

Temperature-Humidity Superposition in Diffusion Phenomena Through Polyamidic Materials

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ABSTRACT: In this work, the diffusivity of three different migrants is investigated in water plasticized polyamides, while changing humidity at a steady temperature, and also in dry polyamides tested at different temperatures close to the glass transition point (T_g). The effect of hydration on the structure and the barrier properties of polyamides are investigated and the results reveal that the diffusion coefficient (D) can be described by a single Williams-Landel-Ferry type equation, expressing D as a function of the $(T - T_g)$ parameter. This correlation is found valid regardless the cause of $(T - T_g)$ variation that could be

temperature increase or T_g reduction due to water induced plasticization. At the same time, the effect of specific interactions between the polyamidic matrix and the diffusing molecules is also investigated, indicating that such interactions are capable of delaying the diffusion process regardless the temperature increase or the extent of plasticization. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2814–2823, 2012

Key words: polyamides; plasticization; diffusion; hydrogen bonding; hydration effects; water content–temperature superposition; fluorescence recovery after photobleaching

INTRODUCTION

The study of the diffusion process of small molecules in macromolecular matrices is fundamental to the basic understanding of the diffusion mechanism and in many operations of polymer science, such as polymerization kinetics, drug delivery, gas separation, textiles, food packaging, and additive migration.^{1–3} As a result, the prediction of diffusivity in polymers has been a key topic for many years, yet it remains tricky to solve due to the numerous parameters that are involved. One of the most widely acceptable theories of molecular diffusion in polymers, the free volume theory,^{4,5} introduced the idea that the mobility of the polymer segments and the migrant molecules in a polymer-migrant mixture are primarily determined by the amount of free volume in the system. In other words, the solution of the diffusivity prediction problem relies on the understanding of the parameters that affect the free volume of a polymer matrix. These parameters can be classified in inherent matrix parameters, like the degree of crystallinity, the chain length or the possible presence of reinforcement agents,⁶ and in external parameters, like temperature variation or humidity

induced plasticization. The latter, has recently gained the interest of the polymer scientific community, due to the influence of hydration on the properties of biodegradable polymers,^{7,8} which are usually polar. However, plasticization is always a classic topic of interest for conventional hydrophilic polymers like polyesters or polyamides,^{9,10} from which valuable experience can be extracted.

Aliphatic polyamides (or Nylons[®]) are important engineering polymers because of their physical and mechanical properties. Their structure consists of amide groups inserted periodically into linear alkane chains; their improved properties are based on the capability of the adjacent polyamidic chains to form hydrogen bonds, the concentration of which is proportional to amide group content. The melting and the glass transition temperature of nylons are higher in comparison to other polymers, like polyethylene, due to the interchain hydrogen bonds, which render the crystalline and amorphous phase respectively more rigid.¹¹ However, the presence of amide groups is the reason for the high absorption of polar solvents, like water and ethylene glycol, which substantially changes polyamides structure even at ambient temperatures, as the strong interchain hydrogen bonds in the amorphous phase are replaced by weaker bonding with polar solvent molecules.^{12,13} As a result, the viscoelasticity of polyamides depends not only on temperature but also on the absorbed moisture, which acts as a plasticizer

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in polyamides, drastically reducing their glass transition temperature. In polyamide 6, for instance, the T_g of dry sample is in the area of 45–60°C and decreases monotonically to almost –15°C as the moisture content in the polyamide increases to the maximum value.^{10,13}

It has been reported that water induced plasticization of polyamides has a similar effect on their properties as temperature has. Onogi et al.¹⁴ for instance, have proved that the relaxation modulus “time-humidity” superposition is almost equivalent to the “time-temperature” superposition for polyamide 6, at least close to the glass transition temperature. Ishisaka and Kawagoe¹⁰ examined polyamide 6 samples in various humid environments and introduced the concept of “time-humidity” superposition, which is able to predict the viscoelastic properties of polyamides. The relevant equation is:

$$\log a_H = -\frac{D_1(M - M_0)}{D_2 + M - M_0} \quad (1)$$

where α_H is the hygroeffect shift-factor, M is the water content at time, t , M_0 is a reference water content, and D_1 , D_2 are the empirical constants related to the matrix. Similarly, Schausberger and Ahner¹⁵ have used the shifting procedure, superimposing temperature and plasticizer concentration during their study on polystyrene, showing that the magnitude of relaxation strength depends on the weight fraction of the plasticizer.

The main idea behind these works lies on the well-known Williams-Landel-Ferry (WLF) “time-temperature” superposition.^{16,17} The principles of this superposition are widely used to study the long-term behavior of polymers. This is done by performing experiments over short, accessible time frames at a given temperature, and then repeating them over the same time frame at different temperatures. This is followed by a shifting procedure that results in a smooth continuous curve known as a master curve that extends over a large time scale. This “time-temperature” correspondence is described by the empirical relationship known as the WLF equation [eq. (2)]:

$$\log \frac{\tau(T)}{\tau(T_0)} = \log a_r = -\frac{C_1(T - T_0)}{C_2 + T - T_0} \quad (2)$$

where τ is the retardation or relaxation time, α_r is the time-scale shift factor, T_0 is the chosen reference temperature, and C_1 and C_2 are characteristic constants of the polymer. Quite often, the glass transition temperature is used as a reference temperature in eq. (2), in which case the characteristic constants are C_{1g} and C_{2g} with values ranging from 15 to 26 for the former and 20 to 130 for the later, depending on the polymer.¹⁷

