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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.

Keywords: Epoxy resin; Plastic deformation; Free volume

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 (methyl-tetra 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 $3.47\times10^{-3}\ \mathrm{s}^{-1}$. 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