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The free volume in acrylic resin/laponite nanocomposite coatings

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ABSTRACT

The morphological features and the free volume properties of an acrylic resin/laponite nanocomposite are investigated using X-ray diffraction and Positron Annihilation Lifetime Spectroscopy. The effects of particle loading on the degree of exfoliation is examined. The measured lifetime spectra and the relative intensities of samples with different particle loading, as well as the shape parameters of the Doppler line broadening are correlated to the free volume in the nanocomposite and the measured CO_2 gas solubility. The effect of the exfoliated nanoclay on the free volume of the composite is found to be very small for clay volume fraction up to 0.2%.

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1. Introduction

One of the most important utilisations of polymer/clay nanocomposites materials relies on their excellent barrier properties to gas permeation [1]. The clay that is used consists of nanoparticles of plate-like shape. Due to the tortuous path that these platelets can create inside the matrix, the gas diffusion process is hindered reducing the permeability of the material [1].

Because of their high aspect ratio, even a small amount of nanoparticles can cause significant reduction of the permeability coefficient. Various models have been proposed for the prediction of the permeability in nano-platelet reinforced materials as a function of particle loading and aspect ratio [1]. Most models are based on the idea that the platelets form a tortuous path for the permeating molecules, and assume that the physical properties of the polymer matrix are not affected by the presence of the inorganic particles.

However, this reduction may not be always possible in nano-clay/polymer composites. The large interfacial regions affect the thermal motions of the polymer side-chains of the matrix. These effects may influence the free volume properties of the polymer and, thus, the rate of the gas diffusion process through the nanocomposite. For example, Yu et al. [2] reported an increase of the free volume in the material when small amounts of bentonite clay was added to the polymeric matrix. This may be attributed to the presence of the extensive polymer/inorganic clay interfaces, where the packing of the polymeric chains was imperfect creating extra free volume. Such an increase of the free volume will cancel out some of the enhancement in barrier properties that the nanoplatelet reinforcement gives to the resin in a nanocomposite coating. On the other hand, Stankovich et al. [3] reported that exfoliated graphene sheets decreased the fraction of the free volume in a polystyrene matrix. It seems that the effect of the nano-platelets interface on the free volume in the composite is not yet fully understood.

The present study examines an acrylic resin/laponite nanocomposite using X-ray diffraction (XRD), Positron Annihilation Lifetime Spectroscopy (PALS) and gas permeability measurements, in order to elucidate the effects of the inorganic phase on the polymer free volume characteristics. The study has two objectives. The first goal is to

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demonstrate the possibility to use PALS in order to measure free volume in complicated systems, such as the nanocomposites. The second goal is to measure any extra free volume present in the composite due to the extensive polymer/clay interfaces.

1.1. Positron annihilation

One of the most accurate ways to measure the free volume in polymers is Positron Annihilation Lifetime Spectroscopy. A good review of this method and its applications has been given by Pethrick [4].

In the method used in the present work the positrons are created by radioactive isotopes, such as the ^{22}Na which decays to ^{22}Ne with the simultaneous emission of a positron, e^+ with energy up to 540 keV, and a γ photon with 1.28 MeV energy, through the reaction:

$$^{22}\text{Na} \rightarrow {}^{22}\text{Ne} + \beta^+(0-540\,\text{keV}) + \nu_e + \gamma(1.28\,\text{MeV}).$$
(1.1)
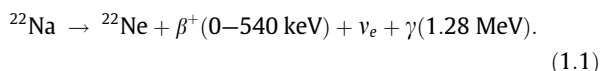
The positrons emitted from such sources have a wide energy distribution (0–540 keV) and are usually called "fast positrons". Fast positrons can be used for bulk measurements as they can penetrate a few tenths of a mm inside the sample. The energy of the injected positrons is decreased within a few picoseconds, due to the inelastic collisions with the surrounding media. On reaching thermal energies ($\sim$0.027 eV), the positron diffuses in the material (diffusion length $\sim$100 nm) before it is trapped in a lattice defect or a free volume hole.