Equation (2) is the basis of many experimental procedures that are used to predict the behavior of polymers varying time or temperature. In addition to this shifting procedure taking into account one pair of test variables, this concept may also be applied to multiple variables simultaneously, provided that the variables involved are independent of each other, and their effect on the polymer behavior is additive.¹⁸ Such is the case in the aforementioned works regarding the “time-humidity” superposition for polyamide 6; both temperature and humidity have a similar effect on the behavior of this polymer, expanding the volume of the amorphous phase either by thermal expansion or by water induced plasticization. Focusing on $(T - T_g)$ as a single parameter in eq. (2), it may be assumed that in fact $(T - T_g)$ is the bridge between the “time-temperature” and the “time-humidity” superposition; the increase of humidity leads to a drastic reduction of T_g , having a similar impact as the increase of T on this parameter, rendering the “time-temperature” and the “time-humidity” superpositions, almost equivalent. Indeed, from a mathematical point of view, eqs. (1) and (2) become identical as long as $(T - T_g)$ is a linear function of M , the water content.

The shift factor of eq. (2) is commonly depicted as the logarithm of $\eta(T)/\eta(T_g)$, where η the viscosity of the matrix. It is then feasible to incorporate D , the diffusion coefficient in the WLF equation by taking into account the Einstein-Stokes equation, which implies that for a given matrix, the ratio $D\eta/T$ is constant. Such a modification of the WLF equation that takes into account D has been previously used successfully in polymer-migrant systems^{19,20}; however, its applicability has only been tested by temperature variation. As a result, it would be interesting to investigate the applicability of the WLF theory on dedicated diffusion data in polymers, by focusing not only on temperature variations, but also in T_g reduction due to water plasticization. In this study, the concept of variable shifting involving temperature and humidity as parameters is used, to investigate the diffusion process in the vicinity of glass transition in two polyamidic matrices, polyamide 6 and 612. Experiments are conducted in different temperatures near the glass transition for dry specimens and in different relative humidity environments, corresponding to lower T_g values of the polyamides. Moreover, specific interactions between the migrants and the polymer matrix are also studied, using two almost identical migrants, which have different capability of forming hydrogen bonds within the polyamidic matrices.

MATERIALS AND METHODS

Materials

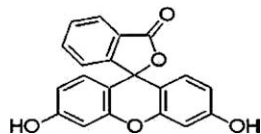
Polyamide 6 (PA 6) and polyamide 612 (PA 612) were provided by DuPont de Nemours International

TABLE I
Structures of the Studied Molecules

Fluorescein

Molecular Weight: 332,1 g/mol

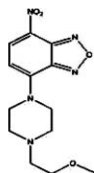
Structure:



NBD-NNOMet

Molecular Weight: 311,3 g/mol

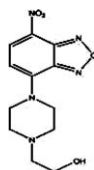
Structure:



NBD-NNOH

Molecular Weight: 295,3 g/mol

Structure:



S.A. (Geneva) in granules, having the commercial name Zytel[®] 7301 NC010 for polyamide 6 and Zytel[®] 158 NC010 for polyamide 612. The studied molecules were fluorescein, and also two homologous molecules based on NBD or 7-nitrobenz-2-oxa-1,3-diazol-4-yl. These molecules were 1-(2-Methoxyethyl) piperazine-NBD and 1-piperazinethanol-NBD. For simplicity, 1-(2-Methoxyethyl) piperazine-NBD will hereafter be called NBD-NNOMet, whereas 1-piperazinethanol-NBD will be noted as NBD-NNOH (Table I). Fluorescein was supplied by Sigma-Aldrich. The other two migrants were synthesized as described elsewhere.²¹ They are two homologous molecules—an alcohol and an ether—synthesized in purpose to have the same geometry with the smallest gap in their molecular weight, yet being able to interact differently with the polyamidic matrices due to hydrogen bonding. NBDNNOH may form stronger hydrogen bonds with the amide groups of the polymeric matrices due to the free hydroxyl group in its olefinic tail, in comparison with the homologous molecule, NBDNNOMet.²²

Sample preparation

The samples for the three-layer tests have to be thin films, in which the migrants are incorporated and

distributed as homogeneously as possible. Additionally, the concentration of the diffusing substances in the samples has to be low for two reasons. Generally, a high concentration of the migrants in the samples may lead to a plasticization of the matrix due to high quantities of the substances resulting to unrealistic estimation of D .^{23,24} In addition, in three layer tests, it is mandatory that the initial concentration of the outer films is lower than the saturation concentration in the experimental temperature.

