Diffusion behavior of water in polyamide 6 organoclay nanocomposites

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Abstract. Research on polymer-layered silicate nanocomposites is currently an expanding field of study because they exhibit a wide range of improved properties over their unmodified starting polymers. Polyamide 6 (PA6)/organoclay nanocomposites have been prepared by exfoliating the organoclay montmorillonite via melt mixing. The exfoliation within the nanocomposites has been monitored using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Water absorption of PA6 nanocomposites and its mechanical performance when saturated with water at temperatures ranging from 40 to 60°C were investigated.

It was found that the organoclay up to 8 wt% was completely exfoliated and well distributed within PA6 matrix as observed by TEM and XRD analysis. Addition of organoclay did not affect the crystallinity of PA6, and better mechanical performances were obtained. It was found that the barrier properties of the neat PA6 exhibited both higher diffusion coefficient and higher maximum water uptake as compared to the filled polymer. For all investigated temperatures the diffusion coefficient was found to decrease as function of organoclay loading. However, the maximum uptake was found to increase without reaching that of neat PA6. A relationship between temperature and diffusion coefficient was also established.

Keywords: nanocomposites, organoclay, polyamide 6, diffusion, water absorption

1. Introduction

In recent years, research on polymer nanocomposites has attracted great interest and is currently an expanding field of study due to the wide range of improved properties over their pristine polymers [1, 2]. These nanocomposites exhibit superior properties such as enhanced strength, reduced gas permeability, and improved flame retardancy [3].

Nylons or polyamides are high performance engineering materials; they are semi-crystalline thermoplastics with attractive physical and mechanical properties that provide a wide range of important end-use performances in many industrial applications.

An original report from the Toyota research team [1] demonstrated such thermal and mechanical properties achieved from polyamide 6 montmorillonite (MMT) composite while another report from Vaia *et al.* [4] suggested that it is possible to melt mix polymers with silicates.

One common property to all polyamides is that they are hygroscopic; they absorb water from the environment, both from the air and from liquid water. This is an important factor to be considered

during material pre-selection, parts design, mechanical performance prediction and optimization. The equilibrium moisture content of PA6 at 23°C in a 50% relative humidity environment is around 2.5 wt% and at 100% relative humidity as high as 9 wt% [5].

In general, the moisture content in nylon is a key variable affecting processing (polymerization, compounding, molding, welding, etc.) and end-use performances (mechanical, dimensional, surface appearance, etc.). The absorbed water in polymer behaves as a plasticizer, which affects material properties such as strength, stiffness, decrease of T_g, modulus and yield stress, while elongation at break as well as toughness, and ductility increase.

PA6 is often filled with mineral fillers or short fibers such as glass, carbon or aramid fibers to increase the modulus. However, layered silicate nanocomposites provide several advantages compared to these traditional filled compounds, such as lower amounts of fillers, therefore, lower density, increased barrier properties, improved transparency and better surface appearance can be observed.

Nanocomposites consisting of exfoliated silicate layers in PA6 can be produced by *in-situ* polymerization, in which organically modified silicate layers were swollen by the monomer i.e. PA6 (or ε-caprolactam) and exfoliated during polymerization [6–8], or by dispersion in the melt state by high shear mixing in a twin-screw extruder [9, 10–11]. Because of the large aspect ratio and surface area of the exfoliated silicate layers they act as efficient barriers against transport through the material [12]. Despite the importance of the influence of moisture in practical applications, only a few papers containing data for mechanical properties of moisture-conditioned nanocomposites have been published [13, 14]. Hence, for a complete understanding of PA6 nanocomposites it is important to understand the mechanism of moisture absorption and its influence on nanocomposites' mechanical properties.

In this paper the influence of the amounts of layered silicate on water diffusion coefficient and maximum amount of absorbed water is described. In addition, the influence of penetrant uptake on the mechanical properties is measured and discussed.

2. Experimental

2.1. Materials and preparation method

A commercially available polyamide 6 (UBE1013B) provided from UBE Industries Ltd (Japan) was used as a test material. The organoclay I.34TCN was from Nanocor, Inc. (USA); it is a methyl dihydroxyethyl hydrogenated tallow ammonium treated montmorillonite.

