

Yield and internal stresses in aluminum filled epoxy resin. A compression test and positron annihilation analysis

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Abstract

The influence of the filler content on the mechanical properties of an epoxy resin composite filled with aluminum powder was investigated. Compressive tests were performed at room temperature and at different strain rates. The response of the composites was also studied by positron annihilation lifetime spectroscopy. The dependence of the yield stress on the filler content is shown. The results are discussed in terms of a proposed model that takes into account the contribution of the filler powder. To this purpose information from positron spectroscopy is important since it allows to correctly evaluate the internal stresses introduced in the composite epoxy lattice by the metal filler.

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1. Introduction

Composite materials made of polymer matrix and rigid particles usually show important residual internal stresses produced during the fabrication process. This phenomenon is a consequence of the differences in the thermal expansion characteristics between the two phases. In the case of a polymer matrix made by cured epoxy matrix with metal powder as filler, this difference is very high.

These internal stresses in the compound have a strong influence on the mechanical behavior of the material and depend on the cure process, filler type, shape, content and dispersion [1–6].

Uniaxial compression tests are a useful tool to characterize the mechanical behavior of particulate composites, since they allow to evaluate the dependence of the yield stress on the strain rate and the filler content. In the literature several models explaining the yield stress behavior have been presented [5,7–9]. However, there is not enough information on the correlation between yield stress and the microstructure of the compounds.

Positron lifetime annihilation spectroscopy (PALS) is an increasingly important analytical technique that can be used as a bulk probe of sub-nanometer voids in porous media and free volume in polymers [10–12]. Ortho-positronium (o-Ps) lifetime is known to be correlated to the size of the free volume holes. More specifically, the spectral component associated with o-Ps is particularly sensitive to variations in the size of the holes; [10–12] therefore, this technique allows to monitor changes of the fractional free volume

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induced by variation of external parameters (temperature, pressure, mechanical stresses, etc.).

The goal of this work is to evaluate the role of the filler content—aluminum powder (Al)—on the mechanical behavior of an epoxy matrix composite. With this aim, the matrix was filled with different amounts of Al and the microstructural behavior was analyzed by means of mechanical testing. To evaluate the experimental data and to take into account the particle contribution to the mechanical response of the samples, a new term was added to a well-known mechanical model for polymers [13–16]. By using positron information, and taking advantage of the useful relationships amongst positron and mechanical parameters, recently obtained by some of the authors of the present paper [17], it was possible to analyze in a more thorough way the microstructural changes in the composites mater as a consequence of Al filling.

2. Experimental

2.1. Material

The material used in this study was an epoxy matrix reinforced with different amounts of aluminum powder (Al 1060–0, min 99.6% Al). The epoxy resin, the curing agent and the accelerator used were a diglycidyl ether of bisphenol A (DGEBA), a methyl tetra hydrophthalic anhydride (MTHPA) and a heterocyclic amine (*N*-methyl imidazol), respectively. All of them were provided by the CIBA Company (Argentina).

A sieve was used to obtain aluminum particle sizes between 106 and 125 μm . The appropriate amount of aluminum particles, dried at 383 K, was mixed with epoxy resin (100 pbw, i.e. part by weight) and hardened (90 pbw) by stirring at room temperature (RT) under vacuum during 30 min. The accelerator (0.7 pbw) was then 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 in a device placed in the axis of a tubular oven. To prevent the settling down of the aluminum filler, the device imposed a rotation to the molds at a frequency of 0.08 Hz during all the curing process. The curing cycle was the following: first, a heating step at 0.8 K/min up to 393 K, then, this temperature was kept constant for 14 h. Finally, the samples were cooled inside the oven down to RT.

Samples with filler volume fractions $\phi = 0, 0.05, 0.10, 0.15, 0.20, 0.25$, and 0.30 were molded.

Optical micrographs of the samples with filler volume fraction of 0.10, 0.20 and 0.30 are shown in Fig. 1. A homogeneous distribution of particles, without the presence of agglomerates or holes, was observed in all samples. The black stains, shown in Fig. 1, are particles started up during the preparation of the samples for the photographs.