The polyamide films were prepared from casting on a glass plate using thick formic acid solutions. The viscous fluid, almost gel, was dried in ambient conditions, providing thin films, which were then cut in circular samples of 2.5 cm diameter. The average thickness of the acquired films was 20 μm for PA6 and 45 μm for PA612. The impregnation of the polyamidic films with the diffusing substances was carried out by immersing the films for 10 min at 50°C in ethanol solutions containing 50 ppm of each migrant, based on preliminary contamination tests. The films were then dried for 4 h in a vacuum oven at 80°C. Finally, the dry samples were also annealed for 30 min at 110°C, to reduce any crystallinity variations within the tested specimens during the diffusion experiments. The annealing conditions were as mild as possible to ensure that no increase in the molecular weight of the PAs would occur.²⁵ With this procedure, dry samples of PA 6 and PA 612 containing each one of the migrants were acquired. Meanwhile samples were also placed in different humidity environments directly after the drying step for three days at 40°C, to have the water content stabilized. The selected environments were 48.4 and 74.7% relative humidity at 40°C, produced by using saturated salt solutions in sealed vessels.²⁶

Methods

Three-layer test

This test has been developed^{3,27} to measure low diffusion coefficients, as the ones expected in the present study. It consists of three superimposed films, which are carefully placed on top of each other in a special cell, which ensures good contact through slight pressure. The two outer films are initially contaminated with a known concentration of the studied migrant, while the inner film is initially virgin. Mass transfer occurs due to diffusion of the migrant from the outer contaminated films to the inner one. If the geometry of the films is the same, then the equilibrium concentration of the inner film (C_2) can be predicted and is expected to be equal to 1/3 of the total concentration of all three films (Fig. 1), where C_1 and C_3 is the concentration of the substance in the two outer films. However, to be sure that this hypothesis is correct, the concentration of

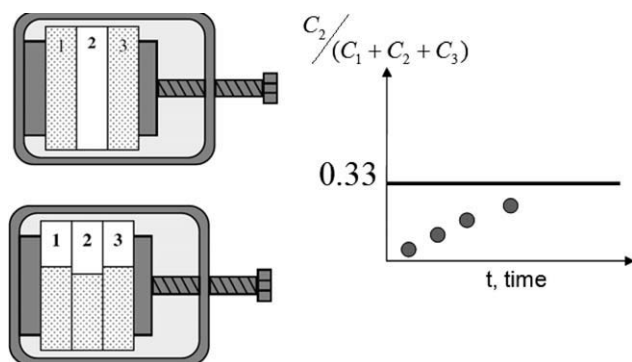


Figure 1 Principle of the three layer test and of predicting the equilibrium concentration of the middle film (C_2).

the outer films has to be as low as possible, and certainly under the saturation point to assume accurately that the equilibrium in the inner film will be equal to 1/3 of the total initial concentration in the outer films.

Three-layer tests were carried out for each one of the three migrants in dry samples at 40, 50, and 60°C, and at 48.4% R.H. and 74.7% R.H., at 40°C, for both PA 6 and PA 612. These conditions were chosen in purpose to facilitate the study of diffusion near the glass transition temperature of the dry polyamides, which is 54 and 52°C for PA6 and PA612, respectively.^{10,22} For each experiment, several stacks of three films were carefully inserted as quickly as possible in a special cell, which ensured good contact of the films. The assembly of the cell was carried out in a glove box in which humidity was controlled, to minimize the possibility of sorption (in the case of dry samples) or desorption of humidity from the prestabilized polyamidic samples. Then, the sealed cells were quickly placed in controlled humidity vessels (or desiccators in the case of dry samples), which were maintained in ovens at the relevant temperature of each experiment.

Ultraviolet-visible spectroscopy

The concentration of the films was monitored through ultraviolet-visible spectroscopy (UV-vis), taking advantage of the fact that all three migrants are fluorescent and thus easily detectable by this method. In predetermined time intervals, a stack was removed from each cell and the three films were separated and dissolved in formic acid. The solutions were then analyzed through UV-vis in a Hitachi® U-2800A spectrophotometer, to determine the concentration in each film. The measurements were carried out in the absorption maximum of the migrants, which was at 465 nm in the case of NBDNOMet, 464 nm in the case of NBDNNOH, and 437 nm in the case of Fluorescein.

Moisture absorption test

To determine the quantity of absorbed water in the hydrated polyamides, a simple gravimetric test was conducted. The test took place in the experimental relative humidity environments and temperature, using annealed polyamidic films. Saturated salt solutions were used to produce various relative humidities environments.²⁶ Two different saturated salt solutions (magnesium nitrate and sodium chloride) for the environments of each relative humidity (48.4 and 74.7%, respectively) were placed into a sealed vessel in an oven at 40°C along with the polyamide 6 and polyamide 612 specimens. A third vessel containing water was also used to produce a 100% R.H. environment. Several specimens were used to nullify the experimental error and left at the appropriate vessels. In regular time intervals, a specimen was removed from the vessel, wiped with a tissue if necessary and weighted by using an electronic analytical balance (Mettler-Toledo AB104) with a resolution of 0.01 mg. This process took place as quickly as possible—typically ~ 5 sec per measurement—and was repeated until equilibrium was reached. The water content, M_t , was determined by:

$$M_t = \frac{W_t - W_0}{W_0} \quad (3)$$

where W_t and W_0 are the weights of wet specimen at exposure time t , and of the dried specimen after drying and annealing, respectively.

