

Temperature and Weight Dependence of Free Volumes in Conducting Composite Polymer Using Positron Annihilation Techniques

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Abstract. Polyvinylidene fluoride-co-hexafluoropropylene (PVdF-co-HFP) with conducting polyaniline (PAni) was studied to measure free-volume intensity (I_3), ortho-positronium (o-Ps) lifetime (τ_3), and Doppler momentum distribution parameters (S and W) as a function of temperature varying from 273 to 373 K and PAni weight percentage varying from 1 %–20 % using the techniques of Positron Annihilation Lifetime Spectroscopy (PALS) and Doppler Broadening Annihilation Radiation (DBAR). It has been observed that the free-volume intensity and the o-Ps lifetime increased sharply with PAni weight percentage up to 4 % after which decreased slowly. DBAR momentum distribution parameters behaved similarly as well and it's assumed that in the studied samples one-type defect was to exist. The thermal expansion coefficient also as a function of PAni weight was extracted from PALS data.

Keywords. Positron annihilation lifetime spectroscopy, free volume, conducting polymers, PAni, PVdF-co-HFP, thermal expansion coefficient.

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1 Introduction

Conducting polymers have been studied extensively in the last few decades for their wide potential use in electronic devices [1], anti-corrosive coating [2] and electrochemical impedance spectroscopy [3]. The conducting polymers are promising materials for various applications such as gas sensors [4], optical devices [5], polymer light emitting

diodes [6], organic transistors [7], microwave absorbers [8], hydrogen storage [9], and biomedical applications [10].

PVdF-co-HFP is a co-polymer matrix and plays important role in achieving essential conductivity when it's added with intrinsically conducting polymer, polyaniline (PAni). The PAni investigated as a potential membrane material for gas separation [11] and probe beam deflection [12] is one of the most important conducting polymers.

A polymer may contain an open-space called “free volume” which occurs due to the change of chemical structure. The concept of the free volume may indeed explain some progresses of physical problems. Therefore, the aim of this work is to study the free-volume intensity, ortho-positronium lifetime, S (sharp) and W (wing) parameters of PVdF-co-HFP as a function of temperature and PAni weight percentage in a vacuum using non-destructing powerful positron techniques yielding invaluable information about the structure and concentration of the free volume [13].

2 Experimental

2.1 Sample Preparation

Commercial aniline (Ani) was purchased from Merck/Germany and it was purified further by vacuum distillation prior use. PVdF-co-HFP with an average molecular weight of 400,000 (Aldrich) was used as a polymer matrix for the composite membranes. Analytical grade ammonium peroxydisulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, was used as an oxidizing agent and supplied from Merck. N-methyl pyrrolidone (NMP), hydrochloric acid (HCl) and acetone were also purchased from Merck and used as received.

First, the Ani was freshly distilled by using rotary evaporator, and 15×10^{-3} mol of the Ani was dissolved in 0.2 L of 1 M hydrochloric acid in a 0.5 L of three-necked round-bottomed flask and then the solution was stirred swiftly for an half-hour. Subsequently ammonium peroxydisulfate was dissolved in 0.2 L of water. Afterward, ammonium peroxydisulfate solution was added dropwise to aniline solution at 273–275 K and the mixture was stirred for 24 hours at this temperature. Next day, the green precipitated PAni was filtrated and washed several times with 0.1 L portions of acetone and ultra pure water to remove all non reacted

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monomer. Then, the PANi in emeraldine salt form was dried in air and then in vacuum oven at 333 K for overnight.

Composite membranes were prepared by solvent-casting technique. Initially, 10^{-3} kg of PVDF-co-HFP was dissolved in N-methyl pyrrolidone (NMP) at 323 K followed by the addition of various amounts of PANi ranging from 1 to 20 %-wt. (PANi/PVDF-co-HFP) and then the mixture was stirred for 3 hours at 308–313 K vigorously. The resulting homogeneous viscous solution was poured on the glass plate. Before the drying step, the films were put in a vacuum desiccator in order to remove bubbles. Then, the composite polymer films were dried in a vacuum chamber at 393 K for 24 hours to remove any trace of solvent (NMP) and stored in a vacuum desiccator prior their use.