The PA6/nanocomposites were prepared via melt mixing method. The PA6 and organoclay were mixed using a KRC-S1 co-rotating twin-screw extruder having an $L/D = 10.2$. The extruder was operated at temperature in the feeding zone of 150°C and in all other zones where heated to 240°C, the screw speed was set to 200 RPM. Different master batches having respectively 2, 4, 6, and 8 wt.% organoclay were thus prepared. The granules obtained by extrusion were injection molded in a laboratory injection molding machine to a rectangular shape having dimension 5×2×2 mm. Before any processing or testing specimens were dried in oven at 50°C for at least 100 hours to ensure that they reached a constant weight condition.

2.2. Sorption process

Diffusion behavior of deionized water was investigated by immersing the specimens in deionized water at 40, 50, and 60°C. Samples were periodically removed, wiped with filter paper to remove excess of the water and then kept at room temperature for 1h before the weight was recorded. This weight is considered to be the wet one. Further analyses were carried out immediately after weight was recorded. Water content was determined using the Equation (1):

$$M_t [\%] = \frac{W_t - W_0}{W_0} \cdot 100 \tag{1}$$

where M_t, W_t and W_0 are the water content at a given time, weight of the sample at the time of the measurement and initial weight, respectively.

2.3. Characterization

X-ray diffraction (XRD) experiments were performed on a Philips Xpert MPD PW3050 X-ray diffractometer with a CuK$_\alpha$ as a radiation source

($\lambda = 1.54$ Å), operated at 40 kV and 30 mA. Samples were scanned at diffraction angles (2θ's) from 2 to 10° at a scan speed of 0.016°/s.

Transmission electron microscopy coupled to energy dispersive X-ray spectrometer TEM/EDS photographs were taken with a JEOL JEM 2010F using an acceleration voltage of 200 kV.

Three point bending test was done according to ASTM D790 using a Shimadzu Autograph AGS-1KNJ machine.

3. Results and discussion

3.1. Morphology

The X-ray diffraction patterns of organoclay and PA6-organoclay nanocomposites are shown in Figure 1 for the 2θ range from 1 to 9°. The XRD pattern relative to pristine organoclay displays a strong diffraction peak at $2\theta = 5°$ corresponding to a basal spacing, d_{001}, of 18 Å. This peak is no more observed on the X-ray diffraction curves of nylon-6 nanocomposites containing up to 8 wt%. The disappearance of such peak within the nanocomposites samples revealed that up to these contents of organoclay, the silicate platelets were well dispersed and well exfoliated within the PA6 matrix.

The evolution of the silicate layers dispersion in the PA6 matrix as a function of the clay content is confirmed by TEM analysis (Figure 2).

A detailed morphological analysis of the nanocomposites has been carried out using TEM micrographs for sample containing 2 wt% (Figure 2), even if little amount of individual exfoliated sheets have been counted in the analysis, most of the tactoids do not contain more than five sheets. This

result is consistent with the X-rays diffraction analysis.

The increase in exfoliation during melt processing is due to the stresses in the extruder that break the organoclay particles into stacks of platelets or tactoids which can be subsequently sheared apart to make smaller platelet stacks. Shear stresses are an important element in these events. Finally, TEM evidence suggests that the platelets on the surface
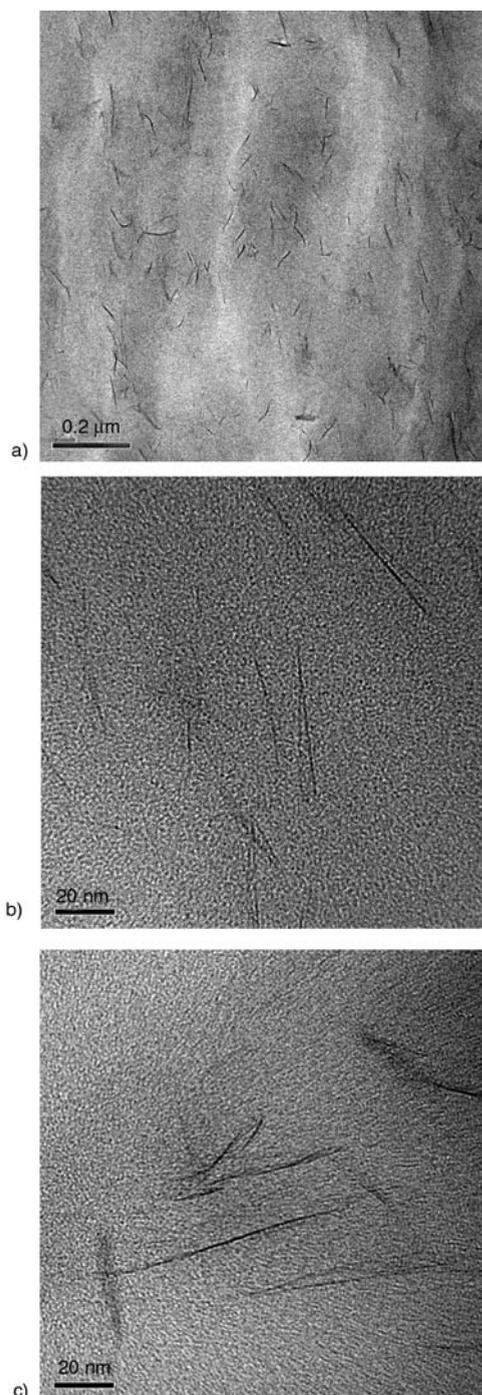
Figure 2. TEM micrograph of PA6 containing 2 wt% organoclay at different magnification

