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On the matrix-particle interphase in epoxy-based composites

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ABSTRACT

A study on the interphase morphology in epoxy-based composites is presented. Composite samples containing a volume fraction of aluminum particles (typical sizes of 100 μm ca.) between 0% and 30% were prepared. As main experimental technique, differential scanning calorimetry (DSC) was used. Specifically, from the thermograms obtained for each composite, the differences between the heat flow at temperatures above and below the glass transition temperature were determined. From these data, for each composite, and following ideas suggested in the literature, the different thicknesses and volumetric fractions of interphase were estimated. The results obtained show that both morphological parameters strongly increase for a filler volume fraction above 15%. On the other hand, using positron annihilation lifetime spectroscopy technique, additional evidence allowed us to confirm the presence of an interphase region in the composites and estimate the associated free volume which was smaller than that corresponding to the epoxy matrix.

1. Introduction

Polymers have lower modulus and strength when comparing with metals and ceramics. In order to improve their mechanical properties, polymers are reinforced with inclusions (fibers, whiskers, platelets or particles), and the final material; i.e., the composite, improves its properties in comparison with those achieved by each individual phase. The study of polymer matrix composites is extremely important due to their multiple industrial applications. This kind of composites are widely used due to its unique attributes such as easy production, light weight, and often ductile nature. However, there are open problems to be solved in the understanding of such polymer-based composites. For example, the study of the region surrounding the inclusions in the matrix phase is subject of an increasing interest of research. In the literature, to describe this region into a polymer matrix-inclusion composite it has been considered as a hybrid phase between main phases (inclusion and matrix), called interphase or mesophase [1]. In particular, this region facilitates a matching for the chemical, physical and mechanical properties between matrix and inclusion [1–3].

For example, the interphases can arise due to preferential adsorption, catalytic influences of a surface, inter-diffusion, phase separation, etc. As a consequence, strong effects can be produced in the thermosetting matrices and, therefore the curing kinetics and the crosslink density can be affected. In such a case, gradients in composition or crosslink density lead to gradients in the microscopic properties of the composites [4,5].

From the experimental point of view, in the study of polymer composites the measurement of the interphase thickness, and therefore its associated volumetric fraction, is very difficult.

Thermal analysis is a suitable technique for the study of the interphase in different composite materials [6]. Specifically, a relationship between the variations of the heat capacity at constant pressure, C_p, and the interphase thickness has been reported in the literature. In such a way, C_p is accepted as a useful experimental parameter to estimate the interphase thickness [1].

In this work, we present a study on the morphological properties of the matrix-particle interphase in epoxy-based composites. The composites were fabricated using different volume fractions of aluminum powder as filler. By means of differential scanning calorimetry, the thickness and volumetric fraction of the interphases in the composites studied were obtained.

Furthermore, in order to go deeper into the interpretation of the experimental data regarding the interphase regions in the composites, positron annihilation lifetime spectroscopy (PALS) was used as a complementary experimental technique. As known, PALS is the most successful technique giving direct information about free volumes in polymers [7,8]. For example, small changes in the microstructure of thermosetting polymers produced by variations in the monomer-hardener epoxy formulation or by the use of several hardeners were studied in detail [9,10]. Thus, and based on

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previous works [11,12], quantitative information regarding the free volume associated with an interphase region is also reported.

2. Experimental

2.1. Sample preparation

The composites studied were prepared using as matrix diglycidyl ether of bisphenol A (DGEBA) epoxy resin, cured with an anhydride (MTHPA) and an accelerator (tertiary amine). In the curing, process the mixture was heated up to 393 K with a 0.8 K/min rate, and at the end of the heating process, the samples were kept at a constant temperature (393 K) for 14 h. The composites were fabricated using aluminum powder with particle diameters between 106 μm and 125 μm and with values for the filler volume fraction ϕ ranging from 0% to 30% in 5% steps. More details about the preparation process are given in Ref. [11].

2.2. Calorimetry

For the DSC scans, a Rheometrics Scientific SP instrument was used. Measurements were made under an Argon atmosphere and the samples of 9 μg weight were located into adequate aluminum pans. The heating rate was of 10 K/min and the temperature range from 293 K until 453 K. For each sample, a glass transition temperature (T_g) was obtained from the calorimetric scans. As usual, at T_g. a step in the heat flow versus temperature plot was observed.