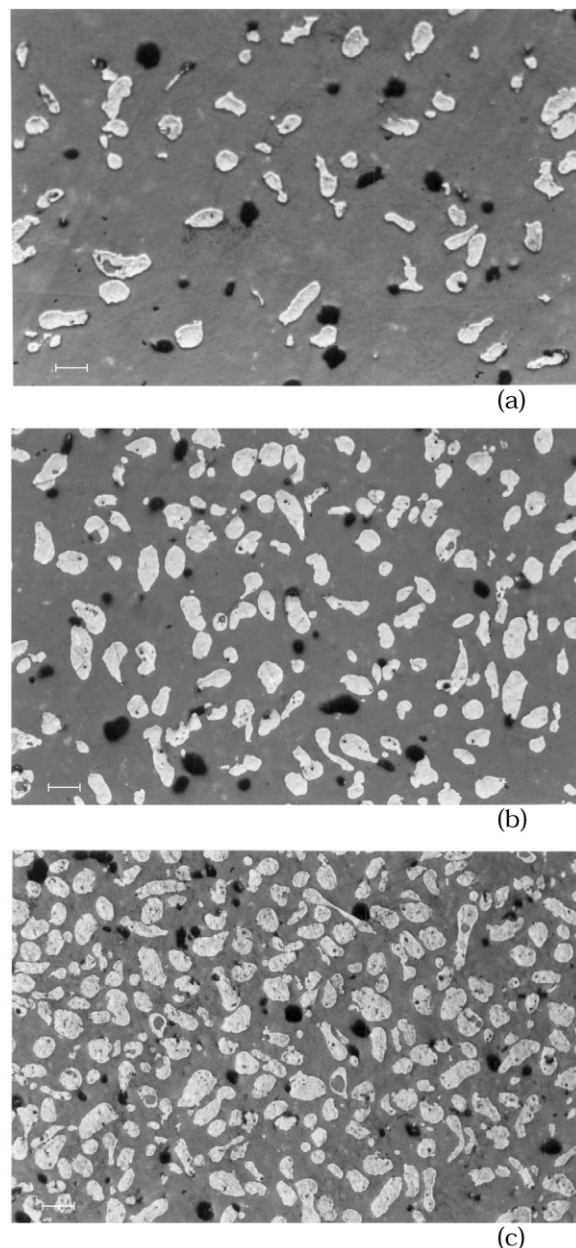


Fig. 1. Microscopic photographs of aluminum filler composite for three different volume fraction (a) $\phi = 0.10$, (b) $\phi = 0.20$, (c) $\phi = 0.30$. Scale = 200 μm .

2.2. Measurements and characterization

2.2.1. Density

The density, ρ , of the composites were measured applying the Archimedean principle considering the weight of the sample in air and water. Fig. 2 shows the values of the density at RT as a function of the volume fraction of aluminum powder in the compound. Usually, the density of a two phases composite is expressed by

$$\rho_c(1 - \phi)\rho_m + \phi\rho_f \quad (1)$$

where the subscripts *c*, *m*, and *f* mean composite, matrix and

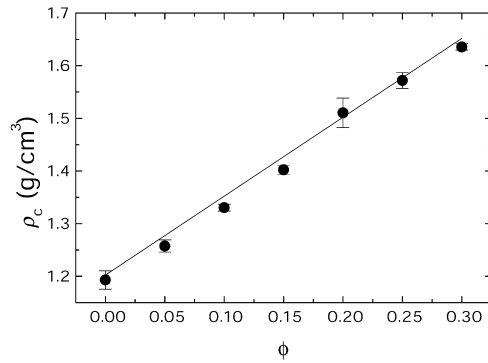


Fig. 2. Density of the composites as a function of filler content.

filler, respectively. A value of $\rho_f = 2.7 \text{ g/cm}^3$ was used for the aluminum filler [18].

