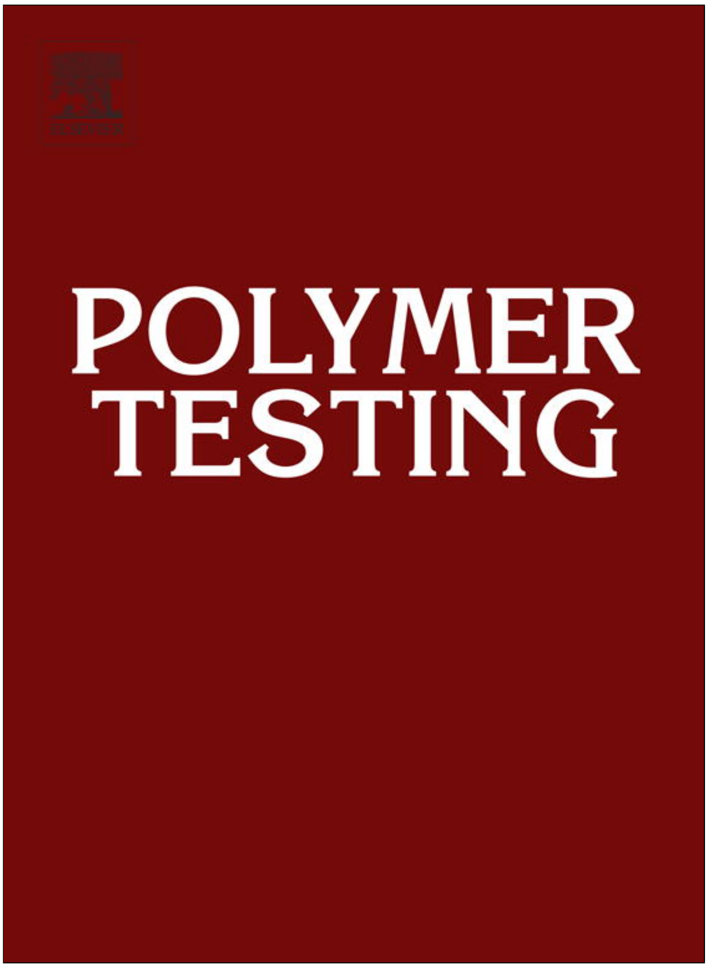

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Material properties

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

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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.

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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:

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

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:

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

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].

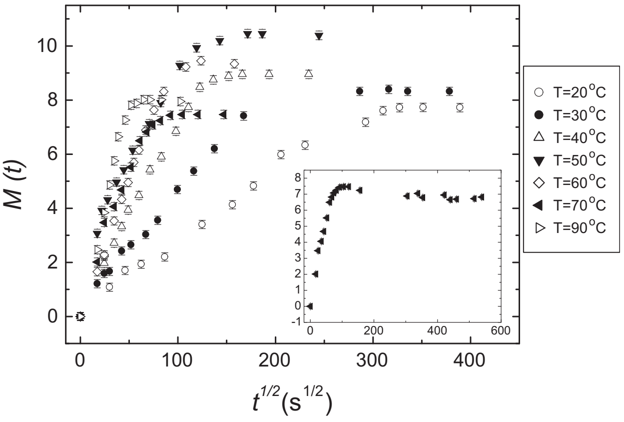

Fig. 1. Water absorption as a function of $t^{1/2}$ for different temperatures in the 0.5-mm-thick sample. In the inset, the water absorption at 70 °C for longer immersion times is shown.