2.2 Positron Techniques

To utilize PALS [13], we prepared a positron source on an aluminium foil (thickness of 5×10^{-6} m) about 25×10^{-6} Ci obtained by the evaporation of aqueous $^{22}\text{NaCl}$ solution and then sandwiched it between two samples. The ^{22}Na source emits positrons (99.93 %) accompanied by a 1274 KeV [14] γ -ray which serves as a starting signal for the timing. The emitted positron enters the material and instantly slows down to the thermal energies. The thermalized positron prefers to occupy any available vacancy in the material because of negative affinity of the surrounding molecules. In the vacancy the positron captures an electron to form either parapositronium (p-Ps) or orthopositronium (o-Ps) with a lifetime 125 ps and 132 ns in the vacuum, respectively. However, in the material positron annihilates with an electron from the surrounding molecules, called pick-off annihilation. Therefore, the lifetime of the o-Ps is dramatically reduced to a few ns in the polymers, but the lifetime of the p-Ps is not changed remarkably so we kept it constant in our calculations. The either annihilation is revealed by two γ -ray, each of energy 511 KeV, serving as a stopping signal for the timing. Conventionally, the positron lifetime is measured as a time difference between two γ -ray. For the PALS, fast scintillation detectors were used: BaF_2 scintillators were combined with Hamamatsu R2059 photomultiplier tubes (PMTs) based by 265 Ortec operated at negative 2200 Volts. As a time signal generator, two constant fraction differential discriminators (Ortec CFDD 583 B) were also used to filter one from the other signal within the selected energy range. A time to Amplitude Converter, TAC, was used to convert pulses of different heights to a time-to-pulse-height signal. The converted signals were fed to a multichannel analyzer (Ortec Model 919E Ethernim MCA). The spectroscopic data yielded from MCA was analyzed using the code of RESOLUTION [15] and PATFIT [15] to obtain the lifetime parameters revealing the information about the free volume.

We employed, then, the DBAR [13] to measure Doppler shift in the photon energy due to the longitudinal component of the momentum of an electron-positron pair. The DBAR generally consists of a germanium (Ge) detector and associated electronics to acquire the spectrum in the energy range around 511 KeV. Under the high voltage of positive 4000 V applied, the signal of the high purity coaxial Ge detector (Canberra GC2519 HP Ge) with an energy resolution of 1.35 KeV (FWHM) for 662 KeV ^{137}Cs was converted by a preamplifier (Model 20022CSI) into an electrical pulse. A spectroscopy amplifier (Model 7611 made by Silena) connected to the preamplifier provided the necessary pulses to a multichannel analyzer (Ortec Model 919E Ethernim MCA). Their amplitudes were measures of the photon energies. The spectrum was analyzed using SP-ver.1 program [16] yielding S parameter (sharp) and W parameter (wing) to obtain momentum distribution of the annihilating electrons. The S and W parameters are sensitive to the changes in the momentum density of lower and higher-momentum electrons, respectively. In a larger size hole in which positronium is localized, a larger S parameter will occur due to smaller momentum uncertainty. Especially in polymers having large defects or voids, the S parameter is a qualitative measure of the defects size and defect concentration.

The PALS technique yields two independent parameters of interest: the free-volume intensity varying with hole number and the o-Ps lifetime varying with hole size. The DBAR technique yields two arbitrary parameters [13]: the S (sharp) and the W (wing) parameters chosen to be ~ 0.5 and ~ 0.25 , respectively. Using both techniques, we measured the parameters starting with a co-polymer PVdF-co-HFP and then continuing with PANi/PVdF-co-HFP with 1, 2, 3, 5, 10, and 20 weight percentages of PANi. For each sample, situated in a sample holder under the vacuum, PALS and DBAR measurements were taken as a function of temperature from 273 to 373 K, provided by a temperature controlled liquid bath and checked by a thermocouple placed on the sample. The PALS measurements with a resolution about 400 ps took approximately 2 hours for one-million counts, however, DBAR measurements took less than an half-hour for two-million counts.

