

On the free volume evolution in a deformed epoxy composite. A positron annihilation study

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Abstract

After fabrication of an epoxy system filled with aluminum powder, followed by inelastic deformations under compression of the specimens, Positron Annihilation Lifetime Spectroscopy (PALS) was used to follow the evolution of the free-volume holes in the matrix. In order to describe the micromechanical deformation mechanism that takes place in the matrix around the inclusions, the experimental free-volume holes data were analyzed in terms of a model specifically developed. This model involves a hydrostatic internal stress resulting from the fabrication process of the composites and the deviatoric part of the applied stress during inelastic deformation. The influence of both kinds of stresses on the modification of the free-volume sizes in the matrix is discussed.

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1. Introduction

With the increasing demands of polymer materials in various technological applications, many polymer composites filled with inorganic materials have been developed. The primary purposes for using inorganic fillers in polymer composites were to reduce the cost and to modify the specific properties such as modulus, toughness, thermal and electrical conductivities, viscosity, opacity and brightness, etc.

In these heterogeneous polymer systems, external load can initiate several micromechanical deformation processes. The character and extent of these deformations play a crucial role in the energy absorption, macroscopic deformation and failure of the material. The prevailing

micromechanical deformation mechanism is determined by the inherent properties of the matrix polymer and by the local stress distribution. Magnitude and distribution of the local stresses are determined by three factors: stress concentration, thermal stresses and interaction of the components [1]. These three factors are frequently discussed from the point of view of continuum mechanics. In the case of metal matrix composites, the discussion is extended to the microscopic viewpoint through the dislocation theory [2]. But, in amorphous matrix composites, like a polymer matrix, the above mentioned theory cannot be applied [3].

Today, the idea that inelastic deformation in amorphous polymers can be viewed as local shear transformations is well-accepted [4]. Such transformations will primarily occur in regions where the local resistance to inelastic rearrangements is low. An excess volume per atom characterizes these regions and the clustering of these excesses over the volume of the region is referred as the local free-volume or as free-volume holes. Moreover, the density and size of these free-volume holes depend on the deviatoric component of the applied stress tensor and

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then, they will change with the further inelastic deformation. The hydrostatic component can only change the size of the holes.

A direct measure of the free-volume holes is uniquely determined by positron annihilation lifetime spectroscopy (PALS). In molecular solids and liquids, a fraction of the positrons injected from a radioactive source forms positronium (Ps), these positrons can annihilate from the *para*-positronium (*p*-Ps), singlet spin state, or from *ortho*-positronium (*o*-Ps), triplet spin state, with a relative formation probability of 1:3 [5–7]. Usually, three lifetime components appear in the PALS spectra of amorphous polymers, they are attributed to the annihilation of *p*-Ps, free positrons (not Ps), and *o*-Ps. *p*-Ps decays mainly via self-annihilation with a characteristic lifetime in vacuum of about 125 ps. The lifetime of *o*-Ps (142 ns in vacuum) decreases in condensed matter, typically to the low nanosecond range due to the pick-off annihilation process. In such a case, it is possible that the positron of the *o*-Ps state can annihilate with an electron other than its bound partner (and opposite spin). Typically, if *o*-Ps is confined to the free-volume holes in amorphous polymers, its lifetime is reduced from the 0.5 to 5 ns range. Besides, the characteristic lifetime of the pick-off annihilation process is highly sensitive to the size of these free-volume holes, for more details see [8–10]. PALS measurements have demonstrated their usefulness for studying the free-volume fraction in polymers as a function of the temperature [11,12]. Furthermore, by using the density and size of the free-volume holes as internal state variables the microscopic mechanical state is characterized [13–15].