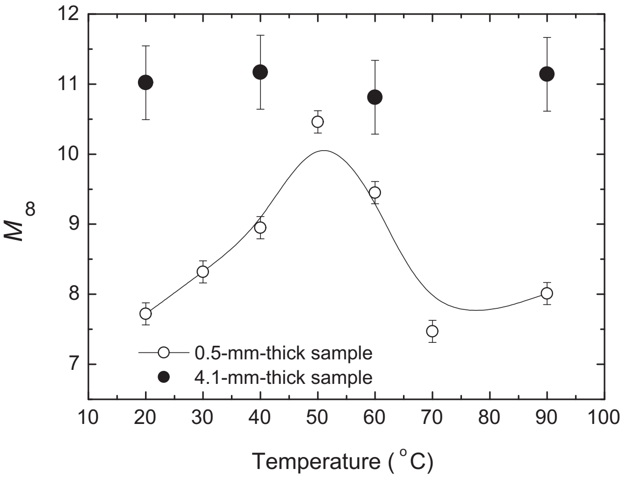

Fig. 2. M_∞ versus the water absorption temperature for the two different thicknesses of samples. The b-spline line represents a guide to the eye.

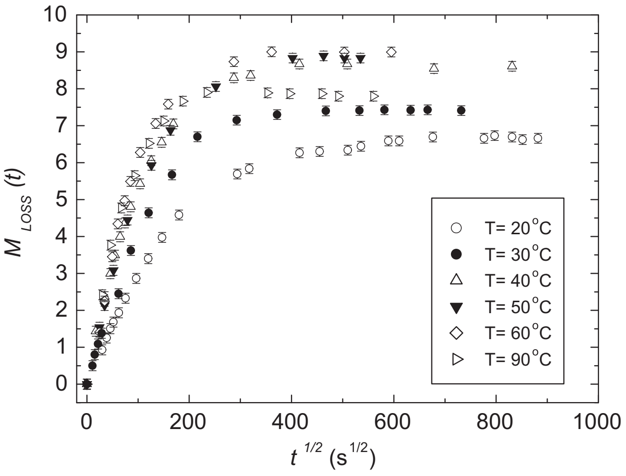

Fig. 3. Water desorption as a function of $t^{1/2}$ for different temperatures (0.5-mm-thick sample).

3.2. Post-saturation stage

After water saturation was reached, the water absorption was observed to decrease for longer immersion times. This behavior was similar for all samples and is exemplified in the plot of water absorption as a function of $t^{1/2}$ at 70 °C that is shown in the inset of Fig. 1. The decrease of the $M(t)$ after the longest immersion time is approximately 1%.

This decrease of absorbed water could be associated with the extraction of additives from soluble materials as a consequence of the plasticization of the matrix.

3.3. Desorption process

The desorption process in the samples with dimensions of $12.0 \times 12.0 \times 0.5$ mm^3 was studied independently of the absorption process. In this case, the loss of water (M_{loss}) was calculated using Equation 3.

$$M_{loss}(t) = \frac{100(W_\infty - W(t))}{W_\infty} \tag{3}$$

In Fig. 3, the values of M_{loss} are presented as a function of $t^{1/2}$ for each temperature. Similar behavior to the absorption process was observed. However, some differences between absorption and desorption processes were observed, and these differences will analyzed in the discussion section.

3.4. Water absorption in large samples

The water absorption measurements at different temperatures were performed using the samples with larger dimensions ($81.0 \times 11.4 \times 4.1$ mm^3).

In Fig. 4, the water absorption and desorption profiles for the large samples are shown as a function of $t^{1/2}$. It can be observed that large samples also present linear water absorption behavior as a function of $t^{1/2}$ in the initial part of the curve. The water saturation values were plotted in Fig. 2 along with the results from the samples that were 0.5-mm-thick. No variation in the M_∞ values as a function of temperature was observed in the large samples; an approximately constant value of $M_\infty = 11.0$ was observed. However, similar to the 0.5-mm-thick sample, the water desorption process is incomplete because the value of the mass saturation during absorption is greater than that during the desorption process.

The samples were weighed to determine their water content and were immediately measured by IET to obtain the E modulus. In Fig. 5, the variation of E (as a percentage with respect to the dry sample) as a function of $t^{1/2}$ is shown for both the absorption and desorption processes. During absorption, first E monotonically decreases as a function of $t^{1/2}$; then E reaches a minimum value and finally slightly increases. Note that the decrease in E is more pronounced for the sample in a bath at 90 °C, which results in a loss of 82% with respect to its initial value. However, the effect of water absorption on E is more important that the effect produced by the temperature. Note that the time required for E to reach a minimum value is significantly less than the time required for water saturation to occur.