3 Results and Discussion

In lifetime analysis, the o-Ps intensity I_3 of a spectrum is obtained using standard computer procedures [17]. In Figure 1, the o-Ps intensity, sensitive to the number of holes, is shown for different weight percentages of PANi/PVdF-co-HFP as a function of temperature. The intensity fluctuated between 273 K and 353 K for each sample but it tended to increase distinctly above 353 K. With increasing PANi weight percentage, the intensity measurably fluctuated up to 4 % of PANi weight, however, after which, continued to

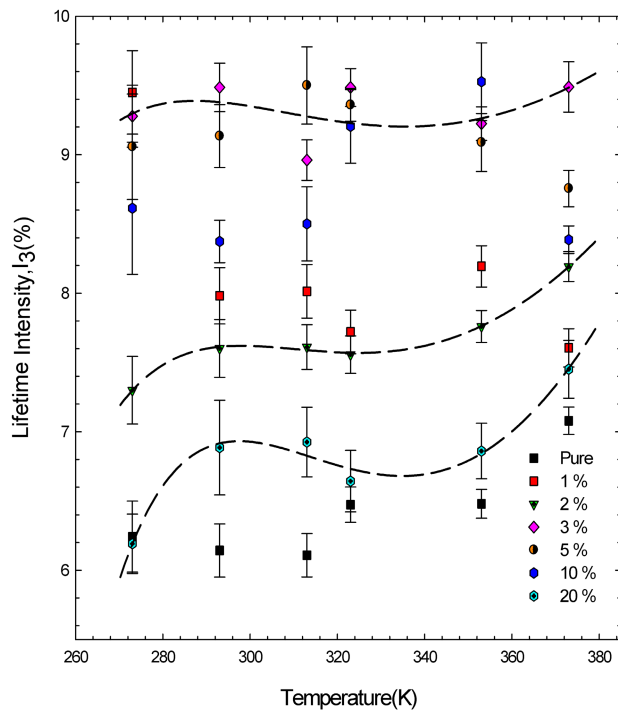


Figure 1. The o-Ps lifetime intensity I_3 as a function of temperature for all samples.

decrease steadily. To see how the intensity changes with weight dependence, the intensity versus PANi weight is plotted in Figure 2. It's clearly seen that the intensity increases sharply up to 4 % but after which decreases firmly. The decrease in the intensity suggests a decrease in the number of holes with increasing PANi weight percentage.

The longest-lived component, o-Ps lifetime, τ_3 [18,19] is obtained from the analysis of the positron lifetime spectra. The o-Ps lifetime τ_3 can serve as a measure of the free volume size, assumed that Ps is in an infinite spherical potential well of radius R . The relation [18] between radius R and the o-Ps lifetime τ_3 allows to find the average volume of the hole, in a spherical approximation. Figure 3 shows a variation of the o-Ps lifetime with temperature for the samples having various weight percentages of PANi. We can state that the o-Ps lifetime increases with increasing temperature and decreases with increasing weight percentage above 4 % of PANi. In Figure 4, the o-Ps lifetime (left vertical axis) and the free volume v_f (right vertical axis) are plotted in terms of PANi weight percentages for all temperatures, and the solid lines are the best fit curves through 273 K, 313 K and 373 K data sets. It is clearly seen that the o-Ps lifetime τ_3 (or the free volume v_f) increases with increasing weight percentages up to 4 % and after which decreases steadily for all temperatures.