Differential scanning calorimetry

The degree of crystallinity of the specimens was measured by Differential scanning calorimetry (DSC) analysis. The experiments were conducted in a DSC 4 (Perkin-Elmer) by heating in a slow rate (10°C min⁻¹). The heats of fusion for the 100% crystalline PA 6 and PA 612 were 190 J g⁻¹ and 197 J g⁻¹, respectively.^{28,29} Measurements were taken for at least five specimens before and after annealing and also in the end of the three layer tests for the extreme cases, that is, for dry specimens tested at 40°C and hydrated specimens tested in the same temperature and 75% R.H.

RESULTS AND DISCUSSION

Hydration of Polyamides

As the three-layer tests were conducted not only in dry but also in hydrated polyamidic samples, it was necessary to investigate the inherent effect of hydration in PA 6 and PA 612. Water absorption was measured at 40°C for both polyamides in three different relative humidity levels, that is, 48.4, 74.7,

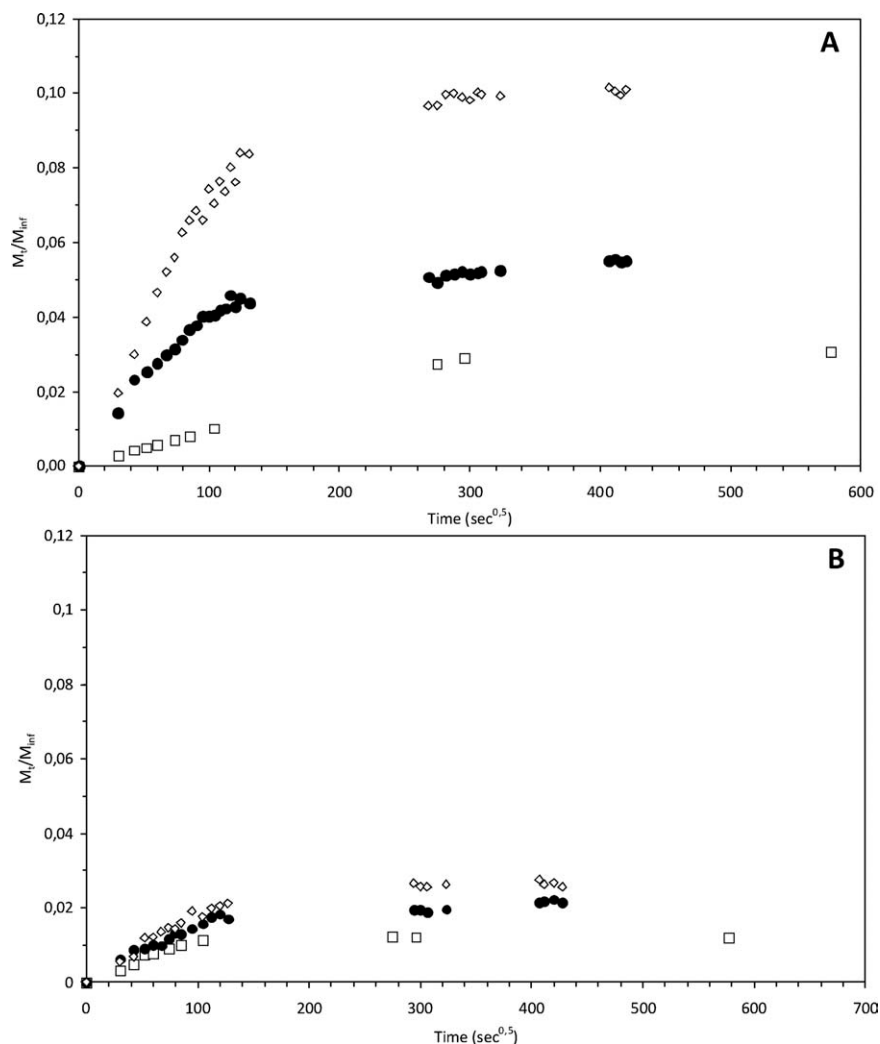


Figure 2 Water uptake for Polyamide 6 (A) and Polyamide 612 (B) at 40°C for the three different relative humidity levels: 48.4% RH (\square), 74.7% RH (\bullet), and 100% RH (\triangle).

and 100%. In all cases, a rapid increase in the water uptake took place in early stages, which gradually reached the equilibrium value M_∞ (Fig. 2). As Fickian diffusion was observed, the water diffusion process in early stages is described by eq. (4)^{30,31}:

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{h^2} \right)^{1/2} \quad (4)$$

The diffusion coefficient is then obtained by eq. (5) from the initial stage of the absorption curves:

$$D = \frac{\pi}{16} (k \times h^2) \quad (5)$$

where D is the diffusion coefficient, k is the initial slope of M_t/M_∞ versus $t^{1/2}$ plot, and h is the initial thickness of specimen.