During desorption, E increases until it reaches a plateau, which is a value that is slightly less (~3%) than the initial E value in the dry state.

The reduction of E in the presence of water in polyamides has been reported in the literature and can be attributed to the plasticizing action of water molecules [11].

4. Discussion

4.1. Absorption kinetic analysis

In the results shown above, it was observed that the saturation mass for the 4.1-mm-thick sample was greater than that corresponding to the 0.5-mm-thick sample. To analyze this behavior, two water absorption models were considered. In both cases, the studied samples have lateral dimensions that are greater than their thicknesses; therefore, one-dimensional absorption was assumed during the analyses.

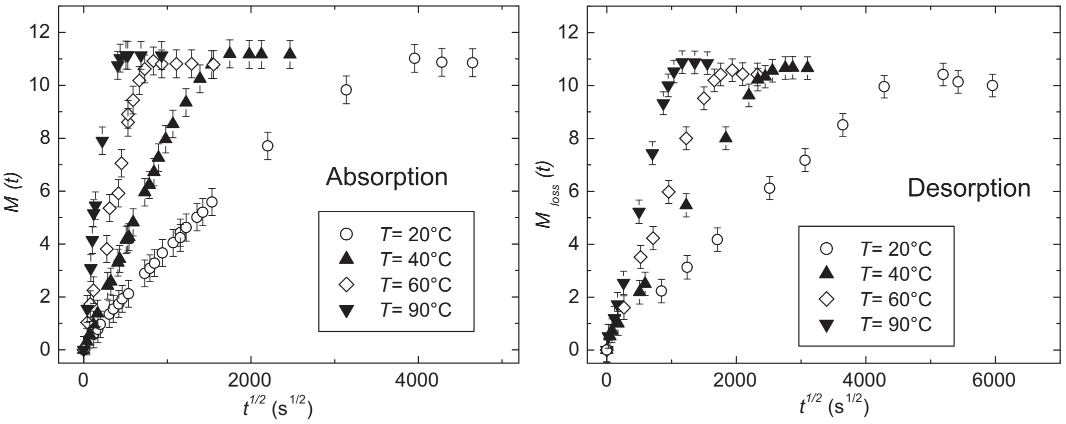

Fig. 4. On the left (right) water absorption (desorption) as a function of $t^{½}$ for different temperatures in the 4.1-mm-thick sample.

The one-dimensional water absorption can be analyzed in terms of the Fickian treatment, where the dependence of M with the time can be described using the following well-known equation [3]:

$$\frac{M}{M_\infty} = 1-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-D(2n+1)^2\pi^2 t}{h^2}\right) \quad (4)$$

where D is the diffusion coefficient, and h is the thickness of the sample.

For short immersion times, Equation 4 can be reduced to:

$$\frac{M}{M_\infty} = 4\left(\frac{Dt}{\pi h^2}\right)^{½} \quad (5)$$

Using this approach, if M is plotted as a function of $t^{1/2}$, the diffusion coefficient can be obtained from the slope of the curve.

However, in some cases, where the Fickian treatment does not provide an acceptable fit to the experimental results, the model developed by Carter and Kibler, which is referred to as the Langmuir model, has been used [4].

In the Langmuir model, it is assumed that the water can be present in the absorbing medium in two states, one free or mobile to diffuse, and the other bound and not free to move [4,5]. Therefore, at a given time and place in a polymer, there are $c(t)$ mobile water molecules per unit volume, which can diffuse with a diffusivity D and become linked or bound in the polymer with a probability γ. At a certain time and place, there are $C(t)$ trapped molecules per unit volume, which become mobile with a probability of α.