The free volume fraction f_v [20] in polymers is linearly related to the o-Ps intensity and the free volume given by $f_v = AI_3v_f(\tau_3)$ where A is the constant. Like the o-Ps

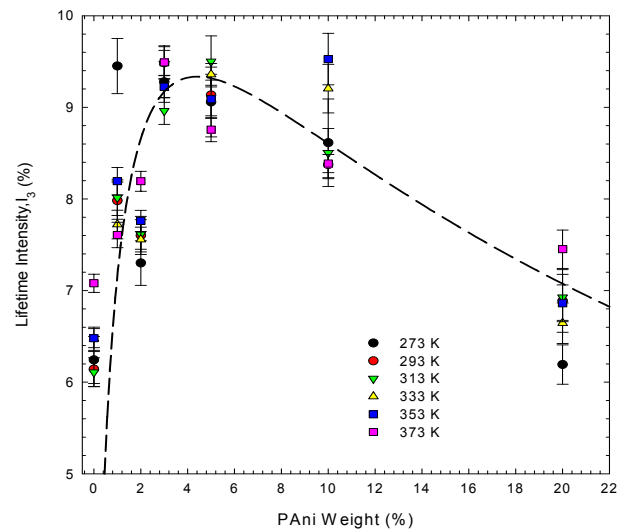


Figure 2. The o-Ps lifetime intensity I_3 versus PANi weight for all temperatures.

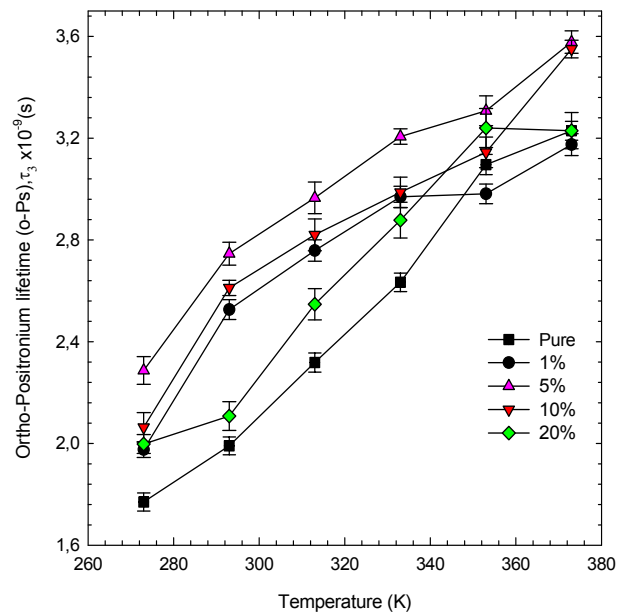


Figure 3. The o-Ps lifetime τ_3 versus temperature for all samples.

lifetime (or the free volume), Figure 5 shows similar variation trend of the free volume fraction f_v versus PANi weight percentage. The free volume fraction increases with increasing PANi weight up to 4 %, and after which decreases steadily. However, for almost all temperatures at 2 % PANi weight the fraction of free volume dropped significantly. Comparison of the results in Figures 3, 4, and 5 suggests that the decrease of the free volume above 4 % PANi weight is mainly due to the shrinking of the free volume which can

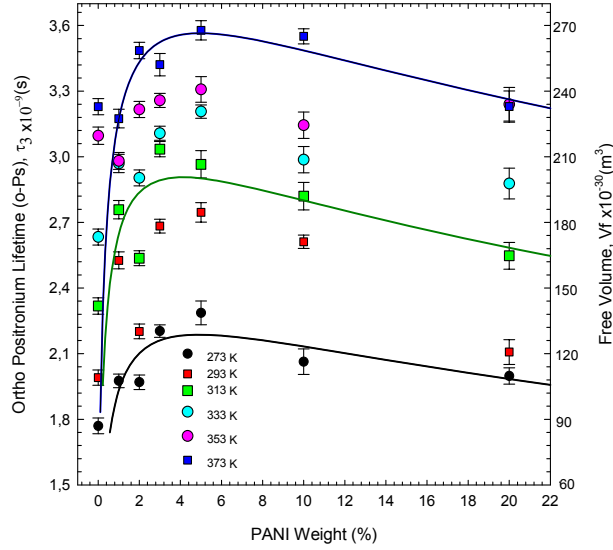


Figure 4. The variation of the o-Ps lifetime τ_3 versus PANi weight for all temperatures.