It results $\rho_m = \rho_c$ for $\phi = 0$. A comparison between the experimental values of ρ_c and those predicted by Eq. (1) is shown in Fig. 2: a very good agreement is obtained. Together with the evidence of the microscopic observations this confirms the absence of macroscopic holes in the samples.

2.2.2. Mechanical test

Compressive tests (ASTM D695M-90) were performed on all specimens at RT with the following strain rates, $\dot{\epsilon}$: 3.47×10^{-5} , 3.47×10^{-4} , 3.47×10^{-3} and $3.47 \times 10^{-2} \text{ s}^{-1}$ using an Instron 4206 testing machine. Samples were cut from the central part of the cured rod. For each filler content, five samples were tested at each strain rate.

The yield stress, σ_y , was evaluated as the stress at the yield point. The values of σ_y are given in Fig. 3 for each test conditions. Each value in the figure is the average of five tests and the statistical error is less than 1.5%.

2.2.3. PALS measurements

PALS measurements were carried out on specimens in the form of discs of 2.5 mm thick, which were cut from the rods used for the mechanical tests, using a low-speed diamond saw. Then, the samples were given a final polish

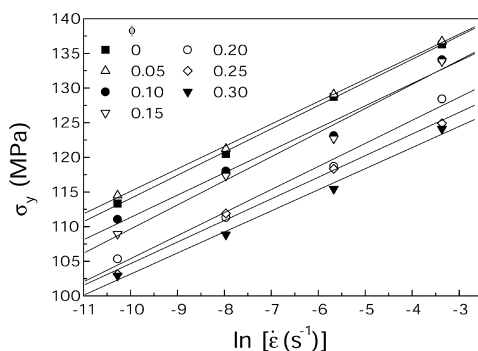


Fig. 3. Dependence of the compressive yield stress, σ_y , on the strain rate, $\dot{\epsilon}$, for samples with different filler Al content. For the sake of simplicity, the error bars are not shown in the figure.

with diamond paste up to $1 \mu\text{m}$ prior to each positron lifetime measurement at RT.

The lifetime spectrometer was a fast-fast timing coincidence system with a time resolution (FWHM) of 255 ps. A $20 \mu\text{Ci}$ source of [22] Na deposited on a thin Kapton foil was sandwiched between two identical specimens. The source contribution and the response function were evaluated by means of the code RESOLUTION [19]. The positron lifetime spectra were measured with a coincidence rate of about 60 cps and a total number of $3\text{--}4 \times 10^6$ coincidence counts. The lifetime spectra were deconvoluted into three components through the LT program [20]. Details about the analysis here adopted are given in Ref. [17]. It was also used the POSITRONFIT program [19] to analyze positron lifetime spectra into three components and the results were in very good agreement with those obtained with LT.

3. Results and discussion

In Fig. 3 the dependence of the yield stress on the strain rate for different volume fractions of the aluminum filler is shown. Both the non-filled and the composite samples show a logarithmic dependence of the compressive yield stress on the strain rate. The same behavior has been reported on different types of epoxy matrices [21–23]. From Fig. 3 it can be deduced that the yield stress decreases by increasing ϕ at a constant strain rate and for filler volume fractions higher than 0.10.

When considering a particulate composite where the particles have a yield stress lower than the matrix ($\sigma_y \approx 28 \text{ MPa}$ for aluminum 1060 [24]), the compressive engineering yield stress of the composite is attained by regarding the true residual cross section between the particles as stress bearing [7–9]:

$$\sigma_c = \sigma_m(1 - a\phi^{2/3}). \quad (2)$$

where σ_m is the yield stress of the matrix. The parameter a depends on the shape, the degree of dispersion of the filler and the adhesion level between matrix and filler.

In the case of unfilled polymers, the yield stress can be written as [13–16]

$$\sigma_m = 2\beta G + \frac{2kT}{V_s} \ln \frac{\dot{\epsilon}}{\dot{\epsilon}_0} \quad (3)$$

where V_s is the activation volume related to the deformation process, G is the shear modulus of the polymer, $\dot{\epsilon}_0$ is a parameter that depends on the microstructure of the material and $\beta \approx 0.076$ [13].

