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Abstract. Positron annihilation lifetime spectroscopy was used to study the effect of water uptake on the free volume of a commercial epoxy exposed to atmospheres with relative humidity ranging from 30.5% to 95.8%. The absorption process was also analyzed by gravimetric measurements. When exposed to humidity the mean hole volume remains constant and the number of holes not occupied by water molecules decrease with increasing of both the exposure time and the relative humidity as indicated by the constancy of τ_3 and the decrease of I_3.

1. Introduction

Epoxy systems are polymers heavily cross-linked in which the cross-linking is derived from reactions of the epoxy group and thus it is a rigid and strong material. They have in general excellent adhesion to many surfaces, superior thermal resistance, a relative low dielectric constant, and ease of processing [1]. Owing to their superior mechanical and dielectric properties, coupled with excellent thermal stability and great chemical resistance, epoxy systems has been widely used in many applications as aircraft components, insulating layers and encapsulants in microelectronics industry, aerospace structural composites and many more [1, 2]. A major drawback of some epoxy systems, like the one used in this work, is their hygroscopic nature which results in the absorption of few percent moisture by weight under ordinary environmental conditions. The absorbed water plasticize the epoxy system, induces differential swelling stresses and generally degrades the physical properties of the epoxy. Some of the effects are a decrease of the glass-transition temperature (T_g), i.e. a decreased thermal stability [3]; a decrease in yield strength, a change of the yield/deformation mechanisms, or both [4]; the creation of micro-cracks or crazes [3, 5]; and chain scission through hydrolysis reactions [5]. Due to these factors it is important to control or inhibit moisture absorption to prevent these undesirable effects. Several studies have been undertaken to investigate the process of moisture absorption in epoxies, but the exact mechanisms that govern humidity-induced water uptake and diffusion of water

molecules within the material are still unclear. It is generally believed that moisture absorption is closely related to the free volume properties of the epoxy [2]. Positron Annihilation Lifetime Spectroscopy (PALS) is a well-established and very sensitive technique for probing sub-nanometer-sized local free volumes between molecular chains in polymeric structures. In the present work, we use PALS to investigate the effect of water absorption process on the free volume in one commercial epoxy submitted different relative humidity environments.

2. Experimental

The samples used in this study were made from one commercial epoxy resin known as SR1500 and one hardener known as SD2505 both produced by Sicomin Composites Company (France). The formulation bases of the epoxy resin SR1500 are bisphenol A and bisphenol F and this epoxy resin has been modified to be crystallization free and have low toxicity. The epoxy resin when mixed with the hardener, upon polymerization, forms the epoxy. The samples used were prepared from one continuous layer of approximately 2 mm of thickness.

The drying of the epoxy samples was performed by placing the samples in a sealed housing containing silica gel at 50ºC for several months (typically for 2 months).

The different relative humidity (RH) atmospheres were controlled between 0% and 95.8% and the temperature was constant at 50ºC except during the positron measurements. To maintain a precisely controlled RH atmosphere over long periods of time, saturated salt solutions were used. The atmosphere above these solutions had RH of 30.5% ($MgCl_2/H_2O$), 74.4% ($NaCl/H_2O$) and 95.8% (K_2SO_4/H_2O), respectively.

To determine the humidity-induced mass uptake in the epoxy samples submitted to different RH environments a precision balance (Perkin-Elmer microbalance, accuracy 0.01 mg) setup was used.

The positron lifetime measurements were carried out at room temperature (24 ºC) using a conventional fast-fast coincidence PALS setup (featuring Pilot-U scintillators and XP2020 photomultipliers) with a time resolution of 260 ps (FWHM). For each experiment, the positron [22]Na source (*ca*. ~30µCi, closed between Kapton® foils) was sandwiched by two identical samples. The lifetime spectra had a total number of *ca*. 2x10^{6} integral counts and were evaluated using the LT (version 9) code [6].

3. Results and discussion

It is generally accepted that the behavior of water absorption in the epoxy is well described by Fick's second law [7],

$$\frac{M}{M_{max}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} exp\left[\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right] \tag{1}$$

where M is the water absorption at time t, M_{max} is the equilibrium water absorption, L the sample thickness and D is the diffusion coefficient. For values of M/M_{max} lower than 0.5, equation 1 takes the simplest form,

$$\frac{M}{M_{max}} = \frac{4}{L}\sqrt{\frac{Dt}{\pi}} \tag{2}$$

The gravimetric results obtained for the relative mass uptake of the samples as a function of the square root of the exposure time for the 3 different RH environments, 30.5%, 74.4% and 95.8%, respectively, are shown in figure 1. The material shows increasing mass uptake from RH=30.5% to 95.8%. Higher RH environment values (74.4 and 95.8%) correspond to higher values of the equilibrium water absorption, achieving *ca*. 1.5% and 3% of relative mass percentage. For the samples submitted to higher RH environments, the water uptake is linearly proportional to $\sqrt{t}$ at the initial stage; for the lowest RH value it is difficult to see clearly this proportionality due to the small amount of uptaken water (less than 0.5%) for the 30.5% RH ambient. It can be also observed that the beginning of the equilibrium water absorption is achieved at approximately the same humidity exposure time ($\sqrt{t}$~20 h$^{1/2}$) and this is an indication that the diffusion coefficient, D, is the same for all samples.
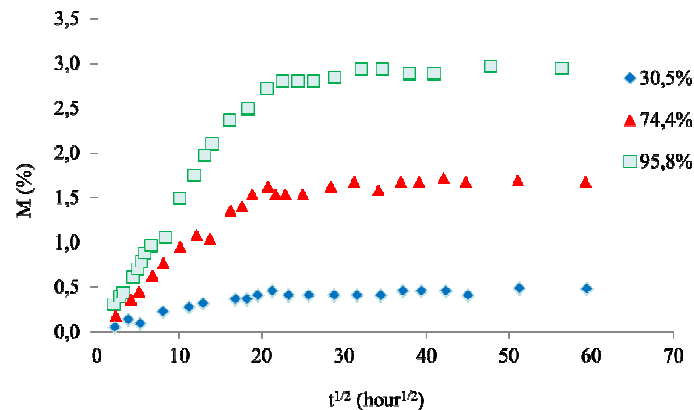
Figure 1. Relative mass uptake as a function of the square
root of exposure time of dry samples placed in different
RH environments.