Figure 1. XRD patterns of the different PA6/organoclay nanocomposites

peel apart by a combination of diffusion of polymer chains and shear which is aided by the fact that individual platelets are not rigid but are quite able to bend away. Of course, the latter step only occurs if the polymer has some affinity for the organoclay surface (a property of both MMT and the organic treatment) and this process may require longer time.

3.2. Effects of clay on polyamide 6 crystallization

Crystalline lamellae are considered to be impermeable to small molecules. It is thus important to take into account any crystalline change in the polymer matrix in presence of clays in order to understand the evolution of the transport phenomenon. In this study, the crystalline structures of the neat PA6 and the PA6-based nanocomposites were investigated by X-ray diffraction (XRD) and differential scanning calorimeter (DSC).

One might expect that the small clay platelets would act as nucleating agents for crystallization of the PA6 matrix. PA6 crystallizes in either α or γ forms [15] resulting from different spatial arrangement in the hydrogen bonding between the oxygen in the carbonyl group of one chain and the hydrogen attached to the nitrogen in the neighboring chain, PA6 exhibits crystalline structure with two types of stable crystalline forms, monoclinic α-crystalline form and monoclinic γ-crystalline form [15, 16]. Formation of the γ-type crystals is favored by low temperatures, stress, and to some extent the presence of clay [17]. For injection-molded bars, the γ-form predominates in the skin, while a mixture of α and γ exist in the core [17].

It was found that the addition of silicates favored the formation of the γ-crystalline phase, suggesting that the formation of γ-crystalline phase of PA6 follows a heterogeneous nucleation mechanism [15]. From the point of view of spacing, the *d*-spacing of α-crystalline phase in the PA6/organoclay nanocomposites are larger than that of γ-crystalline phase in pure PA6, meaning that lattice arrangement in the PA6/organoclay nanocomposites is more ordered than that in pure PA6.

Figure 3 gives the XRD patterns of the injection-molded PA6 and its nanocomposites in the 2θ range from 4 to 40°. All curves showed a major diffraction peak at angular position 21.5°. This diffraction
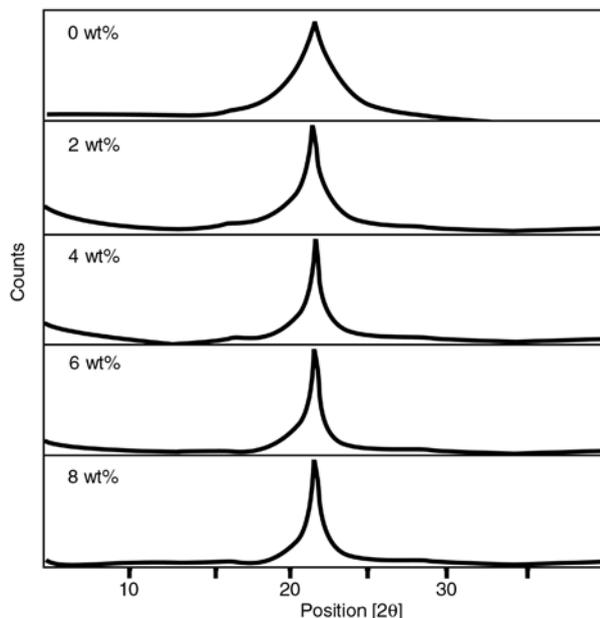
Figure 3. Wide XRD patterns of PA6/organoclay nanocomposites