For the case of 2α and $2\gamma \ll \pi^2 D/h^2$, the water absorption can be approximately described using [4]:

$$\frac{M(t)}{M_\infty} = \left(\frac{\alpha}{\alpha+\gamma}e^{-\gamma t}\left(1-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{e^{\left(\frac{-D(2n+1)^2\pi^2 t}{h^2}\right)}}{(2n+1)^2}\right)\right) + \frac{\alpha}{\alpha+\gamma}\left(e^{-\alpha t}-e^{-\gamma t}\right)+\left(1-e^{-\alpha t}\right) \quad (6)$$

The coefficient D can be obtained from the initial linear water absorption versus $t^{1/2}$ curve using the following equation:

$$D = \left(\frac{\alpha+\gamma}{\alpha}\right)^2\frac{\pi h^2}{M_\infty^2\,16}\left(\frac{dM}{d\sqrt{t}}\right)^2 \quad (7)$$

In Fig. 6, a set of simulated curves that compare the Fick and the Langmuir models and those obtained using

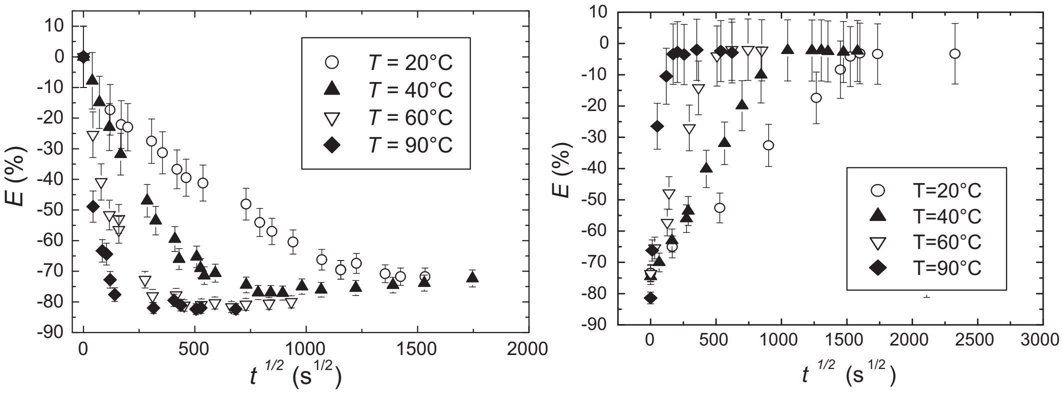

Fig. 5. On the left (right), variations in E during the water absorption (desorption) process with respect to the dry sample as a function of $t^{1/2}$ for different temperatures for the 4.1-mm-thick sample.

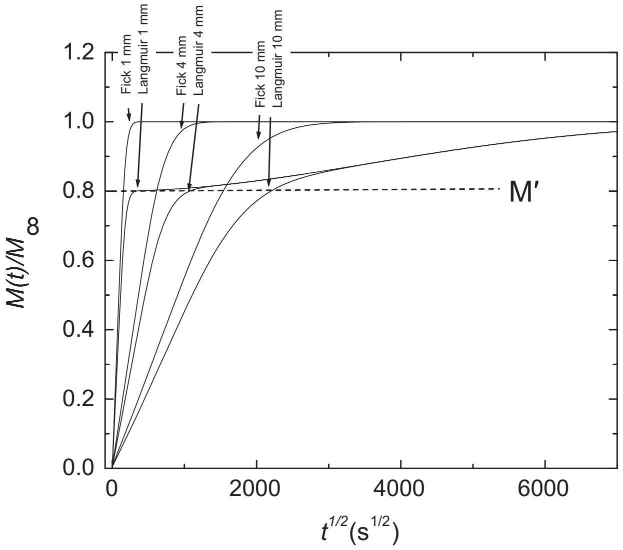

Fig. 6. Simulated water absorption as a function of $t^{1/2}$ for samples of different thicknesses using the Fick and Langmuir models. The values used were as follows: $D = 6.10^{-6}$ mm^2/s. $\alpha = 4.10^{-8}$ 1/s. $\gamma = 1.10^{-8}$ 1/s.

samples with different thicknesses are shown. As observed, when using the Langmuir model and when the thickness of the sample decreases, a plateau zone, which is indicated in the Figure as M', is reached. However, for large samples, the Langmuir curve approximates the Fick curve. The value of M'/M_∞ tends to $\alpha/\alpha + \gamma$ [4].

