Coincidence Doppler Broadening Spectroscopy in Polyvinyl Chloride after Doping with Al_2O_3

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ABSTRACT: Coincidence Doppler broadening of annihilation radiation (CDBAR) and Vickers hardness techniques were performed to study pure Al_2O_3, pure polyvinyl chloride (PVC), and doped PVC with different concentrations of Al_2O_3 (10–50%). The CDBAR ratio curves with respect to pure PVC were presented and reflect the momentum distribution of all the samples. The peak around 14.5 $\times 10^{-3}$ m_oC in the CDBAR ratio curves suggests a large contribution of positron annihilation with the Al_2O_3. There is a linear correlation between the height of this peak and the Al_2O_3 concentration. The S- and W-parameters were extracted from the CDBAR spectra and increase with increasing the Al_2O_3 concentration showing discontinuity at 30% of Al_2O_3 concentration on PVC. The present data confirmed that there is no positronium formation in pure Al_2O_3 as a result of smaller S-parameter. The Vickers hardness increases with increasing the Al_2O_3 concentration in PVC showing a linear dependence with two different slopes depend on the Al_2O_3 concentration range. A correlation between the Vickers hardness (macroscopic data) and the W-parameter (microscopic data) was observed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1307–1313, 2008

Key words: coincidence Doppler broadening; Vickers hardness; polyvinyl chloride; Al_2O_3

INTRODUCTION

Polymeric materials have been widely used in our daily life and industrial areas not only as an efficient alternative to the traditional materials such as wood, stone, glass, natural fabrics, and metals, but they also become indispensable factor to a break through in up-to-date-technologies.[1] The needs for more sophisticated polymeric materials whose functions and properties are precisely tuned for the intended applications drive many researches to enhance the macroscopic properties of polymer products. Polymers in their pure state are excellent electrical insulators, but they can be modified to be relatively semiconductors or good electrical conductors.[2,3] Electrical conductivity in polymers can be improved by adding conductive materials such as metals, metal oxides, and metal salts[4–8] to form a conductive polymer. The conductive polymers are presently of great interest because they offer the promise of combining metallic and semiconducting characteristics with the plastic and elastic properties of organic polymers. They offer many advantages compared with metals. The study on the relationship between the macroscopic and microscopic structure is one of the main research streams for the polymer field.

The positron annihilation spectroscopy has found increasing interest and growing application for studying polymeric materials.[9–12] The reason for this is that it provides a unique probe for subnanometer local free volumes in polymers that arise from their structural disorder. Such free volume holes play a crucial role in determining a variety of properties of polymers.[13,14] By using positron annihilation spectroscopy, many studies indicate that the macroscopic properties of conducting polymers are related to the positron annihilation properties. AL-Qaradawi and Abdel-Hady[15] applied the positron annihilation lifetime (PAL) technique to investigate the behavior of the free volume in pure and doped polyvinyl chloride (PVC) as a function of lead concentration and temperature. The influence of the plasticization process on free volume in PVC using PAL measurement was investigated by Borek and Osoba.[16] The electrical properties of flame retardant PVC were studied by Mostafa et al.[17] In our previous work, the correlation between the dielectric data and the positron annihilation data was established[18] on PVC doped with different concentrations of Al_2O_3.

In the present work, taking into account for the chemical sensitivity of the coincidence Doppler broadening of annihilation radiation (CDBAR) in polymers, the CDBAR technique has been applied to study pure Al_2O_3, pure PVC, and PVC doped with different concentrations of Al_2O_3. In addition, the Vickers hardness of the samples has been measured to investigate a quantitative relationship between the

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mechanical properties and the positron annihilation parameter, which extracted from the CDBAR spectra. Moreover, an attempt is done to establish a correlation between the positron annihilation parameter and the Vickers hardness data.