If the material has a dispersed phase, internal stresses will develop in the epoxy matrix as a consequence of the curing process. They are usually present because of the differences in the mechanical-thermal elastic properties of the filler and the matrix. Polymers usually have a linear thermal expansion coefficient (α) higher than that for a

mineral or metal filler. Specifically, the corresponding values of such a coefficient are $70 \times 10^{-6} \text{ K}^{-1}$ for the epoxy resin matrix, according to the supplier, and $23 \times 10^{-6} \text{ K}^{-1}$ for aluminum [18], respectively. After fabrication, and during the cooling process, large stresses can be developed in both matrix and particles.

The analysis of the thermal residual stress has been mostly performed by the modified equivalent inclusion method. For example, in the generalized self-consistent method (referred as GSCM), the two-phase composite is considered as a sphere perfectly bound to a spherical shell embedded in an effective medium. The residual stress is expressed in terms of the elastic modulus, the thermal expansion coefficient of each phase and the effective medium [25].

Park and Earmme [26] showed that in the GSCM the internal stresses in the inclusion are constant and in the matrix and the effective medium depend on r (the radial coordinate). Therefore, there is an average value $\langle \sigma_i^m(\phi) \rangle$ with respect to its volume in the matrix.

The effect of this average internal stress is to modify the yield stress of the matrix in the following way

$$\sigma_m = 2\beta G + \frac{2kT}{V_s(\phi)} \ln \frac{\dot{\epsilon}}{\dot{\epsilon}_0} + \langle \sigma_i^m(\phi) \rangle \quad (4)$$

From Eqs. (2) and (4), it follows:

$$\sigma_c = \left[2\beta G + \frac{2kT}{V_s(\phi)} \ln \frac{\dot{\epsilon}}{\dot{\epsilon}_0} + \langle \sigma_i^m(\phi) \rangle \right] (1 - a\phi^{2/3}) \quad (5)$$

In Fig. 3, it can be appreciated that the solid lines obtained by using Eq. (5) fit the experimental data very well. Then, the following information can be extracted:

- (i) from the slope, the different parameters involved in the following term

$$\text{slope}(\phi) = \frac{2kT}{V_s(\phi)} (1 - a\phi^{2/3}) \quad (6)$$

and

- (ii) from the ordinate corresponding to $\dot{\epsilon} = 1$,

$$\begin{aligned} \text{ordinate}(\phi) &= \left[2\beta G - \frac{2kT}{V_s(\phi)} \ln \dot{\epsilon}_0 + \langle \sigma_i^m(\phi) \rangle \right] \\ &\times (1 - a\phi^{2/3}) \end{aligned} \quad (7)$$

By using Eq. (6), the variation of the activation volume, with the filler content could be evaluated. However, the value of the parameter a is unknown, and it is not possible to achieve a complete characterization of the material with the mechanical data alone.

For this purpose, the positron annihilation information was used as described below. In a recent paper [17] some of the current authors obtained different expressions that allowed to link directly mechanical and positron parameters

in a simple way as follows:

$$V_s(\phi) = C v_3(\phi) \quad (8)$$

$$\dot{\epsilon}_0(\phi) = v_g \frac{f_v}{v_3} V_s(\phi) \quad (9)$$

where C is a constant; v_g is the number of attempts per unit of time to attain the transformation barrier configuration (for more details, see Ref. [27]). The meaning of v_3 and f_v will be immediately given below.