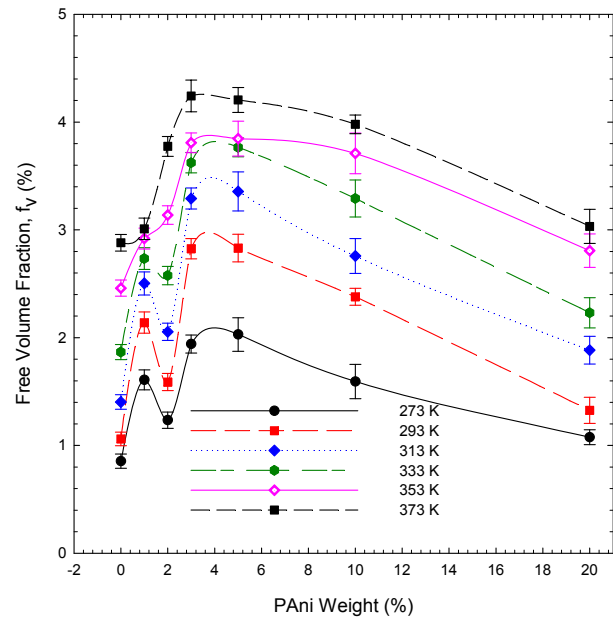


Figure 5. Free Volume Fraction f_v versus PANi weight for all temperatures.

be claimed to the occupation of available free volumes via increasing the additive.

It can be seen that the free volume hole size increases with increasing temperature. This indicates thermal expansion of the free volume hole size. The logarithm of the free volume hole size can be given as a function of temperature:

$$\ln v_f = \ln v_{f0} + \alpha_f T,$$

where $\alpha_f = \partial \ln v_f / \partial T$ is defined as the thermal expansion coefficient of the free volume hole size and $\ln v_{f0}$ is an intercept parameter on the free volume axis.

The fitting parameters of the linear regression for different PANi weight percentage are tabulated in Table 1. Here r^2 is the correlation coefficient squared for the regression. It has some discrepancies in the high temperature region due to scattering of the data. However, we would like to stay at the linear relation of the free volume hole size and know how the thermal expansion coefficients change with the PANi additive. Figure 6 shows the thermal expansion coefficient of the free volume hole size with respect to PANi additive. The resulting graph shows the rapid decrease in the thermal expansion coefficient of the free volume hole size up to 4 % and then modest increase after 4 % with increasing PANi weight. However, there is a sharp rise at 2 % PANi weight agreeing with earlier discussions. We observed similar behavior for the thermal expansion coefficient of the free volume hole size as we discussed before the PALS and DBAR parameters about a turning point at about 4 % PANi weight. This indicates that new free volume holes are increasingly introduced in the PVdF-co-HFP with the increasing temperature as well as the free volume hole size with the additive of PANi after about 4 %.

Using experimental density measurement of the PVdF-co-HFP with molecular weights [21], we fitted the density data at ambient pressure and obtained the following relations for the temperature from 313 to 373 K:

$$\ln V(\text{m}^3/\text{kg}) = \ln V_\alpha + \alpha_T T(K)$$

$\ln V_\alpha = -7.724$ and $\alpha_T = 0.822 \times 10^{-3} \text{K}^{-1}$ for 321 Da and $\ln V_\alpha = -7.737$ and $\alpha_T = 0.880 \times 10^{-3} \text{K}^{-1}$ for 471 Da with the correlation coefficient squared 0.9863 and 0.9926 of the linear regression, respectively. We find that the thermal expansion of the PVdF-co-HFP for 400 Da (our sample molecular weight) is approximately $\alpha_T = 0.851 \times 10^{-3} \text{K}^{-1}$. If we compare it with the thermal expansion coefficient, $\alpha_{v_f} = 11.47 \times 10^{-3} \text{K}^{-1}$ given in Table 1, we can conclude that α_T is 0.0742 times α_{v_f} of which the

PANi weight (%)	$\ln v_{f0}$	$10^3 \alpha_{v_f}$	r^2
0	1.246	11.47	0.9640
1	2.765	7.305	0.7828
2	1.788	10.26	0.9617
3	3.052	6.835	0.8356
5	3.066	6.905	0.8913
10	2.551	8.208	0.8912
20	1.998	9.516	0.9113

Table 1. The linear regression coefficients. r^2 is the correlation coefficient squared for the regression.