After determining the glass transition temperature, the thickness and the volumetric fraction of interphase were estimated from the thermograms following the procedure described below.

To this aim, and in order to model our composites, we have followed ideas reported in the literature in which the geometry of the particles used as filler of the epoxy-based composites is assumed to be spherical with characteristics radii r_f [1]. Besides, it was considered that each particle is surrounded by an interphase, which has an associated thickness Δr_i. So, considering ΔC_p as the difference between the heat capacities (these experimental values were determined from the different thermograms) above and below T_g, respectively; i.e., $\Delta C_p = C_p(T > T_g) - C_p(T < T_g)$ the interphase thickness can be obtained by means of the following expression [1,2]:

$$\Delta r_i = r_f\left(\frac{\lambda_i.\phi}{1-\phi}+1\right)^{1/3} - r_f \tag{1}$$

where

$$\lambda_i = 1 - \frac{\Delta C_p^{\mathrm{Fill}}}{\Delta C_p^{\mathrm{Unf}}} \tag{2}$$

being C_p^{Fill} and $\Delta C_p^{\mathrm{Unf}}$ the differences in the heat capacities mentioned above corresponding to each composite (filled) and the matrix (unfilled), respectively. In our case, the matrix is the epoxy resin.

In this scenario, the volumetric fraction of interphase v_i was calculated using [1–3]:

$$v_i = \left(\left(\frac{\Delta r_i}{r_f}+1\right)^3 - 1\right)\phi \tag{3}$$

2.3. Positron annihilation lifetime measurements

For PALS measurements, a fast–fast timing coincidence system (resolution (FWHM) ~300 ps) and a 20 μCi sealed source of ^{22}NaCl solution deposited onto a thin Kapton foil was used. Positron lifetime spectra were recorded at room temperature with $\sim 2 \times 10^6$ coincidence counts. The spectra were analyzed with an adequate source correction using the constraint parameters LT code [13]. As usual in polymers, PALS spectra were satisfactorily decomposed into three lifetime components. For more details about the analysis see Refs. [7,11]. According to the common interpretation of PALS spectra in polymers, we ascribed the long-lived component to the ortho-Ps (ortho-Positronium) decay in free volume [7,8]. The free volume sizes v_h can directly be estimated using a well-recognized semi-empirical equation through the o-Ps lifetime component as the experimental input and a simple quantum mechanical model (see Refs. [7,8]).

3. Results and discussion

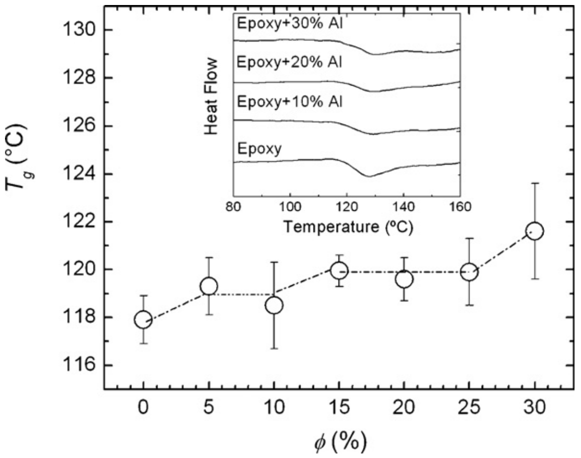

Fig. 1. T_g values (T_g onset) obtained for pure epoxy and the composites samples against versus the filler volume fraction. Lines are only eye guides. In the inset, DSC typical scans for the composite samples are presented.

Thermograms for the composite samples were obtained using DSC. In the inset located at the upper right side of the Fig. 1, the resulting typical thermograms are presented. From them the T_g value for each sample was obtained. In Fig. 1, T_g values (T_g onset) as a function of the volume filler fraction are shown. As can be seen, when aluminum powder is added to the epoxy matrix, the glass transition temperature measured for the matrix increases from 117.9 °C to a valued of about 118.9 °C which were measured for composites containing 5% and 10% of particles. Then, for higher ϕ values ($15\% \le \phi \le 25\%$) T_g remains approximately constant, within the experimental scatter, at a value of 119.8 °C. Finally, a significant increase in the glass transition temperature is observed for the maximum filler content ($\phi = 30\%$).