Recently, the authors of the present paper have reported information about the evolution of the free-volume with the filler content in epoxy composite specimens [16]. Goyanes et al. used the results obtained by means of PALS to explain the yield stress behavior, consequence of the internal stresses, developed in the epoxy matrix when aluminum particles were introduced as reinforcement of the resin during the fabrication process. To gain further insight into the comprehension of the role of the free-volume holes in the plastic deformation mechanism of this kind of epoxy composites, specimens of the same composite system used in the previous paper were plastically deformed under compression at different levels. In such a way, the scope of the present paper consisted of describing the micromechanical deformation mechanism that takes place in the matrix around the inclusions. The changes in the sizes of the resulting free-volumes induced by different levels of micromechanical deformation were experimentally determined by positron lifetime measurements. Then, these values were introduced in a model specifically developed by using the local shear transformation theory. This model involves a hydrostatic internal stress resulting from the fabrication process and the deviatoric part of the applied stress during inelastic deformation. It allows predict how the size and density of free-volume holes in the matrix around

inclusions is modified by the filler content, the fabrication process and the plastic deformation.

2. Experimental

2.1. Materials

The material studied was an epoxy resin reinforced with different amounts of aluminum powder (Al 1060 min 99.6% Al). Particle sizes between 106 and 125 μm were obtained using a sieve. Samples with filler volume fractions ϕ of 0, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 were molded.

An appropriated amount of aluminum particles was dried at 383 K, then mixed with epoxy resin (diglycidyl ether of bisphenol A (DGEBA), 100 pbw) and hardened (methyltetra hydrophthalic anhydride (MTHPA), 90 pbw) by stirring at room temperature in vacuum during 30 min. The accelerator (heterocyclic amine 0,7 pbw) was added to the compound and stirred again during 2 min under vacuum. The degassed compound was poured in a Pyrex tubular mold of 12 mm diameter and 100 mm length. Seven molds were placed in horizontal position around the axis of a tubular oven with the help of an especially made device. This device can also impose a rotation to the molds to prevent the settling down of the aluminum filler during the whole curing process; a frequency of 0.08 Hz was used in all cases. The curing cycle was the following: first a heating step at 0.8 K/min until arriving at 393 K, and after holding this temperature during 14 h. Finally, the samples were cooled inside the oven until room temperature.

2.2. Mechanical test

Samples for compression tests (ASTM D695M-90) were cut from the central part of the cured rods. Mechanical tests were performed at room temperature using an Instron 4206 machine with a strain rate of $3.47 \times 10^{-3} \text{ s}^{-1}$. The tests were stopped at two levels of plastic strain (ϵ_p): 3 and 8%. No barreling was observed at these values of plastic strain.

2.3. PALS measurements and data analysis

Specimens in form of disks of 2 mm thickness and 12 mm diameter were cut from the cured rods and from the deformed samples using a low-speed diamond saw. Then, the samples were given a final polish with diamond paste up to 1 μm prior to each measurement at room temperature (RT).

A lifetime spectrometer with a time resolution (FWHM) of 255 ps was used. A 20 μCi source of ^{22}Na deposited on Kapton foil (7.5 μm thick) was sandwiched between two identical samples of the particulate composite. The source contribution and the response function were evaluated by using the code RESOLUTION [17]. The positron lifetime spectra were recorded with a total number of 3×10^6

coincidence counts. For lifetime data analysis LT [18] and POSITRONFIT [17] programs were used with an adequate source correction. PALS spectra were decomposed into three discrete lifetime components as usual in polymers. The long-lived lifetime component τ_3 is attributed to *o*-Ps annihilation (by pick-off) trapped in the free-volume holes. In the approximation proposed by Tao [19] and Eldrup et al. [20], it is assumed that *o*-Ps resides in a spherical well of radius R_0 with an electron layer of thickness $\delta R = R_0 - R = 0.166$ nm [20] which constitutes the wall of the hole and can overlap with the *o*-Ps wave function. Then, the lifetime component τ_3 is related to the radius of the hole through the following semi-empirical expression:

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

The values of the radii obtained from Eq. (1) should be interpreted only as rough estimates, since real holes are irregularly shaped. Average volume of holes $v_h = (4/3)\pi R^3$ can be obtained from Eq. (1).