The equilibrium water content and the calculated diffusion coefficients are summarized in Table II. It is observed that the diffusion coefficients of PA 6,

which are in good agreement with the literature,³² are not dependent on the moisture concentration and this is also the case for the less hydroscopic PA 612. However, the value M_∞ is clearly dependent on the moisture concentration for both polyamides. The higher M_∞ values observed for PA 6 can be explained by the higher density of hydrophilic amide groups expressed as the ratio of amide groups to methyl groups $[\text{NHCO}]/[\text{CH}_2]$, which is 20% in the

TABLE II
Equilibrium Water Content (M_∞) and the Diffusion Coefficient (D) of Water at 40°C

	R.H (%)	M_∞ (% wt)	D (cm ² /sec)
Polyamide 6	48.4%	3.1 ± 0.1	$3.2 \pm 0.2 \times 10^{-9}$
	74.7%	5.5 ± 0.4	$4.8 \pm 1.1 \times 10^{-9}$
	100%	10.1 ± 0.4	$5.2 \pm 1.5 \times 10^{-9}$
Polyamide 612	48.4%	1.2 ± 0.1	$3.4 \pm 0.1 \times 10^{-9}$
	74.7%	2.2 ± 0.1	$4.1 \pm 0.4 \times 10^{-9}$
	100%	2.6 ± 0.2	$4.6 \pm 1.4 \times 10^{-9}$

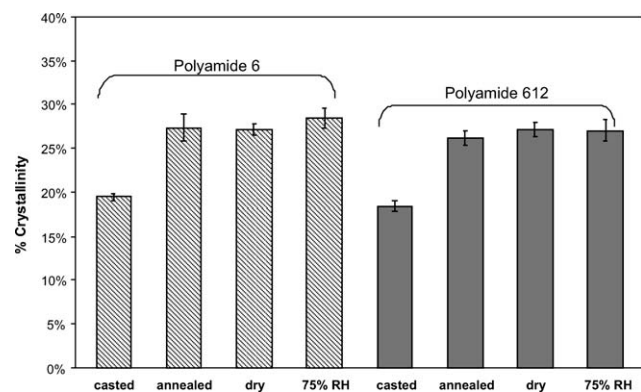


Figure 3 Degree of crystallinity of the polyamidic specimens acquired through DSC; after casting (casted), after annealing (annealed), and after the three-layer tests in the extreme cases of dry and 75% R.H. stabilized samples.

case of PA 6 and 12.5% in PA 612. The greater water absorption in PA 6 is also the reason for the rapid glass transition decrease that has been reported for PA6^{10,13} due to water induced plasticization in contrast with the milder decrease of the less plasticized PA 612.²²

Crystallinity results

It is known that the absorption of water leads to substantial changes in the structure of polyamides even at ambient temperatures, like the experimental conditions in this study.¹³ Water acts as a plasticizer and enhances the macromolecular mobility in the amorphous regions of polyamides, thus crystallization is favored,^{22,33,34} which would result in differences of the degree of crystallinity between the dry and the hydrated samples. However, as crystallinity affects diffusion,⁶ it was necessary for comparative reasons to eliminate the possibility of crystallinity variations between the samples. This was the primary reason for the annealing step that took place before the three-layer experiments, as the annealed samples are expected to be less prone to further post crystallization. The experimental DSC results are summarized in Figure 3. The effectiveness of the annealing step is rather obvious as small variations

are observed before and after the tests, regardless the dry or humid conditions in which the samples were tested.

Three-layer tests

In this study, the diffusivity of the three migrants was evaluated through three-layer tests, involving a “sandwich” of three films, in which the inner film was initially virgin at the start of the experiment, while the two outer films had a known concentration of the migrant. Diffusion coefficients of the tested migrants were determined using “Multwise”, a software that was developed to predict diffusivity in multilayer polymeric films.³⁵ The software was used to simulate the experiments by introducing as parameters the density of the polyamides, the geometry attributes of the films (i.e., thickness and surface area) and the initial migrant concentration of the outer films. The resulting simulation concentration profiles of the three layers over time for various D values were then compared to the experimental results to determine the most adequate D . The obtained values acquired by this procedure are presented in Tables III and IV for dry and hydrated conditions respectively.

Regarding the effect of matrix mobility, that is, comparing the two different polyamide matrices, the results indicate that the diffusion of the migrants is generally slower in PA 6 than PA 612, when both samples are dry (Table III) and the same trend also persists in the hydrated samples (48.4 and 74.7% R.H.; Table IV). This is attributed to the rigidity of the polyamide 6 matrix, derived from its higher density in amide groups and higher thus content of H-bonds in the amorphous phase, which render PA 6 more stiff and resilient to the penetration of the studied molecules.

Turning to the effect of the nature of the migrants, bigger molecules are generally expected to diffuse more slowly in a given matrix, due to the increased free volume requirement for their diffusional jump.^{27,36,37} In both studied polyamides, the acquired diffusion coefficient values however do not

TABLE III
Diffusion Coefficients (cm²/sec) of the Studied Migrants in the Dry State

Polyamide 6	Temperature (°C)		
	40	50	60
Migrant			
Fluorescein	0.6×10^{-13}	0.8×10^{-13}	1.3×10^{-13}
NBD-NNOH	2.0×10^{-13}	2.5×10^{-13}	3.5×10^{-13}
NBD-NNOMet	2.2×10^{-13}	2.8×10^{-13}	5.0×10^{-13}
Polyamide 612	Temperature (°C)		
	40	50	60
Migrant			
Fluorescein	1.1×10^{-13}	2.0×10^{-13}	4.0×10^{-13}
NBD-NNOH	10.0×10^{-13}	24.0×10^{-13}	55.0×10^{-13}
NBD-NNOMet	32.0×10^{-13}	55.0×10^{-13}	90.0×10^{-13}