COINCIDENCE DOPPLER BROADENING SPECTROSCOPY

In molecular materials, the positron preferentially forms and annihilates from a bound state called positronium (Ps) atom. The Ps forms either in the so-called para (antiparallel electron and positron spins: p-Ps) or ortho (parallel electron and positron spins: o-Ps) positronium states.[5–8] Positron annihilation is an experimental method by which one can obtain the microstructure, momentum of electrons, and defect behavior of condensed matter. Because the positron is sensitive to defects, vacancy, surface and interface, it has been turned into the best probe for defect research.[19] The positron annihilation technique has been extensively applied in areas of polymers, solid physics, chemistry, medicine and materials science and so on.[20,21] Since the emerging gamma photons produced by the annihilation of thermal positron with electrons provide information of both momentum distribution and the electron density of materials, the related spectrum can be used to study the microstructure of materials. The width of the gamma ray annihilation spectrum depends on Doppler broadening effects and reflects the momentum distribution of the electrons with which the positrons annihilate.[19–22]

When a positron source is surrounded by a material, the electron and the positron cannot be regarded as entirely free because of the action of an electromagnetic field produced by their surrounding. The most frequent partner for positron, in such annihilation case, is a bound electron. The energies of annihilating γ-ray pairs were denoted by E_1 and E_2. Supposing that the kinetic energy of a thermalized positron can be neglected and E_B means approximately the electron binding energy. The difference in the energy of the annihilation quanta can be express as $\Delta E = E_1 - E_2 = CP_L$ and the sum energy $E_T = E_1 + E_2$ is equal to the total energy of the electron-positron pair prior to annihilation, i.e., $2m_oC^2 - E_B$, where P_L is the longitudinal component of the positron-electron momentum along the direction of the γ-ray emission, m_o is the electron rest mass, and C is the speed of light.[23]

Using only one detector for the Doppler broadening measurements instead of two, the annihilation line would also be spread with the energy but two times smaller ($0.5 \Delta E$). The Doppler spectrum will be additionally distorted by the incomplete charge collection by the detector, registration of the Compton scattered quanta (1.28 MeV) from positron source (^{22}Na), and by the electron binding energy (E_B). In the case of observing both quanta by means of the two detector apparatus, more precise selection of the events is possible, which in turn enables an effective elimination of the background.[23] Taking account of the symmetry measured spectra and the better energy resolution (improved by a factor of $\sim \sqrt{2}$), the apparatus with two detectors is very useful. The CDBAR spectroscopy has been widely applied to study metals and polymers[24,25] in the form of S- and W-parameters. The S- and W-parameters are defined as the ratio of low-momentum region and high-momentum region in the CDBAR spectrum to the total region, respectively. It is commonly accepted to present the CDBAR result as a ratio of the area-normalized counts in each channel of the measured CDBAR spectrum to the corresponding counts from a reference spectrum.[26] The choice of the reference spectrum is of great importance for a correct interpretation of the results. The CDBAR spectroscopy has been proved to be very sensitive to detect polar groups in polymers.[27–31]

EXPERIMENTAL SET-UP

Commercial PVC powder supplied from Alexandria Petrochemical Company, Egypt (K-70). Weakly acidic powder of Al_2O_3 was supplied from Sigma-Aldrich, Milwaukee, WI, USA (particle size $\sim$ 150 mesh, pore size 5.8 nm, surface area 155 m^2/g). Used samples were prepared using a casting method[32] by dissolving the PVC in cyclohexanone at room temperature and adding Al_2O_3 particles. The mixture was cast to a glass dish and kept in a dry atmosphere at 30°C for 2 weeks to ensure the removal of solvent traces. The thickness of the obtained films was in the range 0.4–0.6 mm. The PVC films of the following Al_2O_3 mass fractions were prepared: 0, 10, 20, 30, 40, and 50%.

The CDBAR measurements were carried out using two high purity Germanium detectors. The energy resolution of each detector was calibrated to be 1.1 keV (full width at half maximum, FWHM) at 514 keV γ-line of ^{85}Sr and the channel width was 0.192 keV. Two identical samples were sandwiched around a positron source, prepared by evaporating carrier-free ^{22}NaCl solution on Kapton foil of 7 μm thickness. The sandwiched sample with the positron source was rubbed using Al foils and was set equally at a distance of 20-cm away from each detector. This distance was long enough to avoid any increase in the background due to 3γ-annihilation of the triplet state of positronium (o-Ps). The energies of annihilating γ-ray pairs in coincidence were simultaneously that fulfill the condition $2m_oC^2 - 2.4$

$< E_T < 2m_oC^2 + 2.4$ keV, recorded by two detectors located at an angle of $180°$ relative to each other. Signals from the coincidence circuit were fed into a two dimensional multichannel analyzer (Labo, NT24-DUAL). The CDBAR data were recorded for 22 h resulting in total counts of at least 15×10^6 in the 1024×1024 coincidence matrix at room temperature (about $25°C$).