Instead of the three discrete lifetime components, a continuous distribution of the inverse of the longest lifetime $\xi(1/\tau_{o-Ps})$ can be obtained by analyzing the PALS spectra with the LT program, where in this distribution τ_{o-Ps} is τ_3 . As mentioned in Ref. [21], the continuous long-lived component is related to the radius distribution $f(R)$ by means of:

$$f(R) = 2\delta R \left[\cos\frac{2\pi R}{R + \delta R} - 1 \right] \frac{\xi(1/\tau_{o-Ps})}{(R + \delta R)^2} \quad (2)$$

Then, it is possible to obtain the free volume distribution as

$$g(V_{o-Ps}) = \frac{f(R)}{4\pi R^2} \quad (3)$$

as well as the centroid of the log-normal free-volume distributions $g(v_h)$ and the dispersion $\sigma(v_h)$. Furthermore, the fraction of positrons annihilating in cavities with volumes between V_{o-Ps} and $V_{o-Ps} + dV_{o-Ps}$ is $g(V_{o-Ps})dV_{o-Ps}$ can be obtained [22].

At this point, it is worth mentioning that the distributed and discrete lifetime results obtained in the present work by using LT and POSITRONFIT analysis, respectively, were in very good agreement.

3. Results and discussion

In Fig. 1, the dependence of the average volume of the free-volume V_h on the filler volume fraction ϕ and the level of deformation are shown. The data corresponding to the evolution of V_h with the charge of reinforced aluminum particles for non-deformed specimens were taken from Table 1 of our recent work [16]. In such a case, a behavior characterized by three stages can be observed. The first

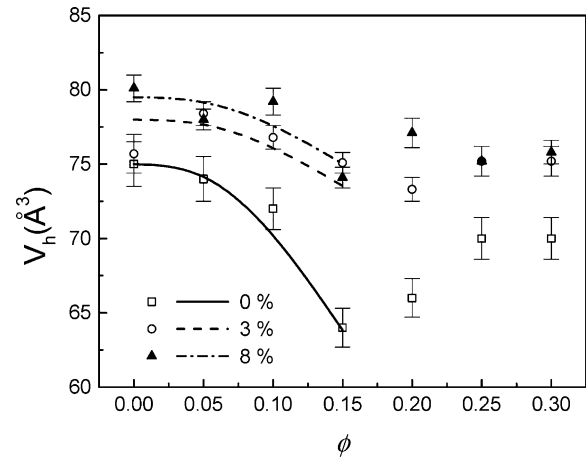


Fig. 1. Dependence of the free-volume fraction obtained from PALS measurements on the filler content and the deformation level. The different lines represent the best fits to the positron data for each deformation level by using the models described in Section 3.

stage, due to the introduction of some few particles inside the matrix, begins with an important decrease of the free-volume reaching a minimum value for a percentage charge content of 15%. Then, during the second stage V_h shows a monotonous increase when the percentage filler content grows up to approximately 25%. After that, the filler volume fraction between 0.25 and 0.30 V_h remains approximately constant, within the experimental scatter.

On the other hand, the plastic deformation introduced by means of compression stress produces a systematic increase of the free-volume in the samples with and without inclusions (Fig. 1). In this figure, only in the deformed composite resins (i.e. when the specimens have inclusions) a change in V_h can be clearly seen. On the contrary, no changes were observed when the material is filler free. Specifically, for 3% deformation the above mentioned change in V_h is significant. This behavior is more noticeable for 8% deformed charged epoxy resins. However, if the absolute V_h values obtained by measuring the 3 and 8% deformed specimens are compared, the difference in the corresponding free volumes is systematically (i.e. for each ϕ) smaller than that revealed comparing the non-deformed and 3% deformed level specimens.

In the following items, we will try to explain these findings.