As previously mentioned, M_∞ is approximately constant for the sample with a thickness of 4.1 mm, with a value of 11.0, whereas the M_∞ for the sample with a thickness of 0.5 mm is appreciably lower. Therefore, the water absorption profile depends on the thickness of the sample, which suggests that a Langmuir-type behavior could be expected for the polyamide samples used in this study.

Furthermore, based on the results presented in the inset of the Fig. 1, a decrease in the water uptake can be expected for longer immersion times (post-saturation time). Therefore, the final part of the curve, i.e., the increase until the final water uptake value is reached, could not be observed.

In this sense, the Langmuir model appears to be an adequate choice for describing the water absorption behavior in polyamide samples. However, this selection introduces the problem that four parameters must be obtained: M_∞, D, α and γ. Therefore, as an estimate, it will be considered that the mass saturation observed for the 0.5-mm-thick samples corresponds to M', and the mass observed for the 4.1-mm-thick sample (11.0) corresponds to M_∞. The decrease in the water absorption for long immersion times prevents the estimation of M_∞. Therefore, the value obtained for $\alpha/(\alpha + \gamma)$ for each sample is calculated from M'/M_∞ independent of the thickness of the sample and, subsequently, D can be calculated using Equation 7 for the water absorption at several temperatures.

In Fig. 7, the values of $ln\ D$ as a function of $1/T$, which were obtained from the water absorption samples, are presented. It can be observed that, although linear behavior is observed in the 4.1-mm-thick sample, in the 0.5-mm-thick sample there is a discontinuity at temperatures close to the T_g.

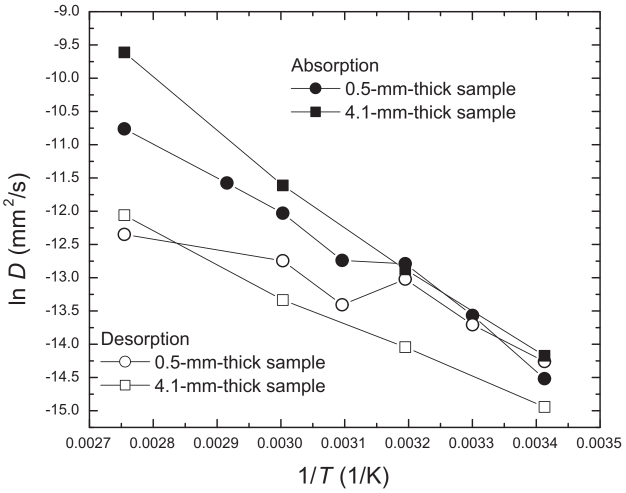

Fig. 7. Logarithm of the diffusion coefficient for the absorption and desorption processes as a function of the inverse of the temperature.

To analyze the dependence of D on the temperature (T), an Arrhenius relationship was used:

$$D = D_0 e^{-E_A/RT} \tag{8}$$

where E_A is the activation energy of the process, R is the ideal gas constant and D_0 is a constant. The 0.5-mm-thick sample was analyzed considering the glassy state and the rubbery state. Using Equation 8 to fit the results presented in Fig. 7, the values for E_A and $ln\ D_0$ were obtained. In Table 1, these values are presented for both of the studied samples.

Based on the Langmuir model, the variation of E with time, which is shown in Fig. 5, can be analyzed. The time when the change in the tendency of E occurs is less than the time where the water saturation is reached, and could be associated with the time when the value of water absorption is M'. Therefore, it can be concluded that the first part of the water absorption curve, which is associated with the mobile molecules of the Langmuir model, produces a decrease of E in the sample. This result is in agreement with those obtained by Popineau et al. [5] for the diffusion of water in an epoxy resin where, paradoxically, the mobile water of the Langmuir model can develop strong interactions, and the water influences E and T_g, whereas the bound water diffusion does not generate changes in the material. Following the ideas introduced by Popineau et al. [5], this

Table 1
Activation energy and logarithm of D_0 for the absorption and desorption processes.