peak can be assigned to the composition of (001) reflection of the PA6 γ-form crystals [18, 19]. However, it was not be possible to conclude if only γ phase exist and that the addition of the organoclay did not influence the crystallinity of PA6. All formulations present a single peak with different broadness as observed in Figure 3, thus, according to XRD results, it can be concluded that both α and γ phases coexist in the neat PA6 and nanocomposites. The introduction of the organoclay in polyamide matrix slightly enhances α-phase formation but does not lead to major modifications in the whole crystallinity index [19]. Nanocomposites containing commercially relevant concentrations of clay, i.e. 3–5 wt%, have comparable crystallization times and temperatures as the pure polyamide with a similar processing history [20].

DSC data were used to complete this qualitative analysis. Figure 4 shows the DSC scan of the neat PA6 and its nanocomposites. A larger endothermic peak could be observed at around *T* = 226°C which is associated with the melting of both α and γ form crystals of PA6 as compared to the neat PA6 which shows a single sharp peak. The broadness of the peak is due to the effect of the organoclay on the crystallinity of PA6 similar effect was reported by Picard *et al*. [20] where they found that the percent crystallinity was not affected by the addition of the organoclay however, Murase *et al*. [21] find that
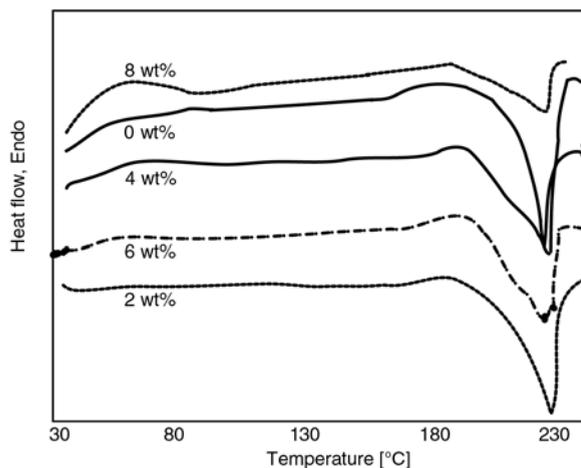
Figure 4. DSC thermograms of PA6/organoclay nanocomposites
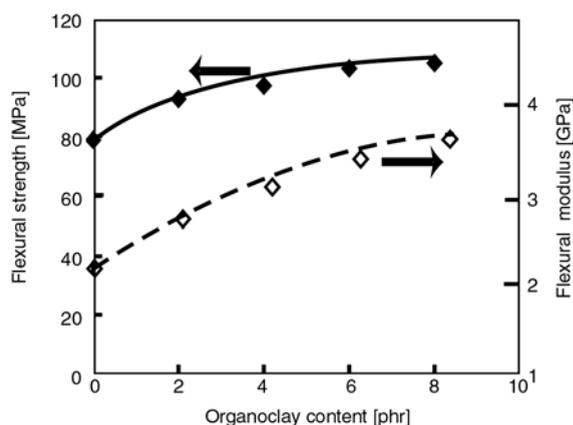
Figure 5. Flexural modulus and flexural strength of PA6 as function of organoclay content

crystallinity value of nylon-6 are much affected by the type of clay incorporated into the polyamide.

It can be concluded form both DSC and XRD measurement that no major modification of the PA6 crystallinity did occur by the introduction of the organoclay even if an alteration of the peak was observed which may be due to the increase of the γ phase. It is believed that the organoclay did not affect the crystallinity of the PA6 which may not alter the moisture absorption as the diffusion may just occur in the amorphous region of PA6 and not within the crystalline ones and the only effect will be the one of the organoclay and the way to prevent the diffusion of water within the matrix.