3.1. Free-volume of the non-deformed composite specimens

The composite material develops internal stresses during the fabrication process as a consequence of differences in the mechanical-thermal elastic properties of the filler and the epoxy matrix. If this internal stress field has a non-zero hydrostatic component, the free-volume fraction f_v of the polymer can be modified according to Ref. [23] as:

$$f_v = f_v^0 - \beta P \quad (4)$$

where f_v^0 is the free-volume fraction of the epoxy resin in the pressure-free state, P is the hydrostatic internal pressure and β is called free-volume compressibility. The free-volume fraction and the average volume of holes can be related by [24,25]:

$$f_v = N_h V_h \quad (5)$$

where N_h is the number of holes per volume unit. If the density of holes does not change with the filler volume fraction of the composite material, Eq. (4) can be rewritten as:

$$V_h = V_h^0 - \frac{\beta}{N_h} P \quad (6)$$

For ϕ values lower than 0.20, the monotonous decrease of V_h when the filler content increases (Fig. 1) can be reasonably explained taking into account a mechanism in which the internal pressure P developed in the epoxy matrix of the composite is considered positive.

In the past, several authors have modeled the thermal residual stresses in particulate composites using different calculation methods. In the model of Park and Earmme [26] a shell of the matrix embedded in an effective medium that surrounds the spherical inclusions is proposed. In this model, the shell elastic constants corresponding to the composite material were used. Then, the mean pressure inside the shell of Eq. (6) can be obtained as

$$P = -\frac{\langle \sigma_{jj} \rangle}{3} = \frac{12K_F K_M (G_C - G_M) \phi}{D} (\varepsilon_{jj}^F)^T + \frac{4K_M [G_C (3K_F + 4G_M) - 3K_F \phi (G_C - G_M)]}{D} (\varepsilon_{jj}^M)^T \quad (7)$$

where

$$D = (3K_F + 4G_M)(3K_M + 4G_C) - 12\phi(G_C - G_M)(K_F - K_M) \quad (8)$$

$$(\varepsilon_{jj}^F)^T = 3(\alpha_F - \alpha_C)\Delta T \quad (9)$$

$$(\varepsilon_{jj}^M)^T = 3(\alpha_M - \alpha_C)\Delta T \quad (10)$$

and K is the bulk modulus, G is the shear modulus, α is the lineal thermal expansion coefficient and, the subscripts and superscripts F, M and C represent the filler, matrix and composite, respectively. At a temperature T_0 , the system is in the free-stress-state.

When the temperature decreases to T , being $\Delta T = T - T_0$, the residual stress develops due to the thermal mismatch. In agreement with Eshelby [27], $(\varepsilon_{jj}^F)^T$ and $(\varepsilon_{jj}^M)^T$ are considered the traces of the ‘thermal transformation strain field’. The fabrication process of the composites studied introduces a new component in the transformation strain as a consequence of a very much smaller thermal expansion coefficient of the mold of Pyrex has than that of the composite material. In the stage of fabrication, the mould

applies an external pressure P_e to the composite at a temperature T_0 (the cure temperature). Thus, during the curing process the system is in a state without stress. When the temperature gets lowered to T this external pressure disappears. Therefore, for each phase the trace of the ‘thermal transformation strain field’ must be rewritten as:

$$\begin{aligned} (\varepsilon_{jj}^F)^{T,P_e} &= (\varepsilon_{jj}^F)^T + (\varepsilon_{jj}^F)^{P_e} \\ &= 3(\alpha_F - \alpha_C)\Delta T + \left(\frac{1}{K_F} - \frac{1}{K_C}\right)P_e \end{aligned} \quad (11)$$

and

$$\begin{aligned} (\varepsilon_{jj}^M)^{T,P_e} &= (\varepsilon_{jj}^M)^T + (\varepsilon_{jj}^M)^{P_e} \\ &= 3(\alpha_M - \alpha_C)\Delta T + \left(\frac{1}{K_M} - \frac{1}{K_C}\right)P_e \end{aligned} \quad (12)$$

In order to evaluate the external pressure P_e , the volumetric change of the composite from room temperature until the end of the curing process must be considered. During the cure cycle, the epoxy resins suffer volumetric changes due to thermal expansion and chemical shrinkage. In the literature [28,29], the last one is usually attributed to polymerization reactions.