The overall energy resolution of the coincidence system was estimated to be ~ 0.9 keV (full width at half maximum, FWHM), which corresponds to the momentum resolution of $\sim 3.52 \times 10^{-3}$ m$_o$C. The coincidence measurements have significant improvement in the peak to background ratio by three orders of magnitude over conventional one detector measurements. The CDBAR spectra were analyzed using CDB-program.[33] The CDBAR ratio curve was obtained by normalizing the CDBAR momentum distribution of the sample to CDBAR momentum distribution of pure PVC sample. To get a better insight in the obtained spectra, S- and W-parameters were extracted from each spectrum. The S- and W-parameters are defined as the ratio of low-momentum region ($P_L < 2.94 \times 10^{-3}$ m$_o$C) and high-momentum region ($11.75 \times 10^{-3} < P_L < 25.44 \times 10^{-3}$ m$_o$C) in the CDBAR spectrum to the total region, respectively.

The microhardness measurements were performed on the standard Vickers microhardness device (Akashi HM-122 and NU-2 microscope and Victor data system display). The indenter is a square-shaped diamond pyramid with top angle $136°$. The standard loading, P was 40 g and the load time was 30 s. The projected diagonal lengths of indentation d (in μm) were measured. The Vickers hardness, H_v was calculated in the unit of MPa using the equation[34]; $H_v = kP/d^2$, where k is a geometrical factor which is equal to 18,186 for this type of indenter. Multiple measurements (more than 6) were taken and averaged to reduce error.

RESULTS AND DISCUSSION

When Doppler broadening of annihilation radiation spectrum of a polymer is compared with that of a metal, two additional components appear; a narrow one due to p-Ps annihilation and a broader one due to o-Ps pick-off annihilation. According to the Tao-Eldrup[35,36] model, the width of the narrow distribution due to self-annihilation of p-Ps reflects the localization momentum of the p-Ps inside the holes. However, the formation of positronium changes significantly the shape of a ratio curve of the CDBAR spectra. It is well known that, positronium will not be able to penetrate deeply in the constituent atoms due to the molecular repulsion force, and hence the
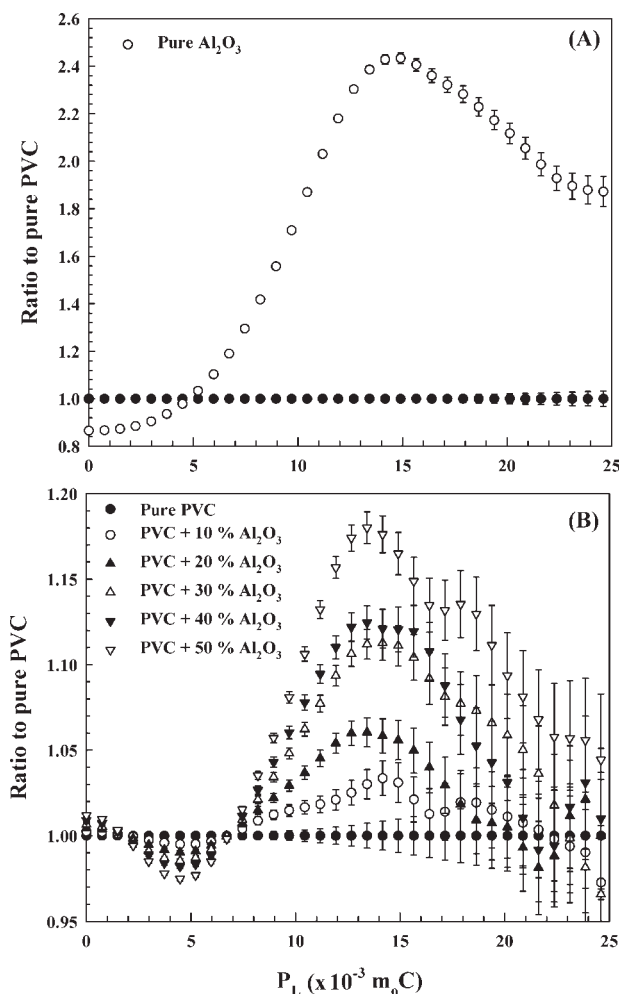