TABLE IV
Diffusion Coefficients (cm²/sec) of the Studied Migrants as a Function of Relative Humidity at 40°C

Polyamide 6	Relative Humidity (%)		
	0	48.4	74.7
Migrant			
Fluorescein	0.6×10^{-13}	2.2×10^{-13}	4.5×10^{-13}
NBD-NNOH	2.0×10^{-13}	5.2×10^{-13}	11.0×10^{-13}
NBD-NNOMet	2.2×10^{-13}	9.5×10^{-13}	15.0×10^{-13}
Polyamide 612	Relative Humidity (%)		
	0	48.4	74.7
Migrant			
Fluorescein	1.1×10^{-13}	3.2×10^{-13}	3.9×10^{-13}
NBD-NNOH	10.0×10^{-13}	27.0×10^{-13}	57.0×10^{-13}
NBD-NNOMet	32.0×10^{-13}	70.0×10^{-13}	78.0×10^{-13}

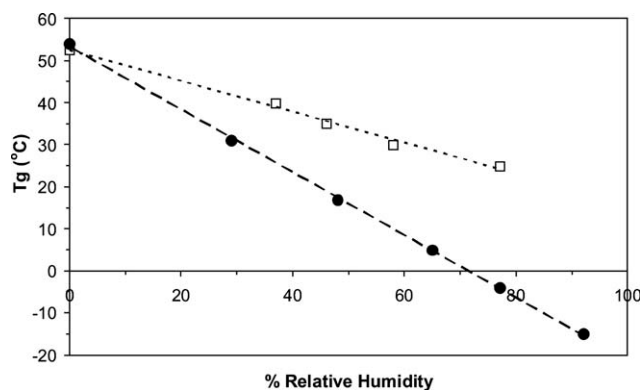


Figure 4 Reduction of the glass transition temperature as a function of the relative humidity level. ● PA6, □ PA612 (data from Refs. 10 and 22).

decrease accordingly to the size of the migrant for the cases of NBD-NNOMet and NBD-NNOH (Table I). The general trend followed is $D_{\text{Fluorescein}} < D_{\text{NBDNNOH}} < D_{\text{NBDNNOMet}}$ regardless the temperature or the humidity environment. In other words, fluorescein, being the bulkiest and heaviest migrant diffuses more slowly in all the studied environments. However, the two homologous NBD molecules demonstrate an inverse trend, as the 10% larger in volume NBDNNOMet diffuses faster than NBDNNOH. This observation is explained by the difference of the characteristic groups of the two molecules and the resulting specific interactions of these molecules with the polyamidic matrices. NBDNNOH may form stronger hydrogen bonds with the amide groups of the polymeric matrices due to the free hydroxyl group in its small olefinic tail (Table I), in contrast with the homologous molecule, NBDNNOMet.

It is interesting to note that the aforementioned finding is in total agreement with previous experiments of our group at 20°C,²² in which diffusion of these two homologous migrants was determined in a confocal microscope through fluorescence recovery after photobleaching (FRAP), again in dry and hydrated polyamides. The affinity of the results is quite remarkable, taking into account that similar diffusion results were acquired with two completely different techniques, a microscopic one (FRAP) and a macroscopic one (three layer tests). The results also indicate that this hydrogen bonding induced “diffusion lag” is dominant in a significant matrix mobility range that includes temperature variations from 20 to 60°C in dry and in hydrated polyamides.

Temperature–humidity induced plasticization superposition

To evaluate the temperature and water content effect on the diffusion process, the experimental data were analyzed more quantitatively by using a modifica-

tion of the WLF relation.^{19,20} As already mentioned, the diffusion coefficient (D), can be incorporated in eq. (2) by taking into account the Einstein-Stokes equation, which implies that for a given matrix, the ratio $D\eta/T$ is constant. As a result, the shift factor a_T can be also defined as the ratio of D at a temperature T , to the D at a reference temperature. If T_g is considered as the reference temperature, then the modification of the WLF relation is:

$$-\log a_T = \log \left[\frac{D(T)}{D(T_g)} \right] = \frac{C'_{1g}(T - T_g)}{C'_{2g} + T - T_g} \quad (6)$$

where C'_{1g} and C'_{2g} are related to the relevant WLF parameters of the polymer matrix [C_{1g} and C_{2g} in eq. (2)] through the coupling parameters ξ and λ :

$$C'_{1g} = \xi C_{1g} \quad (7)$$

$$C'_{2g} = C_{2g} \text{ for } T \geq T_g \quad (8a)$$

$$C'_{2g} = C_{2g}/\lambda \text{ for } T \leq T_g \quad (8b)$$

ξ is interpreted as the ratio of the critical molecular volume V_s^* of the solute jumping unit over the critical molecular volume V^* of the polymer matrix jumping unit, $\xi = V_s^*/V^*$. The jumping units can be interpreted as the discrete steps required for a single migrant or polymer segment to achieve their diffusive motion.^{19,38} The parameter λ ($0 \leq \lambda \leq 1$) describes the character of the change of the polymer volume contraction, which can be attributed to the glass transition. For $\lambda = 1$, the material has an equilibrium liquid structure at all temperatures. For $\lambda = 0$, the specific hole-free volume of the glassy polymer is equal to that achieved at T_g at any temperature below the glass transition.³⁹