		0.5-mm-thick sample		4.1-mm-thick sample	
		E_A (kJ/mol)	$ln\ D_0$	E_A (kJ/mol)	$ln\ D_0$
Absorption	glassy state	64 (±2)	11.9	57 (±3)	9.3
	rubbery state	49 (±3)	5.5		
Desorption	glassy state	47 (±4)	5.1	36 (±2)	0.2
	rubbery state	23 (±10)	−4.6		

bound water may be stored in microvoids or micropores, which create clusters where the water molecules have a weak interaction with the polymer. However, the mobile molecules would have a high probability of interaction with the polymer molecules; one form of interaction could be through hydrogen bonding. It is known that, in polyamides, the water molecules can disrupt the hydrogen bonding present in the polymer network, which affects its mechanical properties [12].

4.2. Desorption process

In the desorption process, the value of the mass that corresponds to the plateau is less than the mass saturation value in the absorption process. Therefore, there is residual water that is not released during desorption at the same temperature as that in the absorption process; this fact has been previously observed [13]. This unreleased water could be related to the bound water of the Langmuir model.

The desorption process also exhibits a linear region in the $M_{loss}(t)$ versus $t^{1/2}$ plot, and the diffusion coefficient could be obtained in this region. In this case, the values of $\alpha/(\alpha+\gamma)$ were assumed to be the same as those obtained for the absorption process, and a value of 10.7 was used for M_∞ because it is the highest value obtained in the 4.1-mm sample.

In Fig. 7, the values of $ln\ D$ as a function of $1/T$ obtained for the desorption process are shown. In this case, for the 0.5-mm-thick sample, the results do not present a linear behavior because, similar to the absorption process, there is a discontinuity at a temperature close to 40 °C, which is close to the glass transition temperature (~45 °C) and, consequently, the desorption parameters change depending on whether the polymer is in the glassy or in the rubbery state. For the 4.1-mm-thick sample, linear behavior was observed, but the slope was less than that in the absorption process. In Table 1, the obtained E_A and $ln\ D_0$ values for the desorption process are presented.

The values obtained for E_A in the desorption process are lower for both samples. In the case of the 0.5-mm-thick sample, E_A decreases when the sample is in the rubbery state. However, although the activation energy is lower, D decreases for high temperatures because there is a change in D_0. In summary, the diffusion is slower in the desorption process.

Different factors can influence the diffusion process, including the polarity, topology or molecular motions. Soles et al. [14] studied the influence of some factors on the water absorption in epoxies with different polarities and topologies. However, in this study, the polarity can be assumed constant, and it can be concluded that the variations between the absorption and desorption are not due to polar changes.

The difference between the absorption and desorption processes could be explained considering that, at the initial time in the desorption process, the water is in the bound state and has more difficulty diffusing. Implicitly, this consideration means that the determination of D from the initial slope of the water absorption curve must be carefully analyzed.

Based on this explanation, the differences observed in D between the 0.5-mm-thick and the 4.1-mm-thick samples could also be explained. Although the initial part of the water absorption curve involves the water in the mobile state in the 0.5-mm-thick samples, in the 4.1-mm-thick samples both the bound and mobile states are involved. The water in the mobile state would be more sensitive to molecular movement and, consequently, more sensitive to the state that the polymer is in, i.e., glassy or rubbery.

5. Conclusions

In the present work, a study on the water absorption and desorption processes in a commercial polyamide is presented. Both processes were performed at several temperatures, and E was simultaneously obtained using the impulse excitation technique. Significant differences were observed in the water mass at saturation in samples with different thicknesses. These differences were analyzed using the Langmuir model and based on the existence of two types of state of the water molecules in the polymer, free and bound. It was observed that the variations in E are primarily produced by the water in the mobile state. Subsequently, the diffusion coefficients obtained for the different temperatures were analyzed using the aforementioned model. The obtained results reveal that there are important differences that depend on whether the sample is in the glassy or rubbery state for the sample with smaller thickness. This study allows the conclusion that the use of the Langmuir model could explain some aspects of the water absorption process in a commercial polyamide.

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