Figure 1 Ratio curve for the CDBAR spectra with respect to pure PVC for (A) pure Al$_2$O$_3$ and (B) PVC doped with different concentrations of Al$_2$O$_3$.

high-momentum component in the CDBAR spectra is associated with the annihilation of free positrons.[37]

Figure 1 shows the ratio curve of the CDBAR spectrum for pure Al$_2$O$_3$ (A) and for different concentrations of Al$_2$O$_3$ on PVC with respect to pure PVC. The higher momentum part was not graphically presented because of the large statistical errors. The ratio curve increases up to 14.5×10^{-3} m$_o$C showing a peak and then decreases. The CDBAR shape of pure Al$_2$O$_3$ is in a good agreement with the data of Kong et al.[38] who presented the ratio curve of Al$_2$O$_3$ with respect to Si. However, they showed that the peak position is at about 11.5×10^{-3} m$_o$C which is lower compared with our data. This attributed to difference reference CDBAR spectrum, Si instead of pure PVC and/or change grain size of the sample used as clear from the data of Dutta et al.[39] and Garay et al.[40]

The ratio curves for doped samples [Fig. 1(B)] decrease up to 2.0×10^{-3} m$_o$C, showing a dip in the
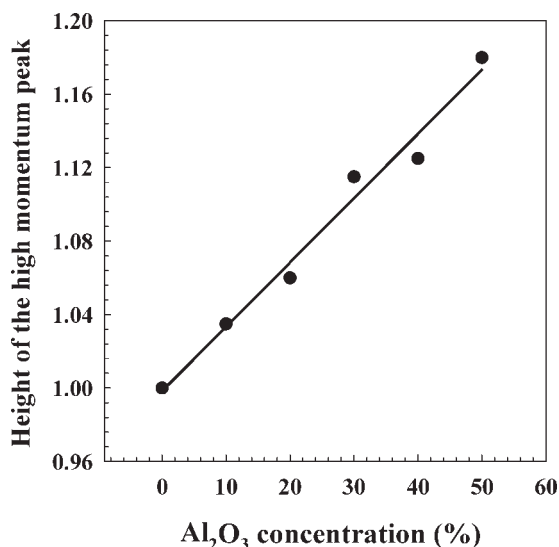
Figure 2   The correlation between the height of the high momentum peak of CDBAR ratio and the Al_2O_3 concentration on PVC.

range $2.0–7.5 \times 10^{-3}$ m_oC, and then showing a peak in the range $7.5–25.0 \times 10^{-3}$ m_oC. The dip deeper decreases and the peak height increases with increasing the concentration of the Al_2O_3 on PVC. In the low momentum region ($> 2.0 \times 10^{-3}$ m_oC), the momentum distribution is proportional to PVC concentration in the sample as a result of increasing the positronium formation. In the high momentum region ($7.5–25.0 \times 10^{-3}$ m_oC), the momentum distribution is proportional to the Al_2O_3 concentration in the sample because of increasing the free positrons annihilate in Al_2O_3.

There is a linear correlation between the height of the high momentum region and the Al_2O_3 concentration as shown in Figure 2. This is in a good agreement with the information that, the CDBAR can identify the chemical environment where the positron is trapped, because the core electrons are tightly bound to the nuclei and are almost unaffected by the chemical bonding and crystal structure.[41] The height of the high momentum region peak for pure Al_2O_3 [Fig. 1(A)] is larger than the value at 50% concentration of Al_2O_3 on PVC (about eight times). This may be due to positrons annihilate in pure Al_2O_3 site without positronium formation.

Figure 3 shows the calculated values of the S- and W-parameters as a function of the Al_2O_3 concentration on PVC. The S-parameter increases with increasing the Al_2O_3 concentration that is due to increasing the positronium fraction corresponding to increasing the o-Ps intensity as presented by Mohamed et al.[18] On the other hand, the increase in the W-parameter is due to increasing of positrons annihilate at the Al_2O_3. It is clear that, the S-parameter value for pure Al_2O_3 is smaller and the W-parameter is larger. This

can be correlated with the data of Petegem et al.[42] and Brauer et al.[43] who confirmed that there is no positronium formation in Al_2O_3. Thus, the S-parameter value for pure Al_2O_3 must be smaller compared with other samples. The high value of W-parameter for pure Al_2O_3 was expected from the idea that more Al_2O_3 leads to more positrons annihilating in it. Thus, the increase of o-Ps formation for doped samples is further confirmed by CDBAR data and agrees with the data of Rao and Chopra[44] who found that the metal doping decreases the degree of crystallinity of the polymer and affects the vibrations of the backbone of the PVC chain or of the side bonds such as C—Cl and C—H.