It is known that in polymeric composites, the glass transition temperature can increase or decrease relatively to that of the pure polymer depending on the type of chemical and/or physical bonding between filler and matrix in the interphase [14]. When the composite has a larger T_g than the matrix, it can be concluded that the bonding occurring in the interphase region is strong. On contrary, when the bonding in the interphase of the composite is weak a lower T_g value is obtained.

Considering that the glass transition temperature is associated with bulk properties of polymers, in the literature it has been pointed out that when only a surface layer of the polymeric matrix surrounding the inclusions is affected, a very small change in T_g should be expected [1]. In this frame, the relative T_g values measured are giving a first characterisation of the interphases present in the polymeric composites.

To go deeper into the analysis of the interphases, morphological information was looked for. The results obtained are presented below.

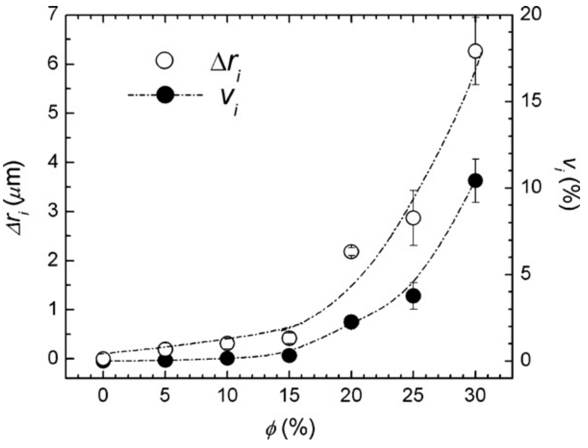

Fig. 2. Interphase thickness and volumetric fraction of interphase as a function of the filler volume fraction. These values were obtained using Eqs. (1)–(3). Lines are only eye guides.

In Fig. 2, the thickness and the volumetric fraction of interphase as a function of the filler content are shown. For each composite, the Δr_i. and v_i parameters were estimated using Eqs. (1)–(3). As can be seen, both parameters increase when the filler content increases, first slightly and then rapidly when ϕ is higher than 15%. The highest value of the interphase thickness (~6 μm) in correspondence with the highest filler content ($\phi = 30\%$) approximately represents 10% of the typical particle radii. This result, is in a good agreement with results reported in the literature [1,3].

On the other hand, the maximum value of v_i (10%) reached for $\phi = 30\%$ is equivalent to 15% ca. of the total volume of the matrix.

Summarizing, the contribution of the volumetric fraction occupied by the interphase into the matrix becomes significant especially for filler contents higher than 15%.

In Fig. 3, the variation of the average free volume as a function of the filler volume fraction is shown. As can be seen, there is a complex and non-monotonic behavior of v_h when ϕ increases. The plot can be divided into three regions. In the first, when the filler content is lower than 10%, v_h rapidly decreases from 76.8 Å^3 to 71.7 Å^3. Then this parameter increases up to 74.4 Å^3 when $\phi = 15\%$. Finally, in the third region, characterised by filler volume fractions higher than 15%, the average free volume decreases (initially slightly and then more markedly) until reaching an absolute minimum value of 69.6 Å^3. This v_h versus ϕ plot is slightly different, especially in the absolute values of v_h, from that previously reported by the authors of the present work [11]. However, such differences should be assigned to uncontrollable changes during the fabrication procedure of the samples at laboratory scale, such as the mechanical stresses generated as a consequence of the different expansion/contraction of the resin and recipient used for the curing of the polymer. However, the main issue we want to emphasize is that in all the epoxy particulate composites studied we have always found a minimum around 10–15 vol.% in the free volume against filler content plots.

It is well known that in composites there is a strong residual stress due to the different thermal expansion coefficients of the matrix and inclusion [15,16]. Therefore, it is possible to assume that this residual stress influences the average free volume. This assumption allowed Goyanes et al. [11] to satisfactorily explain the decrease in v_h for ϕ values up to about 10–15%. However, an explanation on the further behavior of the average free volume for highest aluminum powder content is still an open issue. In fact, DSC results shown in Fig. 2 indicate that the contribution of the interphase is detectable, within the experimental scatter, for ϕ values higher than 15%.

