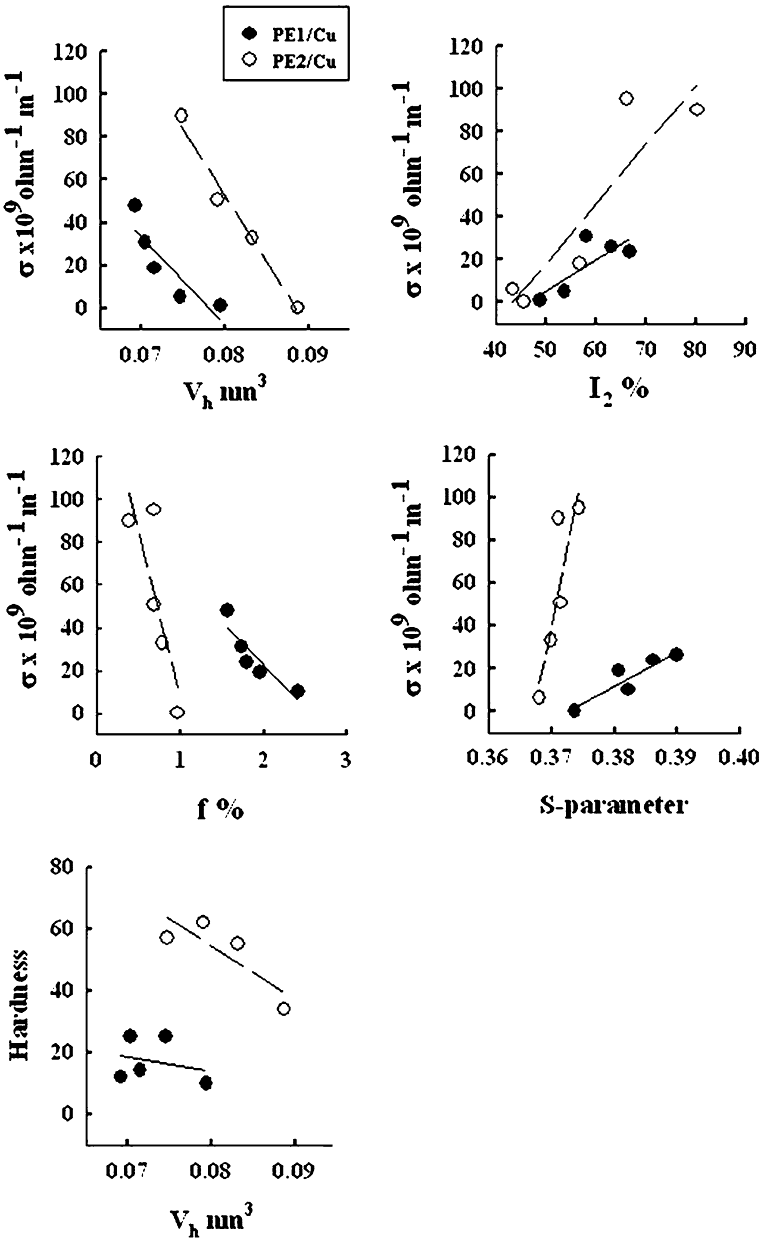


Fig. 5 Variation of *S*-parameter and *W*-parameter as a function of filler content

Since, the *S*-parameter is the characteristic parameter which shows the electron momentum density, the increase of *S*-parameter at 10 wt% for PE1 containing Cu and Al suggests that the probability of positron and Ps annihilating with low momentum valence electrons increases. On the other hand, a decrease in *S*-parameter is observed in case of PE2. These initial trends can be explained on the basis of inhibition of Ps formation by the metals filled PE2 due to

Fig. 6 Correlation between, *f*%, I_2, *S*-parameter and σ as well as V_h and hardness. The *lines* are drawn to guide the eye



the formation of high electron density region. With increasing wt% of metals the increase in *S*-parameter in case of Al as a filler is due to inhibition of Ps formation implies increased annihilation in free or trapped positron states in the crystalline–amorphous interfaces, and the amorphous regions of the metals–polymer complexes. This can be visualized as a shift from annihilation of the positron in the Ps state for the pure PE samples to annihilation of free or trapped positron as a consequence of reaction between the localized negative charges in the polymer molecule with the positrons. The opposite trend of *W*-parameter reflects the decrease in positron annihilating with highly momentum core-electron, thus is considered to be sensitive to the degree of order in microstructure of polymer. In the relatively ordered structure where the concentration of positron-trapping defects such as microvoids, chain ends is relatively high, so, *W*-parameter is larger in case of PE2 because the probability of a positron annihilating with core electron has increased. Consequently, the addition of filler to PE decreases disorder structure resulting as a decrease in free-volume hole size.

From the above figures one can observe that, for both polyester composite samples containing Zn, the values of lifetime parameters (V_h and *f*), *S*-parameter and *W*-parameter are randomly distributed around the value of unfilled PE samples. This confirmed the electrical and mechanical results which showed that PE composites samples containing Cu and Al have good electrical and mechanical properties compared with those containing Zn.

Correlation between electrical conductivity, hardness and lifetime parameters

Figure 6 shows a correlation between σ, hardness and lifetime parameters where composite samples containing Cu are taking as an example.

Because the intermediate lifetime component is attributed to the annihilation of positrons trapped with free electrons at the polymer matrix–metal interface, the trapping sites might be voids in the amorphous regions of the polymer composites. The intensity I_2 of the intermediate lifetime component and S-parameter are an indicator of the electric conductivity σ, so the larger the I_2 and S-parameter value, the greater is σ [27]. This indicates that the formation of large amounts of micro-crystalline boundary leads to an increase in conducting path or the increase in the number of transfer paths and hence better conductivity. On the other hand, the high values of S-parameter correspond with high conductivity, it suggested that the chance of positron annihilating with electrons with low momentum electrons evidently increased in the conductor. These electrons with low momentum should be dislocated π- and d-electrons. They act as carrier resulting in high conductivity. Figure 6 shows that σ is positively correlated with I_2, S-parameter and negatively with free-volume parameters (V_h and f) of polyester composites.

A negative correlation between the free-volume size (V_h) and hardness was observed in Fig. 6. This means that, polyester composites exhibit good electrical and mechanical properties at small free-volume hole size and low fraction.

Conclusion

The introduction of metal particles into PE1 and PE2 decrease the tensile strength by increasing the concentration of fillers. On the other hand the hardness of these composites increased with increase of filler up to 20% and then decreased with further loading.

The permittivity (ε'), dielectric loss (ε'') and the conductivity (σ) increase by increasing Cu and Al content in the two styrenated polyesters. No significant increase is observed in case of Zn content.

A significant change is observed in the free volume parameters (V_h and f%) and the valence electron density (S-parameter) with filler content for two styrenated polyesters. On the other hand, the size distributions in polyesters samples are found to vary from 0.068 nm^3 to 0.083 nm^3 and are affected by wt% of filler.

The correlation between V_h and f% with σ and hardness shows the electrical and mechanical properties of two styrenated polyesters are affected by the filler content.

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