It is interesting to observe a relatively larger increase of o-Ps intensity, I_3 (taken from Ref. 18) as compared with W- and S-parameters. For example, the relative increase of I_3 at 50% Al_2O_3 to pure PVC is about 36.4% while there is only a 0.24% increase
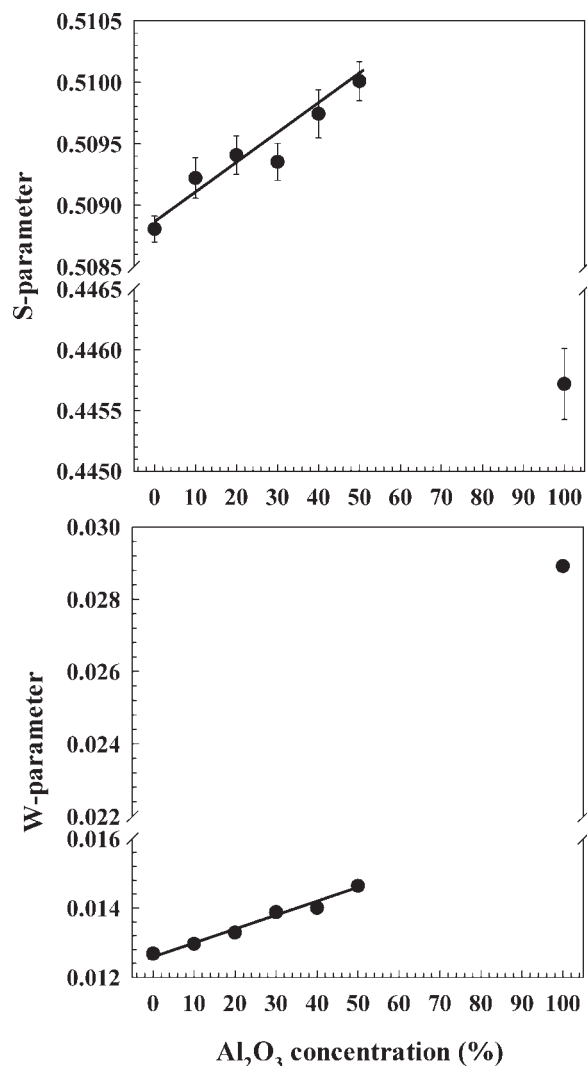

Figure 3 S- and W-parameters as a function of the Al_2O_3 concentration on PVC.
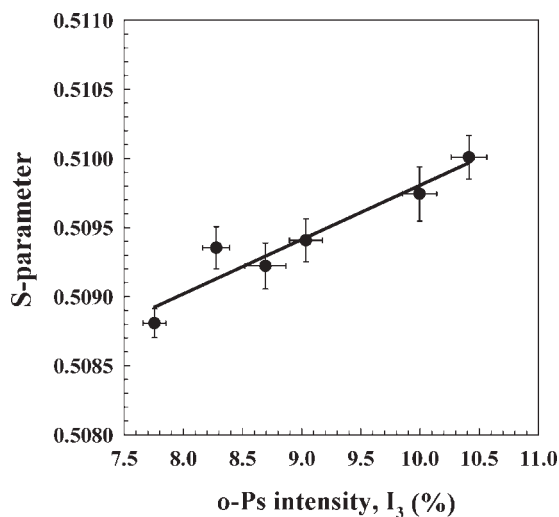
Figure 4 Relationship between the S-parameter and o-Ps intensity, I_3 in PVC doped with different concentrations of Al_2O_3. Solid line represents a linear fitting of the experimental data. The o-Ps intensity, I_3 data was taken from Ref. 18.

in S-parameter. This is because the origin of signals contributing to the I_3 and S-parameter is quite different and the comparison cannot be taken quantitatively. The variation of S-parameter comes from the momentum density change while the variation of the I_3 result comes from the electron density change. Qualitatively, S-parameter is a composite parameter related to both o-Ps lifetime and its intensity. The correlation between the S-parameters and the o-Ps intensities, I_3 is shown in Figure 4. As can be seen from this figure, the S-parameter is well correlated with the o-Ps intensity, I_3. This correlation is reasonable because the p-Ps self-annihilation accompanies a very low momentum and gives a sharp annihilation peak with a large value of S-parameter. This is in a good agreement with the data of Sato et al.[45] who used PAL and coincidence Doppler broadening of annihilation spectroscopes for the studies of many polymers.

