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Material properties

Study of the water absorption and its influence on the Young's modulus in a commercial polyamide

L. Silva [a,b], S. Tognana [a,c,*], W. Salgueiro [a,c]

[a] IFIMAT – Universidad Nacional del Centro de la Provincia de Buenos Aires, Pinto 399, B7000GHG Tandil, Argentina
[b] Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina
[c] Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, calle 526 entre 10 y 11, 1900 La Plata, Argentina

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ABSTRACT

The water absorption and desorption processes of a commercial polyamide were studied in the temperature range of 20-90 °C. A strong influence of the temperature on the water mass saturation, primarily in the region of the glass transition temperature, was observed. Differences in the parameters related to the diffusion process were also observed between samples with different thicknesses. The results were analyzed using the Langmuir model, which considers two states of absorbed water in the polymer: bound and mobile. The obtained diffusion coefficients were analyzed in terms of the temperature and the state of the polymer, either glassy or rubbery. The influence of the absorbed water on the Young's modulus was evaluated using the impulse excitation technique. It was observed that the water absorbed in the bound state generates the most significant changes in the Young's modulus.

1. Introduction

The number of applications for polymeric materials has increased over time, and an increasing number of materials have been selected for use in different structures or products. Specifically, the study of polyamides (PA) is of great importance due to the demand for these materials in many applications, such as the fabrication of components and products in diverse areas of industry, including agriculture, electrical, automotive and transportation. The polyamides family is comprised of different polymers that are differentiated by the number of methyl groups that exist to either side of the nitrogen atoms (amide groups). In other words, the properties of the polyamides are influenced by the number of methyl units.

One characteristic of these polymers is their ability to absorb water from the environment, either in the liquid or gaseous state [1,2]. It is known that all polymers can absorb water in a wet atmosphere, and the amount of water that is absorbed depends on the composition and hydrophobicity of the polymer. However, this feature becomes more important in PA because the water molecules can form polar bonds with the amide groups. Additionally, the water molecules can displace the PA molecules, which causes plasticization of the material. The swelling can introduce internal stresses, which lead to degradation of the physical properties of the polymer. Therefore, it is extremely important to analyze the behavior of these types of polymers during the absorption and desorption of water, with the goal of obtaining information about the diffusion of water when it enters or leaves the material. Also, sustainability is important in the choice of the materials and, consequently, the influence of environmental conditions (such as moisture or temperature) on the mechanical properties of materials is an active field of research.

* Corresponding author. IFIMAT – Universidad Nacional del Centro de la Provincia de Buenos Aires, Pinto 399, B7000GHG Tandil, Buenos Aires, Argentina. Tel.: +54 249 4439670; fax: +54 249 4439679.
E-mail address: stognana@exa.unicen.edu.ar (S. Tognana).

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There are several theoretical models for analyzing the interactions of water molecules in polymers and for obtaining the characteristic parameters that describe the general behavior of the materials [3]. In general, the diffusion of water can be characterized based on whether it exhibits Fickian behavior. When the diffusion of water does not exhibit Fickian behavior, the Langmuir model has been used by some authors to characterize the diffusion process [4,5]. This model assumes that the absorbed water can remain in the polymer in a mobile or immobile form such that only a fraction of the water molecules are free to move and diffuse in the material.

In this work, the absorption and desorption of water in a commercial polyamide at different temperatures, both less than and greater than the glass transition temperature, and variations in the Young's modulus were studied. Two different sized samples were used for this study, and different saturation values of water absorption were observed in each case. Based on the obtained results, the Langmuir model was used to analyze the absorption/desorption curves. Important variations were also observed in the water absorption behavior when the sample was in different states, such as glassy or rubbery.

2. Experimental methods

For the water absorption measurements, the samples were cut from an as-received commercial bar (trademark Grilon) using a low-speed diamond saw, and then polished with 1200-grit grinding paper. Two different sized rectangular specimens were used: $12.0 \times 12.0 \times 0.5$ mm^3 and $81.0 \times 11.4 \times 4.1$ mm^3. The error associated with the measurement of the dimensions was 0.05 mm.