3.3. Strength evaluation

Three points bending test of neat PA6 and that of PA6/nanocomposites was performed, this bending test will help to evaluate the strength of specimens either before or when immersed in a specific water. It gives also an idea about the degree of degradation of the polyamide as well as the degree of enhancement of the organoclay. By measuring the mechanical properties one can determine the extent of damage that may be caused by the absorption of liquid within polymer. Knowing that this damage may be mainly due to the plasticizing effect, hence, the measurement of mechanical properties have to be done at both states: wet (sample immediately removed from the water) and dry state (immersed sample dried for enough time to enable complete drying). If the strength or modulus recovers to the initial state one can postulate that no degradation did occur on the other hand if recovery is not 100% achieved this will be attributed to the degradation of the sample. Addition of organoclay may enhance the mechanical properties and also avoid to some degree the degradation of the polymer matrix.

Nevertheless in this study just wet condition were measured, as shown in Figure 5 illustrating the flexural modulus and the flexural strength of the different formulations. It is observed that both flexural modulus and strength increased as the organoclay content increases, this is mainly due to the benefit of the clay as reinforcing agent and also to the well dispersion and exfoliation of the organoclay. This is may be due to the constraint of the polymer chains by their interaction with the clay surfaces [22].

The extent of the enhancement is directly related to the degree of exfoliation. For PA6, recent research has demonstrated that comparable levels of exfoliation and performance, at least in terms of stress-strain behavior, can be achieved by melt processing as found by the chemical approach [13]. It is important to appreciate that additional effects caused by matrix-filler interactions, including changes in matrix crystal structure or chain mobility, may also be involved because of the high surface areas and small dimensions. The increased modulus could be contributed to the reduced mobility of a constrained polymer phase close to the silicate layers. The large surface area of the exfoliated platelets is considered to be responsible for this constrained polymer phase with a higher modulus [23].

3.4. Diffusion behavior of water in PA6/organoclay nanocomposites

Polyamides are well known to be hygroscopic materials and that they absorb water easily even at room temperature.

Weight change of PA6 and PA6/organoclay nanocomposite as function of immersion time in deionized water at 40°C as function of square root time is shown in Figure 6. It is observed that after a linear increase, the equilibrium is reached at about 140 h of immersion time in the case of the immersion at 40°C. Similar behavior is observed at elevated temperature with shorter immersion time needed in order to reach the weight change equilibrium.
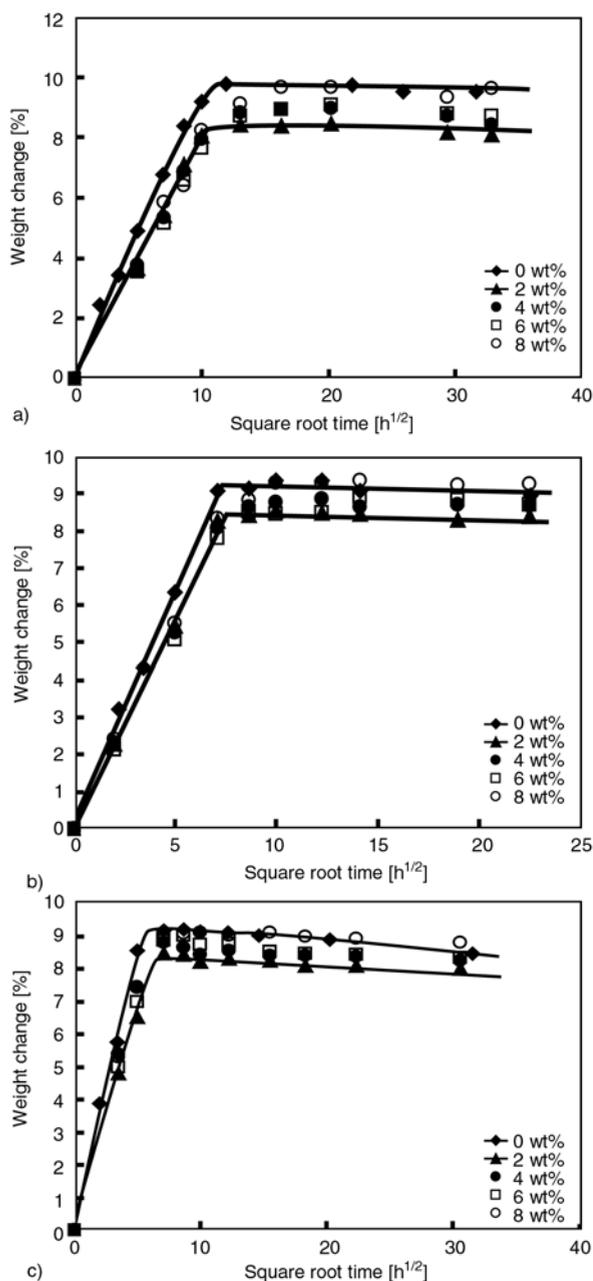
Moisture absorption is generally considered to be independent of moisture concentration, the diffusion of moisture is generally considered to obey Fick's law [24, 25], see Equation (2):