An idealized outline of the volumetric changes of epoxy resins due to thermal expansion and chemical shrinkage can be described as follows: In the first stage, when the liquid resin is instantaneously heated from RT until the cure temperature T_0 , before any chemical shrinkage occurs, the volume increases as a natural consequence of the thermal expansion. During the second stage, when the temperature is maintained constant the volume decreases due to the chemical shrinkage. Finally, when the samples are cooled till to RT, the thermal contraction produces another volume decrease. Taking into account the above analysis, the total volumetric change of the epoxy resin corresponding to the whole curing process can be estimated by:

$$\left(\frac{\Delta V}{V}\right)_M = 3\alpha_M^{\text{above}}(T_0 - T) + \left(\frac{\Delta V}{V}\right)_M^{\text{shrinkage}} \quad (13)$$

where α_M^{above} is the thermal expansion coefficient of the epoxy resin above T_g and $(\Delta V/V)_M^{\text{shrinkage}}$ is the chemical shrinkage of the epoxy resin at T_0 . For composite materials, the volumetric change should also be estimated using Eq. (13). Then, the external pressure P_e present in Eqs. (11) and (12) can be evaluated according to:

$$\begin{aligned} P_e &= -K_C \left(\frac{\Delta V}{V}\right)_C \\ &= -3\alpha_C^{\text{above}} K_C (T_0 - T) - \left(\frac{\Delta V}{V}\right)_C^{\text{shrinkage}} \end{aligned} \quad (14)$$

where α_C^{above} is the thermal expansion coefficient above T_g of the epoxy composite material and $(\Delta V/V)_C^{\text{shrinkage}}$ is the chemical shrinkage of the composite material at the temperature T_0 .

Finally, inserting Eqs. (7), (8), (11), (12) and (14) in Eq. (6) a detailed expression for the dependence of the free volume on the filler volume fraction can be obtained. The capability of prediction of this model is strongly dependent on the thermal, elastic and swelling properties of the composite material.

The coefficients K_C , α_C , G_C and $(\Delta V/V)_C^{\text{shrinkage}}$ can be evaluated using the Hashin and Strikman relationships obtained for a two-phases compound [31]

$$K_C = K_F + \frac{(1-\phi)}{\frac{1}{K_M - K_F} + \frac{3\phi}{3K_F + 4G_F}} \quad (15)$$

$$\alpha_C = \alpha_M + \frac{\alpha_F - \alpha_M}{\frac{1}{K_F} - \frac{1}{K_M}} \left(\frac{1}{K_C} - \frac{1}{K_M} \right) \quad (16)$$

$$G_C = G_F + \frac{(1-\phi)}{\frac{1}{G_M - G_F} + \frac{6\phi(K_F - 2G_F)}{5G_F(3K_F + 4G_F)}} \quad (17)$$

$$\left(\frac{\Delta V}{V} \right)_C^{\text{shrinkage}} = \left(\frac{\Delta V}{V} \right)_M^{\text{shrinkage}} \left(1 - \frac{\frac{1}{K_C} - \frac{1}{K_M}}{\frac{1}{K_F} - \frac{1}{K_M}} \right) \quad (18)$$

Assuming that the α_C^{above} coefficient follows a mixture law, it can be estimated by

$$\alpha_C^{\text{above}} = \alpha_M^{\text{above}}(1-\phi) + \alpha_F(\phi) \quad (19)$$