If the regions used for the calculation of the S- and W-parameters are adjacent a linear relationship between S- and W-parameter can occur when in metals or semiconductors exists only one defect type with varying concentration, and the slope of the line is a characteristic feature of the defect type.[46] Analogous situation could be found when polymer sample is under study where positrons annihilate from different states in polymers. Linear relationship between S- and W-parameters can occur if the fraction of annihilation from a definite state varies predominantly for the expense of the annihilation from the other states. The S–W plot for pure and doped PVC with different concentrations of Al_2O_3 is shown in Figure 5. It is clear from this figure that, there are

two regions. First region represents the relation at low concentration of Al_2O_3 and second region represents the relation at high concentration of Al_2O_3. The result at 30% Al_2O_3 concentration on PVC sample is deviated from these two lines, which means that a transition structure could happen in this concentration. Similar transition was seen for AC electrical conductivity measurements.[18] The slopes of these two lines are different because the appearing of the Al_2O_3 concentration changes the average electron momentum distribution and could be indicating different types of positron traps. This is consistent with the data of Misheva et al.[47] who measured annealed and nonannealed thin films. They found the slopes of the two straight lines in S–W plot, however, are different and presume different kind of defects in the annealed and nonannealed films.

Polymers usually have poor resistance to abrasive sliding attack because of their relatively low levels of hardness and strength, high plasticity, and low thermal conductivity. Fillers will certainly improve these properties therefore promote the hardness. The mechanisms revealing how fillers improve hardness are not well established. There appear to be two broad explanations. One of them stems from the observation that excess filler concentration is noticed on the composite surface after prolonged sliding. Based on this observation the bulk of the load is supported by the concentrated filler resulting in increased hardness of the composite. The second suggestion is that fillers may improve the adhesion of the transfer film to the counter face and thereby suppress the hardness. While the first explanation might be accepted easily by common sense, the second is complicated. In a broad sense, it is considered to be either physical or chemical in nature. Physical interaction involves van der Waals forces and is
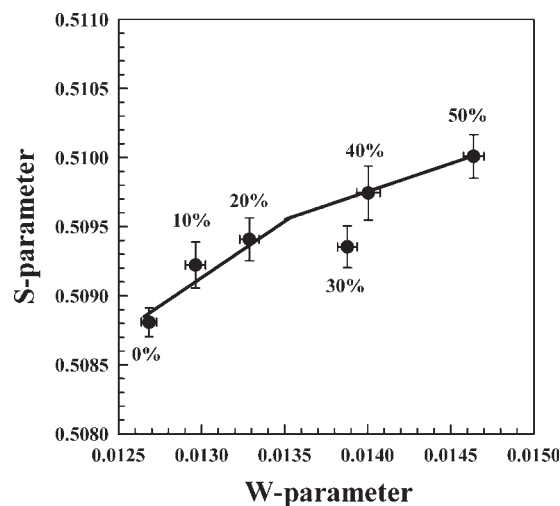

Figure 5 Correlation between the S- and W-parameters at different concentrations of Al_2O_3 on PVC.

comparable in strength with the forces between molecular chains within the polymer itself.

The Vickers hardness, the resistance of a material to deformation, is a very important mechanical property.[48] It is a measure of the local resistance of the material against the indenter penetration and is connected with the local irreversible deformation. Figure 6 shows the Vickers hardness of the samples as a function of Al_2O_3 concentration on PVC. The Vickers hardness increases with increasing the Al_2O_3 concentration which is in good agreement with the data of Yang and Hlacvacek.[49] They found that PVC/Al_2O_3 composites demonstrated a strong wear resistance. Our data also agree with the data of Yan et al.[50] who found that the tensile strength and break elongate ratio values of the membrane improved more than 50% for the polyvinylidene fluoride ultrafiltration membrane that consisted of 2% (weight) Al_2O_3 particles. The hardness of the filler and firm bonding between filler and polymer provided these composites with enhanced mechanical properties. The load is supported by the concentrated filler, which protects the specimen from being abraded, resulting in the increased wear resistance of the composite. It is clear that, there are two regions with different Al_2O_3 concentration dependence of Vickers hardness. The slopes of these two regions met at 30% concentration of Al_2O_3. The slope value in the first region (up to 30%) is smaller than that value in the high region (30–50%). This may be due to change of the sample structure from dispersive to distributive type after doping with high concentration of Al_2O_3, which leads to higher Vickers hardness dependence.