In the systematic LT analysis it was observed that all spectra were well fitted with three components: two short-lifetime components (τ_1, I_1) and (τ_2, I_2) are normally assigned to self-annihilation of *p*-Ps and free/trapped positron annihilation, respectively; the longest lifetime component (τ_3, I_3) is due to the annihilation of *o*-Ps. τ_3 is considered to be related to the size of intermolecular-space holes, and a semi-empirical relationship between τ_3 and the size of holes for Ps localized on spherical holes [8] has been used to estimate the volume created among polymer chains. I_3 is often treated as a measure of the density of holes [9].

In our analysis the value of τ_1 was varying systematically around 155 ps and it was fixed to that value in order to reduce the artificial effects. Assuming that the pick-off annihilation is the only *o*-Ps quenching process the ratio between I_1 and I_3 is 1/3 and in the analysis the value of the intensity I_1 was forced to be equal to $I_3/3$.

The second lifetime component τ_2 was a free parameter in the fitting process and it had a regular value around 360 ps.

Since only the long-lived *o*-Ps lifetime could be related to the properties of the free volume size in the samples, the following discussion are mainly based on the annihilation characteristics of τ_3 and I_3.

Assuming that the holes are spherical, the relationship between τ_3 and the radius (R) is described as [8,10,11]

$$\tau_3 = 0{,}5\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1} \quad (ns) \tag{3}$$

where ΔR=0.166 nm is the thickness of a homogeneous layer for the pick-off annihilation and the radius of the finite spherical potential is $R+\Delta R$.

The free volume fraction, F_v, is directly related to I_3 and τ_3 through the expression [8],

$$F_v = C\,\frac{4}{3}\pi R^3 I_3 \tag{4}$$

where C is an empirical scaling constant that reflects the probability of *o*-Ps formation.

Figure 2 represents the values of τ_3 and I_3 as a function of the square root of the exposure time of the dry samples in different relative humidity atmospheres. It can be seen that the value of τ_3 is independent of the amount of absorbed water of each sample even in the non-saturation regimen $(\sqrt{t}<20\ h^{1/2})$. On the other hand, the values of I_3 decrease monotonically with the exposure time and become constant approximately for $\sqrt{t}>20\ h^{1/2}$ when the water uptake saturation regimen is achieved. The decrease in I_3 is more pronounced for samples exposed to atmosphere with higher relative humidity revealing that the water molecules are occupying the free holes in the epoxy. It is well known that the inclusion of water in polymers has an effect of reducing positronium formation process and consequently in a reduction of I_3. A linear relation between the relative variation of I_3 and the

relative variation of the uptake water mass seems to exist and this behavior maybe suggest that the water absorption is determined mainly by the free volume fraction of the material, but we have only 3 different RH atmospheres and more data are needed to confirm this sentence.

The constant value of τ_3 is 1.76±0.02 ns and, according to equation 3, corresponds to "spherical" holes with an average radius of 2.63±0.02 Å, which is comparable to the kinetic diameter of a water molecule, 3 Å. The constancy in τ_3 and the behaviour of I_3 with the RH atmosphere reveal that each occupied hole accommodates only one water molecule and in the occupied hole there is no more Ps formation.
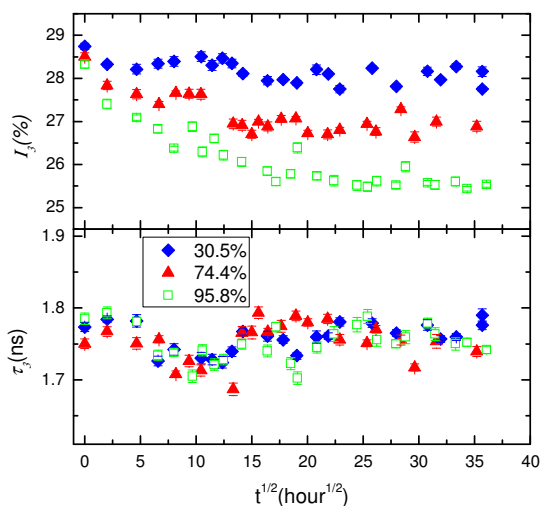

Figure 2. o-Ps lifetime and intensity, τ_3 and I_3, as a function of the square root of exposure time of initially dry samples in different humidity atmospheres.

4. Conclusion

The positron annihilation lifetime technique has been applied to study water absorption in a commercial epoxy exposed to atmospheres of controlled relative humidity. The epoxy shows increasing mass uptake from 30.5% to 95.8%, with a maximum mass uptake of approximately 3% at RH of 95.8%. PAL measurements indicate a decrease in intensity I_3, which is strongly dependent on the atmosphere exposure time and on the relative humidity. The value of τ_3 is constant and independent of RH and the exposure time revealing that in the hole occupied with water there is no Ps formation.

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