From the analysis of the positron lifetime spectra, the values of the longest lifetime component τ_3 and those of the associated intensity I_3 , shown in Table 1, were obtained. According to the common interpretation, this component has been assigned to *ortho*-Ps decay. The lifetimes τ_1 and τ_2 (not shown in Table 1) are associated with the annihilation of positrons located into regions characterized by different electron densities. τ_1 should be considered as a weighed mean of two different components, since it also contains annihilations from *para*-Ps. The mean size of the holes forming the free volume can be roughly estimated by means of a simple quantum mechanical model: [28,29] *ortho*-Ps in a hole is approximated to a particle in a spherical potential well with radius R_0 . It is assumed that an electronic layer forming a thickness δR is present on the walls of the hole, whose effective radius is consequently reduced to $R = R_0 - \delta R$. The following equation relating R (Å) and τ_3 (ns) is usually used: [28,29]

$$\tau_3 = 0.5 \left[1 - \frac{R}{R + \delta R} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R + \delta R} \right) \right]^{-1} \quad (10)$$

with $\delta R = 1.66 \text{ Å}$ [30]. The semi-empirical Eq. (10) allows to find the average volume of the hole, in a spherical approximation. The intensity of the longest component, I_3 , is often claimed to be linearly correlated to the density of holes, so that the free volume fraction f_v of the polymer is written as follows:

$$f_v = C_3 I_3 v_3 \quad (11)$$

being C_3 a constant and v_3 the average spherical volume of the hole. However, Eq. (11) has been criticized, since I_3 is so sensitive to different factors (such as thermal history [31], source exposure time [32] and exposure to visible light [33])

Table 1

Dependence of positron parameters (τ_3 and I_3) on the filler metal content. In this table, the average hole volume v_3 obtained from the positron parameters by using Eq. (10) is also included

ϕ (% Al content)	τ_3 (ns)	I_3 (%)	v_3 (Å ³)
0	1.73 ± 0.03	19.7 ± 2.0	75 ± 1.5
5	1.72 ± 0.04	16.5 ± 0.7	74 ± 1.5
10	1.70 ± 0.02	13.8 ± 0.2	72 ± 1.4
15	1.61 ± 0.02	10.2 ± 0.2	64 ± 1.3
20	1.63 ± 0.03	11.5 ± 0.2	66 ± 1.3
25	1.67 ± 0.03	10.6 ± 0.4	70 ± 1.4
30	1.68 ± 0.03	10.5 ± 0.4	70 ± 1.4

that its changes cannot be exclusively accounted for free volume variations. For these reasons the following equation has been recently used by various authors [34–36]:

$$f_v = Av_3 \quad (12)$$

and we will follow the same approach in the present work.

Table 1 also includes the corresponding values of the hole volume v_3 , for all the measured samples.

By using Eqs. (8) and (6) can be rewritten as

$$\text{slope}(\phi)v_3(\phi) = \frac{2kT}{C} - \frac{a2kT}{C}\phi^{2/3} \quad (13)$$

A good fit to the experimental data by using Eq. (13) is observed in Fig. 4, from which the values of $a = (0.34 \pm 0.02)$ and $C = (32 \pm 1)$ could be estimated.

Once obtained the parameter a , Eq. (7) can be written as:

$$h(\phi) = \frac{\text{ordinate}(\phi)}{(1 - a\phi^{2/3})} = \left[2\beta G - \frac{2kT}{Cv_3(\phi)} \ln \dot{\epsilon}_0 + \langle \sigma_i^m(\phi) \rangle \right] \quad (14)$$

It is obvious that for $\phi = 0$, $\langle \sigma_i^m(\phi) \rangle = 0$ and then

$$h(0) = 2\beta G - \frac{2kT}{Cv_3^0} \ln \dot{\epsilon}_0^0 \quad (15)$$

where the superscript 0 is associated with the parameters when $\phi = 0$. By using Eqs. (8), (9), (12), (14) and (15), it is easy to obtain

$$\langle \sigma_i^m(\phi) \rangle = h(\phi) - 2\beta G + \frac{2kT}{Cv_3(\phi)} \ln \left(\frac{v_3}{v_3^0} \right) - \frac{v_3^0}{v_3(\phi)} (h(0) - 2\alpha G) \quad (16)$$

By inserting in Eq. (16) the experimental data from the mechanical tests and positron lifetime measurements, it is possible to obtain the variation of the internal stress with the filler amount which is shown in Fig. 5. The value of the shear modulus G for the polymer was estimated from the Young's modulus E measured from the compression tests. In the range of the strain rates evaluated a value of