The positron is the anti-particle of the electron and it will be annihilated upon collision with an electron to generate photons of a specific energy as determined by the mass-energy conversion law of Einstein, $E = m_0c^2$. When the two particles are annihilated in vacuum, the annihilation occurs via three different processes. The first is the direct annihilation which results in the creation of two γ photons of 511 keV energies that are emitted in opposite directions, around the centre of mass of the system. The other two processes employ the formation of a temporary pair between the two particles that is called a positronium, Ps. A Ps is similar to a hydrogen atom with a binding energy $\sim$6.8 eV and a radius of 1.06 Å. Depending on the spin state of the two particles, there are two possible Ps atoms: the $p - Ps$ positronium corresponds to the antiparallel, while the $o - Ps$ positronium to the parallel spin configuration. In vacuum the annihilation of these positronium atoms occurs within lifetimes of 0.125 ns for the $p - Ps$ (2γ-annihilation) and 140 ns for the $o - Ps$ (3γ-annihilation), respectively.

When the positrons are injected in the material, similar processes of annihilation occur as above. In this case the Ps formation can be achieved only in low electron density regions like in voids or in the free volume of the polymers. If no such areas are present, then the positrons will be annihilated via the direct annihilation process. The lifetimes of the free and the $p - Ps$ positrons remain the same as in the case of vacuum but the $o - Ps$ lifetime is very much reduced now.

The reduction of the lifetime of the $o - Ps$ is due to the "pick off" reaction, in which the electron with the parallel spin is exchanged with an electron with antiparallel spin from the cavity wall. This reduction depends on the overlap of the wave-functions between the $o - Ps$ and the surrounding electrons. In materials with small voids, such as in polymers, the overlap is strong and thus, the reduction is large, from 140 ns to 2–5 ns.

The whole process, from the time of generation of the positron until its annihilation, can be divided into four stages: The first stage is the generation of the positrons, according, e.g. to the reaction (1.1). This generation is accompanied by the emission of a γ photon at 1.28 MeV. The detection of this photon marks the starting point for the measurement of the lifetime. The second stage is the implantation of the positrons in the material and their acceleration through inelastic collisions. The third stage is the diffusion process of the positrons through the polymer, which leads to their trapping and the formation of Ps. The final stage is the annihilation of the positrons and the detection of the γ 511 keV photons.

1.2. Measurement of free volume using PALS

The measured lifetime of the positron is the time difference between the detection of the 1.28 MeV γ photon and the detection of the 511 KeV photon. The lifetime spectrum can be resolved into N Debye decaying processes by fitting the curve by a sum of N exponentials:

$$F(t) = \sum_{i=1}^{N} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right).$$
(1.2)

Here I_i is the relative intensity and τ_i is the lifetime of the ith Debye process. In polymers, the lifetime spectrum (Eq. (1.2)) is resolved into three terms (Fig. 1). The first term (I_1, τ_1) has a relaxation time (lifetime) $\tau_1 \sim 0.125$ ns and is related to the fast annihilation of the p-positronium and the free positrons. The second process (I_2, τ_2) has a relaxation time $\tau_2 \sim 0.4$ ns and corresponds to the direct annihilation of the free positrons. Finally the third process (I_3, τ_3) is the pick-off annihilation process of the o-positronium and has a relaxation time τ_3 in the range of 1–5 ns.

According to the model of Tao–Eldrup the lifetime of the $o - Ps$ is related to the size, R, of the free volume hole, where it is trapped and the annihilation takes place (Fig. 1), via the relation:

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{\sin 2\pi \frac{R}{R_0}}{2\pi}\right]^{-1},$$
(1.3)

where $R_0 = R + \Delta R$, with $\Delta R \sim 0.1656$ nm [4] the electron layer thickness around the hole that is assumed to be uniform.

The fractional free volume in polymers is related to the intensity of this annihilation process, I_3 [4]:

$$V_f = CV_hI_3,$$
(1.4)

where $V_h = (4/3)\pi R^3$ in Å^3 is the volume of a spherical hole, while C is an empirical parameter (inverse volume) that depends on the polymer. Pethrick [4] reported a value