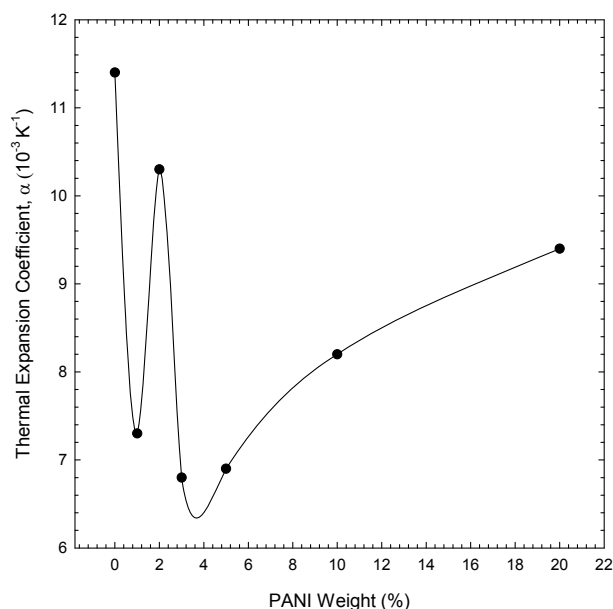


Figure 6. The thermal expansion coefficient of the free volume hole size with respect to PANi weight percentage additive.

difference can be attributed to the occupied spaces not considered in the latter. For this reason, specific volume can be written as $V = V_0 + V_f = V_0 + N_h v_f$ [22] where V_0 is the specific occupied volume, V_f is the total free volume, and N_h is the total hole number per unit mass. From this relation, we can obtain $\alpha_T = f_\alpha \alpha_{v_f}$ where $f_\alpha = V_f / (V_0 + V_f)$ will be called as “thermal expansion fraction” and N_h is assumed to be constant. In this case, $f_\alpha = 0.0742$ and it can be presumably employed to estimate the thermal expansion coefficient of the PVdF-co-HFP with PANi additives in Table 1.

The S (sharp) parameter in Figure 7 fluctuates between 273 K and 373 K and varies with PANi weight percentages. As the S parameter increases, the W (wing) parameter decreases [13]. Thus, for convenience, we did not show the plot of W versus temperature. We plotted the S parameter as a function of PANi weight percentages in Figure 8 to see the effect of weight dependence on the S parameter. It shows that the S parameter behaves like the o-Ps intensity and o-Ps lifetime. However, the S parameter drops deeply at 2 % and then increases sharply up to 5 % and after which decreases progressively.

All these results above indicate the presence of defects or voids (free volume). To understand what type(s) of defects in our sample, the S parameter versus the W parameter was plotted and shown in Figure 9. In the Figure 9, the S parameter depends linearly on the W parameter; it can be explained that one straight line (fitting line) may indicate that there is mainly one type of defects [23].

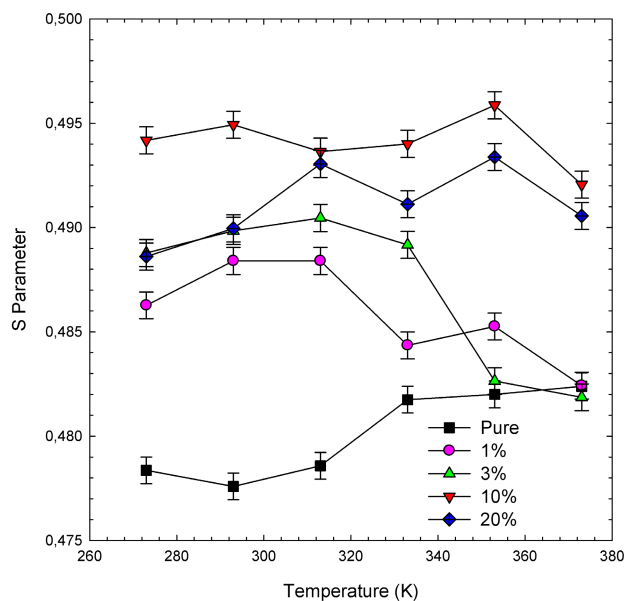


Figure 7. The W parameter as a function of temperature for all samples.