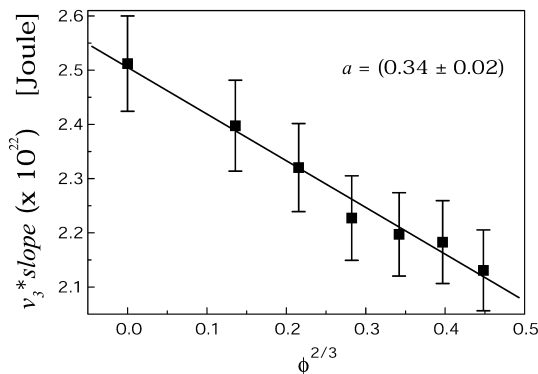


Fig. 4. Linear fitting of the product $v_3(\phi) \cdot \text{slope}(\phi)$, obtained by using Eq. (12) and the experimental data, as a function of $\phi^{2/3}$.

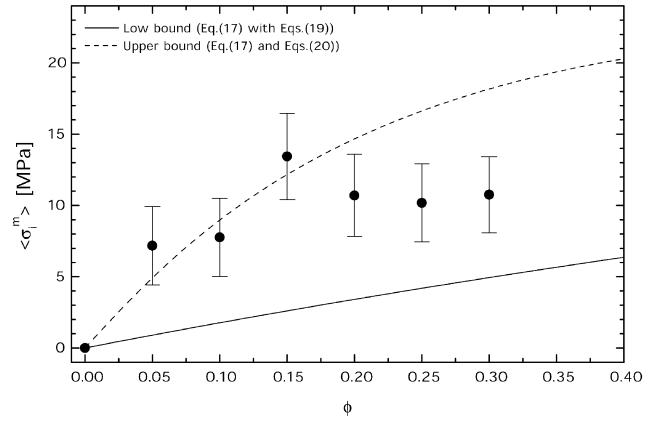


Fig. 5. Dependence of the internal stress with filler volume fraction calculated from Eq. (16). The lines represent the values of $\langle \sigma_i^m(\phi) \rangle$ predicted by Eq. (17) with Eqs. (19a–c) (solid) and (20a–c) (dashed), respectively.

$E = (2.85 \pm 0.05)$ GPa was obtained. Then, by considering $G = E/[2(1 + \nu)]$ and with the Poisson ratio $\nu = 0.35$ as indicated by the resin supplier, a value of $G = (1.06 \pm 0.02)$ GPa was obtained. The bulk modulus of the polymer can be estimated from the relationship $K = E/3(1 - 2\nu)$.

From Fig. 5 can be noted that the average internal stress increases up to 15% of the filler content and then remains approximately constant. As working hypothesis the system was considered as dilute for low values of ϕ . As ϕ increases, the matrix is locally distorted and the average stress is likely to be higher. At a given level of filler content the interaction between fillers could become important and the internal stress levels up. However, further work must be done in order to elucidate this point.

For comparative purposes, it should be noted that the values obtained are similar to those previously reported in the literature for other particulate composites [1,3]. On the other hand, if the thermal expansion coefficients and the modulus of filler and matrix previously mentioned are used, it is possible to estimate the internal stress by using GSCM [26]. According to this method in the case of a particle having a higher shear modulus than the matrix, the mean internal stress in the matrix is expressed as [26]

$$\langle \sigma_i^m(\phi) \rangle = \frac{36K_f K_m}{D} (G_m - G_c)(\alpha_f - \alpha_c)\Delta T \phi + \frac{12K_m}{D} \times (\alpha_m - \alpha_c)[3K_f \phi(G_c - G_m) - G_c(3K_f + 4G_m)]\Delta T \quad (17)$$

with

$$D = (3K_f + 4G_m)(3K_m + 4G_c) - 12\phi(G_c - G_m) \times (K_f - K_m) \quad (18)$$

where ΔT is the difference between the cure temperature and RT, K the bulk modulus and the subscripts f , m and c represent the filler, matrix and composite, respectively.