$$\frac{M_t}{M_\infty} = \left[1 - \sum_0^\infty \frac{8}{(2n+1)^2 \pi^2} \exp\left(\frac{-D(2n+1)^2 \pi^2 t)}{4l^2} \right) \right] \quad (2)$$

where M_t is the mass gain at reduced time and M_∞ is the maximum mass gain at the equilibrium state and l is half the thickness of the polymer sample.

The solution for Fick's law short times then reduces to the Equation (3) for the initial stage of diffusion:

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{\pi l^2} \right)^{1/2} \quad (3)$$

In the initial stage of the absorption, up to approximately $M_t/M_\infty = 0.5$ the increase in mass shows a linear relationship with the square root of time [26–28].

As observed, the plot of M_t/M_∞ vs. $t_{1/2}/2l$ is linear at the initial stage and the diffusivity can be calculated from its slope, hence, the diffusion behavior of water may be considered to follow the Fickian type diffusion. Diffusion coefficient could be determined from the slope of the normalized weight change using Equation (3).

Table 1 summarizes the diffusion coefficient at different temperatures. The diffusion coefficients D can be used to compare the diffusion rate in the unfilled polymer to the nanocomposites one, and to estimate how much time total moisture saturation of a sample takes, depending on the dimensions.

It is observed from the plotted data of the diffusion coefficient in Figure 7 that the diffusion coefficient decreased as the amount of organoclay increased, according to the values are reported in Table 1 the diffusion coefficient falls to about a half in the case of immersion at 40°C, on the other hand the equilibrium weight change is not so much affected, the highest decrease is obtained with the lowest filling content, and as the organoclay content increases this equilibrium increases even despite the fact that it remains below that of the unfilled PA6. These

Figure 6. Weight change of PA6 and PA6/organoclay nanocomposites at a) 40°C, b) 50°C and c) 60°C

Table 1. Diffusion parameter for PA6 and PA6/organoclay nanocomposites

Formulation	40°C		50°C		60°C	
	M_∞ [%]	D [m²/s]·10⁻¹²	M_∞ [%]	D [m²/s]·10⁻¹²	M_∞ [%]	D [m²/s]·10⁻¹²
0 wt%	9.547454	2.25693	9.356305	3.81366	9.004974	7.91952
2 wt%	8.259288	1.86913	8.433146	3.77303	8.152024	5.44119
4 wt%	8.759826	1.56598	8.728609	3.29763	8.401829	6.47927
6 wt%	8.876960	1.36672	8.672343	2.99715	8.606046	5.24040
8 wt%	9.564869	1.25389	9.282899	2.95311	9.000577	5.31154
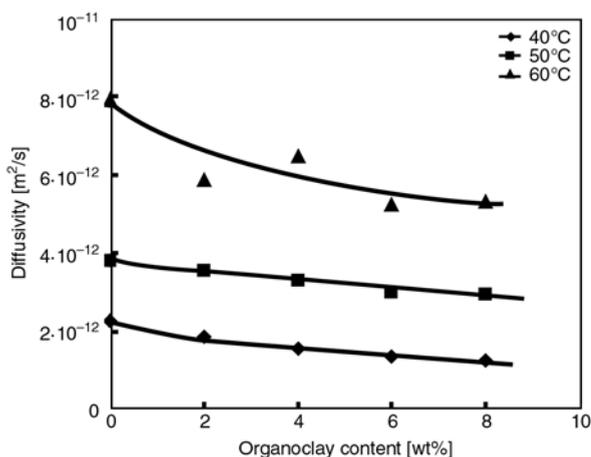
Figure 7. Diffusion coefficient at different temperature as function of organoclay content

results point to the effect of hydrophilic clay on the equilibrium water uptake i.e. even if the clay is treated to be hydrophobic and organically treated to have the ability to exfoliate within the polymer matrix some of the hydrophilicity may remain, that will attract water and thus the final water absorption may reach that of the unfilled polymer when considering longer immersion time.