Previously collected diffusion data of the same migrants in PA 6 and PA 612, which were acquired at lower temperatures ($\sim 20^\circ\text{C}$) through the FRAP technique,^{22,37} were also used for this analysis. The diffusion coefficient data for each migrant were fit to eq. 6. For dry samples only the T was varied, while T_g remained constant, whereas for hydrated samples at a given temperature the T_g was reduced as a function of relative humidity using previously published data (Fig. 4).^{10,22} The results of this process are listed in Table V. For each fit above the glass transition temperature, the values of ξ and $\log D(T_g)$ were determined, while the WLF parameters were held constant, using $C_{1g} = 20.9$ and $C_{2g} = 120 \text{ K}$.⁴⁰ The acquired parameters were then used for data referring to temperatures under the T_g to acquire λ according to eq. (8b). As Figure 5 implies, the application of eq. 6 in the experimental data seem quite successful. The acquired ξ values, presented in Table V, generally follow the trend $\xi_{\text{Fluorescein}} >$

TABLE V
Acquired Parameters from the Application of eq. (6) to the Experimental Data

Polymer	Migrant	Molecular Weight (g/mol)	Molar Volume (\AA^3)	ξ	λ	$\log D (T_g)$
Polyamide 6	Fluorescein	332.1	313.3	0.09	0.9	-12.9
Polyamide 6	NBD-NNOMet	311.3	296	0.07	0.9	-12.3
Polyamide 6	NBD-NNOH	295.3	270.2	0.07	0.9	-12.5
Polyamide 612	Fluorescein	332.1	313.3	0.14	0.8	-12.6
Polyamide 612	NBD-NNOMet	311.3	296	0.13	0.8	-11.2
Polyamide 612	NBD-NNOH	295.3	270.2	0.13	0.8	-11.6