Lower (–) and upper (+) bounds of α_c , K_c and G_c can be evaluated using the Hashin and Shtrikman relationships [37] for two-phase media as

$$\alpha_{c(-)} = \alpha_m + \frac{\alpha_f - \alpha_m}{\frac{1}{K_f} - \frac{1}{K_m}} \left(\frac{1}{K_{c(-)}} - \frac{1}{K_m} \right) \quad (19a)$$

$$K_{c(-)} = K_m + \frac{\phi}{\frac{1}{K_f - K_m} + \frac{3(1 - \phi)}{3K_m + 4G_m}} \quad (19b)$$

$$G_{c(-)} = G_m + \frac{\phi}{\frac{1}{G_f - G_m} + \frac{6(1 - \phi)(K_m + 2G_m)}{5G_m(3K_m + 4G_m)}} \quad (19c)$$

$$\alpha_{c(+)} = \alpha_m + \frac{\alpha_f - \alpha_m}{\frac{1}{K_f} - \frac{1}{K_m}} \left(\frac{1}{K_{c(+)}} - \frac{1}{K_m} \right) \quad (20a)$$

$$K_{c(+)} = K_f + \frac{(1 - \phi)}{\frac{1}{K_m - K_f} + \frac{3\phi}{3K_f + 4G_f}} \quad (20b)$$

$$G_{c(+)} = G_f + \frac{(1 - \phi)}{\frac{1}{G_m - G_f} + \frac{6\phi(K_f + 2G_f)}{5G_f(3K_f + 4G_f)}} \quad (20c)$$

Using this set of equations and Eqs. (17) and (18), the variation of $\langle \sigma_i^m(\phi) \rangle$ with the filler content were calculated taking into account that

$$K_i = \frac{E_i}{3(1 - 2\nu_i)}$$

and considering the reported data for the filler properties [38], $E_F = 70 \times 10^9$ Pa, $\nu_F = 0.35$. The results are shown in Fig. 5 the values of the internal stress obtained, combining the mechanical and positron data, lie between the two curves.

Therefore, it can be concluded that the estimation of the internal stresses obtained in the range of filler content considered in the present work is reasonable.

4. Conclusions

The main contribution of PALS technique to this research is to give information about the modifications of the free volume by the presence of filler. Besides, the changes of the free volume reflect those corresponding to the activation volume in the material which is strongly related to the deformation plastic process. This information is the key of the characterization of the polymer matrix in the composite to analyze the yield stress behavior with the filler content.

It is known that during the fabrication process of the composite, residual internal stresses are produced when cooling the material from the cure temperature to the service

temperature. Usually, these internal stresses are considered in expressions that describe the behavior of the composite yield stress with the strain rate, temperature, filler content, etc. Internal stresses are generally evaluated by means of theoretical approaches which consider the fabrication process variables as well as material physics characteristics. In this paper, it has been introduced a new way to obtain internal stresses through information on the free volume given by PALS together with well known relationships of the yield stress with the strain rate. It is clear that the approach proposed implies additional experimental effort, but the results of the variation of the internal stresses with the filler content show a reasonable agreement between the values of the internal stresses estimated from the generalized self-consistent method and those obtained in the present research.

Finally, it could be asserted that the combination of the two techniques, PALS and compression test, gives an interesting tool for a better understanding of the process involved in the plastic deformation of particulate composites.