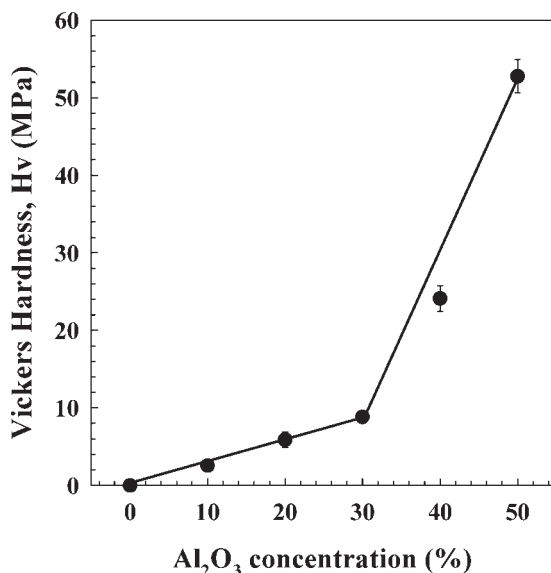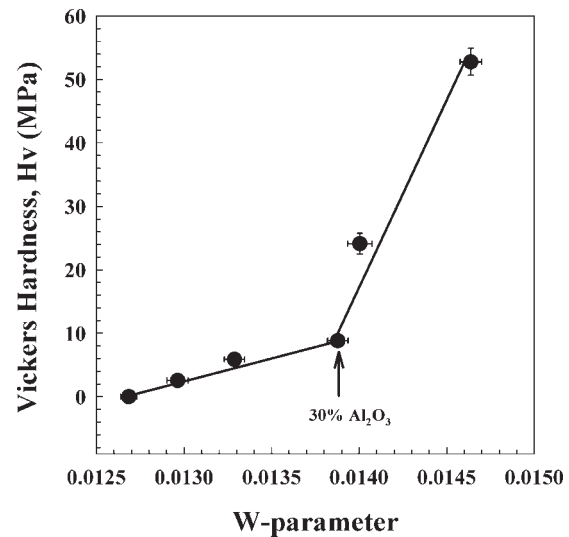It is interesting to see the correlation between the microscopic tool (W-parameter) and the macroscopic

Figure 7 Correlation between the W-parameter and the Vickers hardness in PVC doped with different concentrations of Al_2O_3.

tool (Vickers hardness) as shown in Figure 7. The behavior of this correlation is similar to the trend in Figure 6. Increasing the Al_2O_3 concentration on PVC leads to increase the hardness and increase the W-parameter as a result of increasing the chemical composite in the samples (increasing the positron annihilating at Al_2O_3). This correlation also has two different slopes that depend on the hardness of the samples (i.e., Al_2O_3 concentration on PVC). It is important to notice that, the meeting point for this correlation was at 30% Al_2O_3 concentration on PVC too. Thus, the nature of positron annihilating at up to 30% Al_2O_3 concentration is different compared with that at higher concentration of Al_2O_3.

CONCLUSIONS

CDBAR has been measured for pure Al_2O_3, pure PVC, and doped PVC with Al_2O_3. It provides information about the positron momentum distribution. With increasing the Al_2O_3 content, the S-parameter increases due to higher positronium fraction corresponding to increasing of the o-Ps intensity. On the other hand, the W-parameter increases due to increasing of positrons annihilating at Al_2O_3. At higher concentrations of Al_2O_3 (> 30%), the sample structure might be changed from dispersive state to distributive state. This conclusion has been supported by the observed two straight lines in the S–W plot. The hardness of the samples increases with increasing the Al_2O_3 concentration on PVC. There is a linear correlation between the Vickers hardness and the W-parameter implying a positive correlation between the macroscopic mechanical properties and the positron annihilation parameters was achieved.

Figure 6 Vickers hardness as a function of Al_2O_3 concentration on PVC.

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