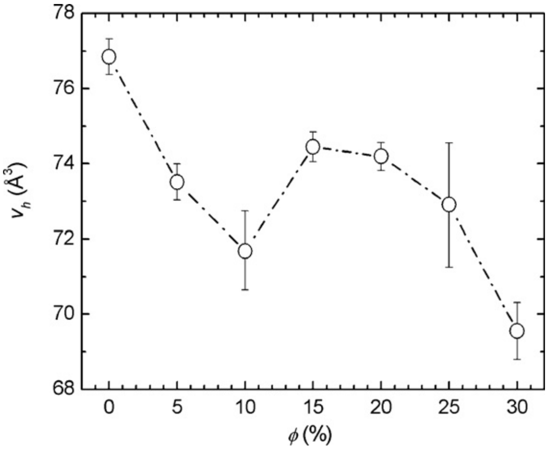

Fig. 3. Average free volume v_h versus filler volume fraction obtained from PALS measurements. Lines are only eye guides.

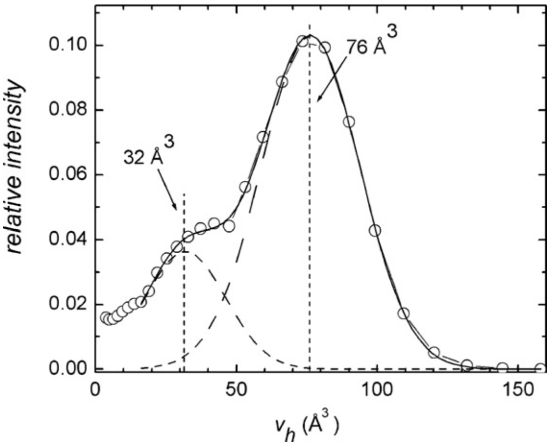

Fig. 4. Free volume distribution for the composite containing 15% of filler volume fraction (see text).

From a joint analysis of the DSC and PALS data, it could be assumed that the existence of a second contribution to the free volume size distribution due to the interphase is the responsible for the decrease in the average free volume for $\phi \geq 15\%$. In such a case, the average free volume in the composite (interphase and matrix), would be smaller than those of the matrix.

In order to reinforce this assumption with quantitative information on the average free volume distribution, positron annihilation lifetime spectra were re-analyzed using a free-constraint PALS spectra analysis code (MELT) [17]. In particular, samples containing a volume filler fraction of 15% were studied. This specific filler content was selected on the basis of DSC results, especially those presented in Fig. 2, since the volume fraction selected corresponds to the ϕ threshold from which a detectable contribution of the interphase is revealed. As a result, a bimodal-like distribution of the free volume was obtained (see Fig. 4). These results were estimated from the o-Ps lifetime component. Quantitatively, using a simple Gaussian fitting procedure, represented by dashed lines in the figure, the more intense distribution shows a well-defined free volume maximum around 76 Å^3, while it can reasonably be inferred that there is a less intense distribution with a smaller size located around 32 Å^3. Taking into account the discussion given above, the smaller v_h distribution can be associated with the contribution of the interphase region, while the larger one with the contribution of the polymeric matrix. Additional information obtained using PALS is not given here because it is out of the scope of the present work.

4. Conclusions

In the present work, some topics related to the matrix-particle interphase in epoxy-based composites filled with different amounts of aluminum powder content were studied. From the results obtained, the following items deserve to be pointed out.

- From calorimetric measurements, the thickness and volume fraction of the interphase region surrounding the filler were calculated. These parameters show an important increment for filler contents higher than 15%.
- The glass transition temperatures increase for the highest filler contents. This increment agrees with the assumption that in a polymer composite the interphase has a modified structure in comparison with that corresponding to the matrix. Furthermore, it was found that for the composites studied, there is a filler content threshold for which the presence of the interphase is detectable.

- Using positron annihilation lifetime spectroscopy, quantitative information on the matrix-particle interphase was obtained. In particular, from the composite containing 15% filler volume fraction a bimodal-like free volume distribution was revealed with maxima relative intensities located at 32 Å^3 and 76 Å^3. The smaller distribution was associated with the interphase region and the larger one to the epoxy matrix free volume, respectively.

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