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References

- [1] Gupta VB, Brahatheeswaran C. J Appl Polym Sci 1994;52:107.
- [2] Nakamura Y, Yamaguchi M, Okubo M, Matsumoto T. J Appl Polym Sci 1992;44:151.
- [3] Low IM. J Mater Sci 1990;25:2144.
- [4] Lutz MP, Zimmerman RW. J Appl Mech 1996;63:855.
- [5] Nielsen LE, Landel RF. In: Shojiro O, editor. Mechanical properties of polymers and composites. New York: Marcel Dekker Inc; 1994. p. 398. Chap. 7.
- [6] Lilholt H. In: Shojiro O, editor. Mechanical properties of metallic composites, 17. New York: Marcel Dekker Inc; 1994. p. 425. Chap. 17.
- [7] Tavman IH. J Appl Polym Sci 1996;62:2161.
- [8] Bazhenov S. Polym Engng Sci 1995;35:813.
- [9] Ramsteiner F, Theysohn R. Composites 1984;15:121.
- [10] (a) Jean YC. Microchem J 1990;42:72. (b) Jean YC. Mater Sci Forum 1995;175–178:59.
- [11] Dlubek G, Fretwell HM, Alam MA. Macromolecules 2000;33:87.
- [12] Mogensen OE. Positron annihilation in chemistry. Berlin: Springer; 1995.
- [13] Brown N. In: Brostrow W, Corneliussen RD, editors. Failure of plastics. Hanser: Munich; 1986. p. 112–3.
- [14] Seitz JT. J Appl Polym Sci 1993;49:1331.

- [15] Gonzales G, Benites GM, Goyanes SN, Rubiolo GH, Marzocca AJ. *An Assoc Quim Argent* 1996;48:105.
- [16] Benites GM, Goyanes SN, Terzzoli MC, Rubiolo GH, Marzocca AJ. *Proceedings of Fifth Latin American and Third Ibero American Polymer Symposium*, vol. 1. Argentina: Mar del Plata; 1996. p. 292.
- [17] Rubiolo GH, Somoza A, Goyanes SN, Consolati G, Marzocca AJ. *Phys Rev B* 1999;60:3792.
- [18] Lide DR. *Handbook of chemistry and physics*. London: CRC Press; 1993. p. 130, Chapter 12.
- [19] Kirkegaard P, Pedersen NJ, Eldrup M. In: Dorikens-Vanpraet L, Dorikens M, Segers D, editors. *Positron annihilation*. Singapore: World Scientific; 1988. p. 642.
- [20] Kany J. *Nucl Instr Meth A* 1996;374:235.
- [21] Miwa M, Takeno A, Yamazaki H, Watanabe A. *J Mater Sci* 1995;30:1760.
- [22] Truong VT. *Polymer* 1990;31:1669.
- [23] Harding J. *Composites* 1993;24:323.
- [24] Shackelford JF, Alexander W, Park JS. *Materials science and engineering handbook*. Boca Raton, Florida United States: CRC Press Inc; 1994. p. 429.
- [25] Cristensen RM. *J Mech Phys Sol* 1990;38:379.
- [26] Park SJ, Earmme YY. *J Comp Mater* 1999;33:1205.
- [27] Kocks UF, Argon AS, Ashby MF. In: Chamlers B, editor. *Progress in materials science*, vol. 19. Oxford: Pergamon Press; 1975.
- [28] Eldrup M, Lightbody D, Sherwood N. *ChemPhys* 1981;63:51.
- [29] Tao SJ. *J Chem Phys* 1972;56:5499.
- [30] Nakanishi H, Ujihira Y. *J Phys Chem* 1982;8:4446.
- [31] Wang CL, Hirade T, Maurer FJH, Eldrup M, Pedersen NJ. *J Chem Phys* 1998;108:4654.
- [32] Suzuki T, Miura T, Oki Y, Numajiri M, Kondo K, Ito Y. *Radiat Phys Chem* 1995;45:657.
- [33] Hirade T, Maurer FJH, Eldrup M. *Radiat Phys Chem* 2000;58:465.
- [34] Schmidt H, Maurer FJH. *Polymer* 2000;41:8419.
- [35] Bandzuch P, Kristiak J, Sausa O, Zrubcova J. *Phys Rev B* 2000;61:8784.
- [36] Dlubek G, Saarinen K, Fretwell HM. *J Polym Sci B* 1998;36:1513.
- [37] Hashin Z, Shtrikman S. *J Mech Phys Sol* 1963;11:357.
- [38] Kaye GWC, Laby TH. *Tables of physical and chemical constants*. New York: Longman; 1995. p. 44.