For non-deformed specimens, the best fit to the free-volume experimental data (see the solid line in Fig. 1) were obtained inserting the terms evaluated from Eqs. (15)–(19) and the parameters given below in the detailed expression of Eq. (6):

$$K_F = 77.8 \times 10^9 \text{ Pa} \quad G_F = 25.93 \times 10^9 \text{ Pa}$$

$$\alpha_F = 23 \times 10^{-6} \text{ K}^{-1}$$

$$K_M = 3.2 \times 10^9 \text{ Pa} \quad G_M = 1.07 \times 10^9 \text{ Pa}$$

$$\alpha_M = 60 \times 10^{-6} \text{ K}^{-1}$$

$$\Delta T = -100 \text{ K} \quad \beta = 3.13 \times 10^{-10} \text{ Pa}^{-1}$$

$$\left(\frac{\Delta V}{V} \right)_M^{\text{shrinkage}} = 0.069$$

$$\alpha_M^{\text{above}} = 210 \times 10^{-6} \text{ K}^{-1} \quad V_h^0 = 75 \text{ \AA}^3$$

$$N_h = 1.2 \times 10^{21} \text{ cm}^{-3}$$

Characteristic coefficients of the mechanical and thermal properties of the matrix were given by the supplier with the exception of α_M^{above} which was obtained from Ref. [30]. In

the case of the filler these coefficients were obtained from the literature [31]. From Refs. [24,30] the values of β and $(\Delta V/V)_M^{\text{shrinkage}}$ were, respectively taken. From the fitting procedure, the values of the remaining parameters V_h^0 and N_h were got. It is worth noting that the value of the holes density N_h resulting from the fitting is in very good agreement with those recently reported for different epoxy systems [32].

In the present work, the model proposed to analyze non-deformed epoxy-resin composites predicts a systematic decrease of the average volume of the holes beyond 15% of volume filler fraction. However, the experimental values show a contrary behavior. This discrepancy in the prediction of the model suggests that for volume filler fractions higher than 15%, the particles of the filler percolate and, therefore, some fraction of the polymeric matrix become occluded. In such a way, the chemical shrinkage of the occluded matrix would induce a negative hydrostatic pressure on itself. Using Eq. (6), this negative hydrostatic pressure should induce an increase of the free-volumes inside the occluded matrix and the average volume of the holes in the overall composite material growth. It is reasonably to expect that the fraction of occluded matrix continue growing with the increment of the filler content. Consequently, the free-volume in the composite material should reflect the same behavior as the data shown in Fig. 1.

3.2. Effect of the plastic deformation

When the matrix is only plastically deformed, no changes are present in the trace of the ‘thermal transformation strain field’ given by Eqs. (11) and (12). This behavior can be assigned to the null trace of the plastic transformation strain. However, the size and number of free volumes in the polymer matrix must change as a consequence of the plastic deformation. In Fig. 2(a) the $g(V_{o-Ps})$ in the blank polymer as a function of V_{o-Ps} for the different plastic deformation levels are shown. From this figure, it can be concluded that there exists an increase in the size of the free-volumes when the deformation increases. This result agrees with those previously reported on similar studies [33,34]. For the composite epoxy resin the same behavior was found. As a representative case, the free volume distribution functions with a percentage filler content of 15% against the deformation were chosen (Fig. 2(b)). However, it must be considered that for blank and charged materials measured the term $(\partial V_h^0 / \partial \epsilon)$ is very different. In our opinion, this difference can be attributed to the inhomogeneity of the plastic strain field produced in the matrix around the inclusions as a consequence of a stress concentration.

Let assume that till 15% of percentage filler content the particles do not percolate. Then, for a given plastic deformation of the composite material, the stresses concentration around the inclusions should be independent of the volume filler fraction. Therefore, the values of V_h^0 and N_h should be constant. In fact, specifically the model