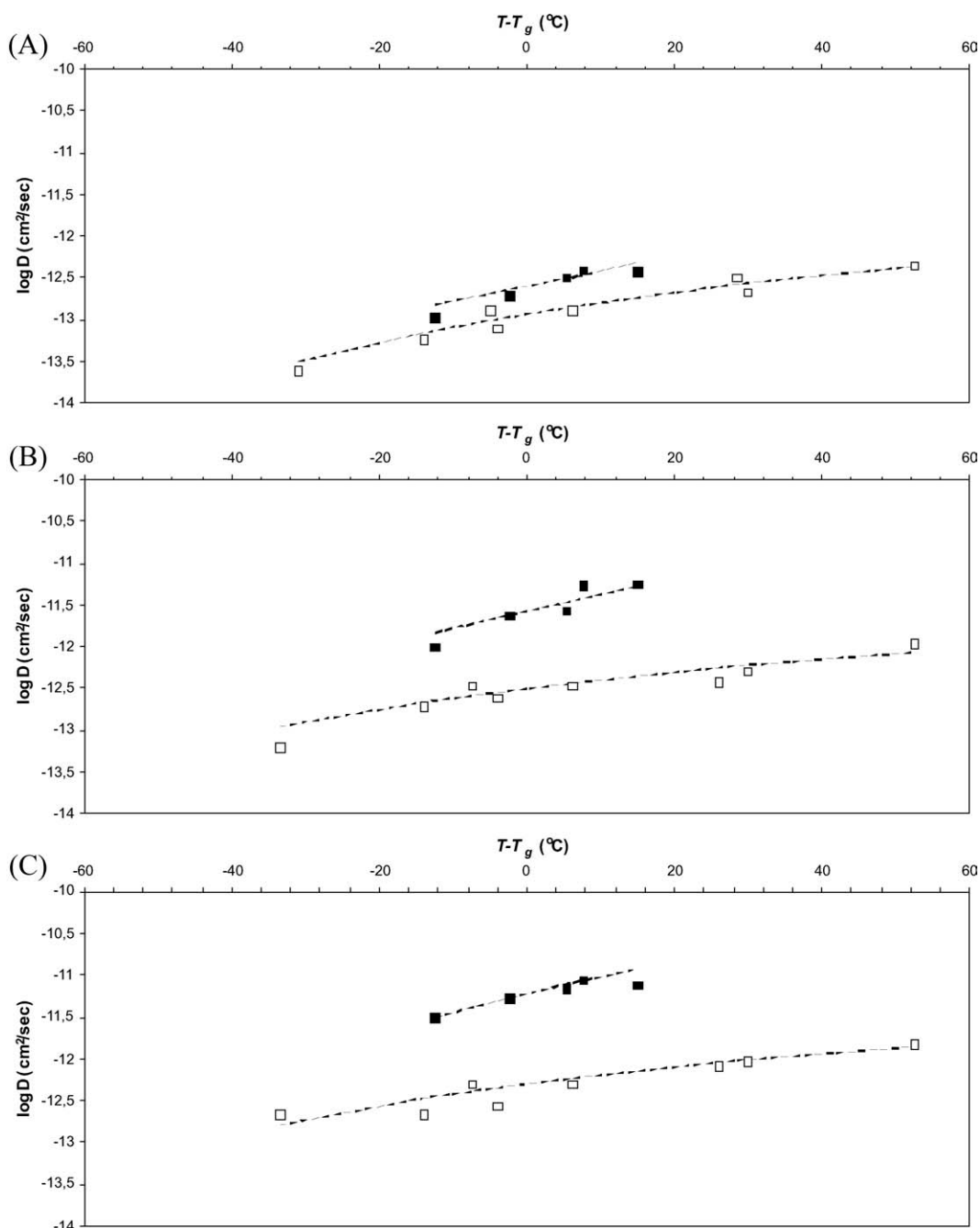


Figure 5 Correlation of the diffusion coefficient with the $(T - T_g)$ parameter for Fluorescein (A), NBD-NNOH (B), and NBD-NNOMet (C). Results for PA6 are indicated with white points (\square) and for PA612 with black points (\blacksquare). The dotted lines represent the fit of eq. (6) to the results. Data from this work and from Refs. 22 and 37.

$\xi_{\text{NBD-NNOMet}} \cong \xi_{\text{NBA-NNOH}}$ for a each polyamide. For comparison, in the same table the molar volume values of each migrant are included, calculated by using the software "Spartan 08" (Wavefunction). It can be observed that the difference in the molar volume of the two NBD molecules, being only 10%, is not substantially affecting the calculated ξ value. In general, the calculated ξ values are in fact following almost the same trend as the molar volumes of the migrants for a given matrix. This verifies the definition of ξ as the ratio of the critical molecular volume V_s^* of the solute jumping unit over the critical molecular volume V^* of the polymer matrix jumping unit.

It is remarkable to note the fact that the modified WLF [eq. (6)] has been used to describe diffusion data acquired in different temperatures but also in different hydrated states of the two polyamides. Typically, this equation has been used to investigate the temperature dependence of the diffusion coefficient for a certain polymer by adjusting the experimental diffusion temperature. In our case, not only temperature, but also T_g , the glass transition temperature is altered as shown in Figure 4 due to water induced plasticization. To our knowledge, this is the first time that this equation is used to describe diffusion data in the vicinity of T_g , in a polymer where not only T , but also T_g varies. This implies that temperature increase and water induced plasticization have a similar impact on the diffusion process, by increasing matrix mobility, in the investigated range of temperature and humidity and for bulky diffusing molecules as the ones investigated. In the case of lower molecular weight diffusing molecules, like oxygen or other gases for instance, this may not be the case as for substances with molecular weight lower than 100 g/mol, diffusion is controlled mainly from the mobility of the diffusing molecule and not from the mobility of the polymeric matrix.³

The results also lead to the assumption that temperature increase does not directly act on the mobility of the migrant but mainly in the free volume of the matrix and that humidity-induced plasticization has a temperature like effect in the diffusion process, as both these parameters mainly affect the polymer matrix mobility. If temperature directly acted to the mobility of the migrant, then the measured diffusivities in dry samples at elevated T (where also thermal expansion occurs) would have been substantially higher compared to the diffusivities measured in hydrated samples at lower T , where only water-induced plasticization of the matrix occurs. However, Tables III and IV indicate this is not the case. However, it is interesting to note that Reynier et al.⁴¹ have made a similar observation by studying the diffusion in virgin and in swollen polyolefins. In fact, this is consistent with the fundamental idea of the free volume theory, which implies that a diffusing

molecule can only move from one position to another one when, in its neighborhood, the local free volume exceeds a certain critical value, thus the molecular transport results from the redistribution of free volume and not from a thermal activation of the migrant-polymer matrix system.⁶

CONCLUSIONS

The objective of the presented experiments was to investigate the effect of water-induced plasticization and of temperature increase in the barrier properties of polyamides near the glass transition temperature. For this purpose, the diffusivity of three migrants was studied through polyamide 6 and polyamide 612, at three different temperatures in the dry state and in different relative humidity environments at a steady temperature. The study was conducted by the three-layer tests technique, a film contact procedure that is specifically designed to determine low diffusion coefficients. The obtained diffusion data were correlated with the $(T - T_g)$ parameter, which due to the experimental conditions was altered either by temperature increase, or by T_g reduction due to water induced plasticization. It is shown that the acquired diffusion results can be described by a single WLF type equation that relates D with the $(T - T_g)$ parameter, regardless the cause of $(T - T_g)$ variation. This implies that temperature increase and water induced plasticization have a similar impact on the diffusion process in the studied conditions, by increasing matrix mobility. However, a comparison of the diffusivities of two homologous migrants demonstrated that the diffusion process is retarded by specific interactions, like hydrogen bonding between the matrix and the diffusing molecules, regardless the temperature or water content variation. These results, acquired by a macroscopic film contact tests, were correlated with previous experiments at a lower temperature,²² in which diffusion was determined although FRAP, indicating that the hydrogen bonding diffusion lag effect is persistent in a wide temperature range, in dry and hydrated polyamidic materials. Finally, all diffusion data collected using FRAP were also well correlated with the aforementioned WLF type equation proving nicely the temperature-humidity superposition by combining two completely different experimental techniques, namely three layers tests and FRAP, to evaluate diffusion.

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