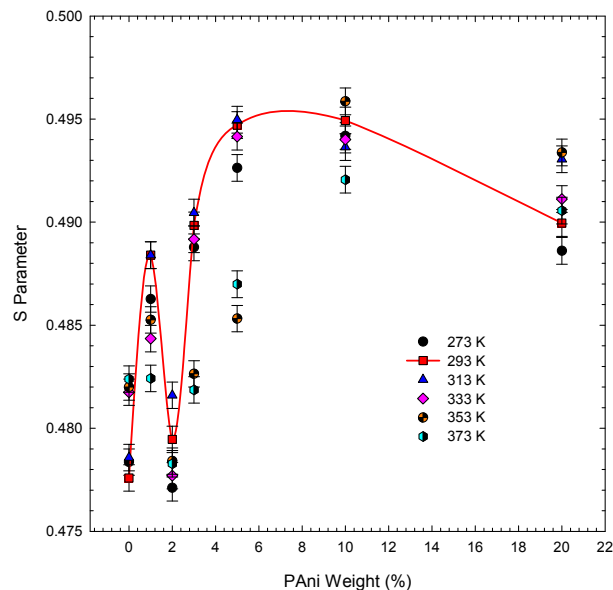


Figure 8. The S parameter versus PANi weight for all temperatures.

4 Conclusions

In conclusion, the positron annihilation lifetime spectroscopy (PALS) and the Doppler broadening annihilation radiation (DBAR) have been successfully applied to measure the free-volume properties such as the o-Ps free volume intensity, the o-Ps lifetime, the S and W parameters at all temperatures for conducting composite polymer samples. The results yield information about the free-volume contents. Increasing the percentage of PANi added to polymer

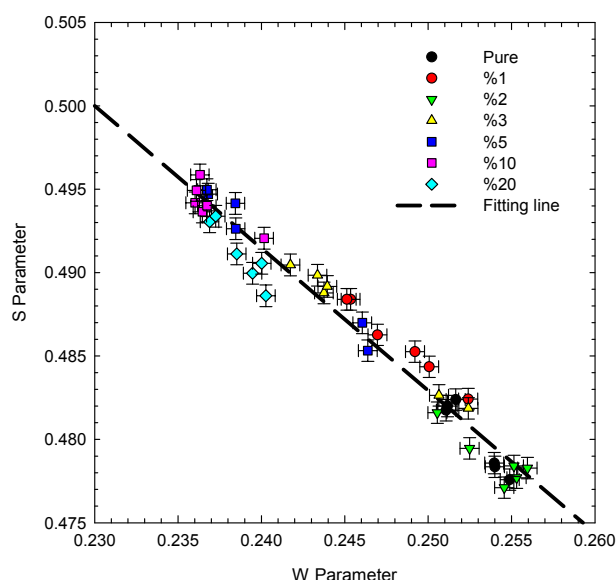


Figure 9. The S parameter versus the W parameter for all samples.

matrix, PVdF-co-HFP, affected the fraction of free volumes, free volume intensity. It was found that I_3 and τ_3 increased with increasing temperature as a function of weight percentages below 4 % and after which decreased constantly. It can be concluded that the free volume increases with an increase in the size of the open spaces which occurred due to weight percentages when below 4 %. From the DB parameters, we can suggest that there is one type of defect in the samples. We also calculated the thermal expansion coefficient of free volume hole size as a function of PANi weight extracted from PALS data.

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