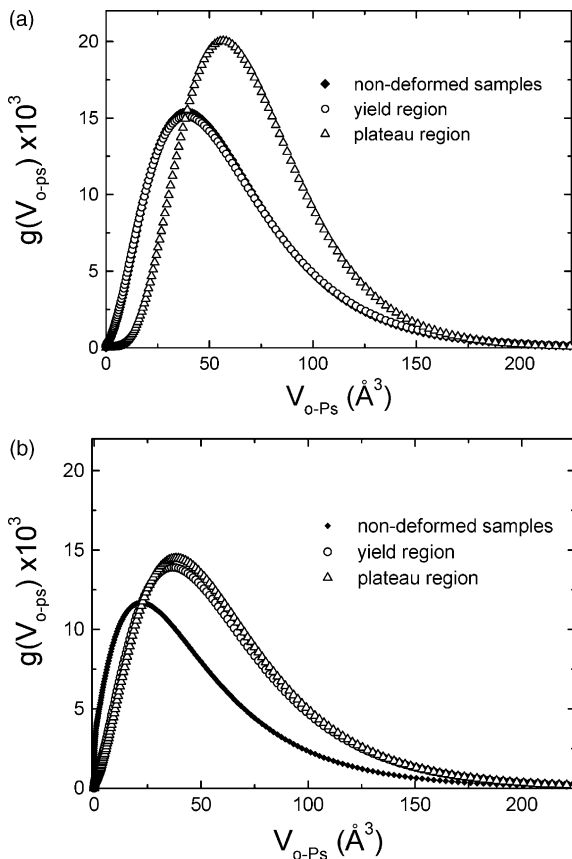


Fig. 2. Free-volume distribution functions $g(V_{o-ps})$ as a function of the plastic deformation. (a) Blank epoxy resin, (b) epoxy matrix composite filled with 15% volume fraction of aluminum powder.

proposed in the present work reasonably fits the data for the deformed composite specimens up to a filler volume fraction $\phi=0.15$ (see the fitting dash and dot-dashed lines in Fig. 1). Furthermore, except V_h^0 and N_h , the same parameters used for non-deformed samples were also used to satisfactory fit the experimental data obtained for all plastic deformed samples. Therefore, it must be considered that V_h^0 and N_h are dependent on the deformation level as demonstrated for the corresponding values obtained from the best fits of the experimental data given below:

- For 3% of deformation level,
 $V_h^0 = 78.0 \text{ \AA}^3$, $N_h = 3.13 \times 10^{21} \text{ cm}^{-3}$.
- For 8% of deformation level,
 $V_h^0 = 79.5 \text{ \AA}^3$, $N_h = 3.13 \times 10^{21} \text{ cm}^{-3}$.

Finally, it is worth mentioning that, in agreement with the experimental data shown in Fig. 2, the values of V_h^0 grow when the plastic deformation increases.

4. Conclusions

The present work contributes to understand the deformation mechanism that takes place around the inclusions in

a polymer matrix composite. To obtain information regarding the microscopic point of view, the local shear transformation theory was used. Taking advantage of the high sensitivity of the Positron Annihilation Lifetime Spectroscopy, it was possible to measure the average volume of the free-volume holes in the neighborhood of the site in which the plastic deformation can be located. Specifically, this deformation rises as a consequence of the action of the deviatoric component of the external stress applied.

For non-deformed composites, the experimental data show that the size of these holes depends on the filler content in the composite. In this case, it was demonstrated that this behavior is a consequence of a hydrostatic internal pressure induced over the polymeric matrix during the curing process. Specifically, we propose that this hydrostatic internal pressure results from the mismatch among: (i) the thermal expansion of the mold; (ii) the thermal expansion of the composite specimens and (iii) the chemical shrinkage of the polymer matrix. In particular, it can be concluded that the minimum in the free-volume values for filler contents 15% ca. appears as an onset of the percolation process of the filler particles. It can be assigned to the chemical shrinkage of the occluded matrix, giving place to a positive hydrostatic component of the internal stress over the matrix.

In the case of deformed specimens, it was shown that the action of the deviatoric component also changes the size and density of the free-volumes; but, it does not modify the influence of the hydrostatic internal stress on the size of the holes.

Finally, from the different fitting procedures to the experimental data, values of the holes density N_h for non-deformed and deformed samples were reported. For epoxy deformed systems, the values obtained represent an additional contribution to the knowledge of the microstructure of such composites.

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