The samples were dried at 80 °C until constant weight was achieved. Then, the samples were immersed in water at a fixed temperature and periodically weighed using a precision balance. The water gain (M) at a specific immersion time (t) was determined using the following equation:

$$M(t) = \frac{100(W(t) - W_d)}{W_d} \quad (1)$$

where $W(t)$ is the weight of the sample at time t, and W_d is the weight of the dry sample.

The Young's modulus (E) of the polyamide was measured using the impulse excitation technique (IET) [6–8]. An experimental setup was constructed specifically for measuring E. In this device, the sample is placed on two sharp supports that are located at a distance of 0.224 of the total sample length from the ends of the sample. The impact of a small polymer ball on the center of the sample was used to excite the vibration of the bar. When the sample is impacted by the ball, the frequencies that are not in resonance are attenuated. A commercial microphone was used to detect the vibrations of the bar. The signal was amplified and monitored using an oscilloscope and then recorded using the soundboard of a personal computer. The frequency spectrum was obtained using Fourier analysis, and from this spectrum the fundamental resonance frequency (f) was determined. The fundamental resonance frequency in an isotropic material with a bar shape is related to E through the following equation:

$$E = 0.9465\left(\frac{mf^2}{b}\right)\left(\frac{L^3}{t^3}\right)T \quad (2)$$

where m, b, L and t are the mass, width, length and thickness of the sample, respectively, and T is a correction factor that depends on Poisson's ratio and the dimensions of the sample. In this work, T was calculated using an equation for a rectangular bar that is given in the literature [9].

The glass transition temperature of the sample (T_g) was obtained through differential scanning calorimetry (DSC) measurements using a TA instrument at a heating rate of 10 °C/min in an argon atmosphere.

3. Results

3.1. Water absorption

In Fig. 1, the results obtained from the water absorption process are shown as a function of the square root of time, $t^{1/2}$, for different temperatures between 20 °C (room temperature, RT) and 90 °C in the samples with dimensions of $12.0 \times 12.0 \times 0.5$ mm^3. A linear trend in the water absorption with $t^{1/2}$ was observed until the saturation point was reached.

From the water absorption curves presented in Fig. 1, the saturation mass (M_∞) was determined for each temperature. In Fig. 2, the results obtained for M_∞ as a function of temperature are shown. The M_∞ increases up to $T = 50$ °C, where it reaches a maximum value. The value of M_∞ at 50 °C is approximately 50% greater than the value obtained at room temperature.

From the DSC thermograms, a T_g of 45 °C was obtained for these samples; therefore the maximum M_∞ is reached at a temperature that is close to the T_g. The significant increase of M_∞ when the temperature reaches the T_g suggests a process that is influenced by molecular movement, unlike other works where the principal process was assumed to be an interaction where water diffuses through the material by successively binding to the hydrophilic groups [10].

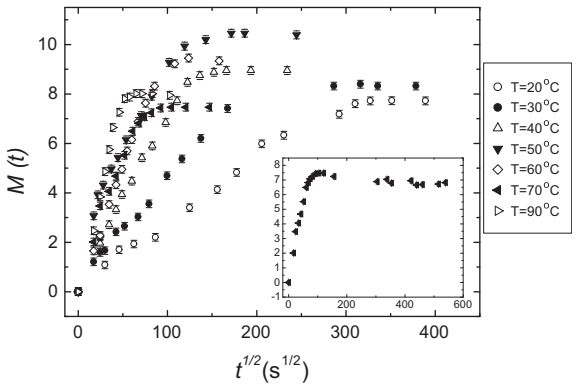

Fig. 1. Water absorption as a function of $t^{1/2}$ for different temperatures in the 0.5-mm-thick sample. In the inset, the water absorption at 70 °C for longer immersion times is shown.