The excellent resistance to water permeation of the PA6 organoclay nanocomposites is caused mainly by the decrease in diffusion coefficient (*D*) compared with nylon-6. A dispersion of impermeable filler and crystallite decrease the diffusion coefficient by increasing the average path length required to transport the specimen [29].

The rate of water absorption in PA6 nanocomposites is reduced compared to the unfilled polymer because of the impermeable silicate layers in the polymer. These layers increase the path-length for diffusion through the polymer. The increase in the path length predicts better barrier properties for nanocomposites. The maximum amount of water that can be absorbed by PA6 nanocomposites is not too much reduced; only the rate of absorption is

reduced due to the lower diffusion coefficient [29, 30].

The speed of water absorption in PA6 nanocomposites is reduced compared to the unfilled polymer because of the impermeable silicate layers in the polymer. These layers increase the path-length for diffusion through the polymer [30]. This increased path length predicts the better barrier properties of nanocomposites very well [31]. In PA6 the water is absorbed in the amorphous phase, because the crystalline part is inaccessible for water [30]. The amorphous fraction is not much different in nanocomposites as evidenced by XRD and DSC and therefore the amount of absorbed water can reach approximately the same level as in unfilled polyamide, if sufficient time is available [30].

Temperature plays a very important role in the diffusion of penetrant molecules through polymeric membranes. Diffusion, like reaction rates, may be thought of as an activated process following an expression of the Arrhenius form given by Equation (4):

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \tag{4}$$

where the activation energy E_D depends on the polymer and size of the penetrant. The diffusion behavior is found to be temperature dependent as illustrated in Figure 8. It is found that the coefficient of diffusion becomes lower as temperature decreases, diffusion coefficient can be formulated as: $D_T = 0.0025 e^{-6528.9/T}$ where D_T is the diffusion coefficient [m²/s] and *T* is temperature [K].

Activation energy (*E*) could be estimated from the diffusion coefficient equation (Equation (4)) the data are reported in Table 2. It is found that the activation energy globally increases as the organoclay content increases.

Table 2. Activation energy for PA6 and PA6/organoclay nanocomposites

Formulation	Activation energy E [kJ/mol]
0 wt%	54.28
2 wt%	46.43
4 wt%	61.54
6 wt%	58.31
8 wt%	62.65

Diffusivity [m²/s] vs Temperature [1/K]

0 wt%=0.0025e$^{-6528.9T}$
2 wt%=0.0001e$^{-5584.9T}$
4 wt%=0.0293e$^{-7402.1T}$
6 wt%=0.0076e^{-7014T}
8 wt%=0.0371e$^{-7535.5T}$
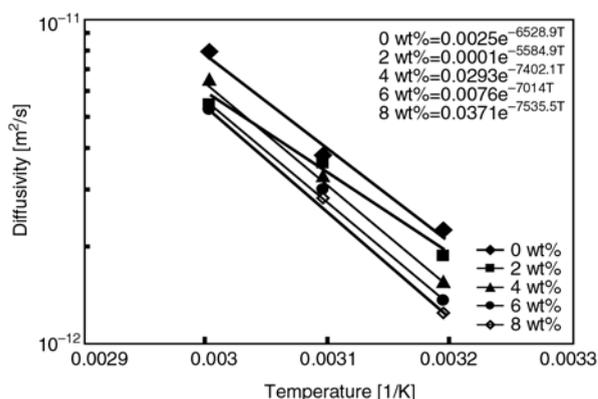
Figure 8. Relation between diffusivity and temperature of PA6/organoclay nanocomposites

It noticed that the diffusion coefficient increases as function of the immersion temperature; this is due to the fact that increasing the temperature leads to a decrease of the interaction energy. Exception is observed for the data 2 wt% where a decrease is observed this mainly due to the fact that at this concentration and at immersion temperature of 60°C showed the lowest diffusion coefficient, which did alter the calculation of the activation energy done via curve fitting as seen in Figure 8.

In the case of the PA6/organoclay nanocomposites, there are mainly two interaction groups: the interaction of water molecules with the amide groups of the PA6, i.e. matrix and the interaction of water molecules with the hydrophilic clay group i.e. the filler. Although the clay has been modified to be more organophilic, it may still interact and bind to water molecules, even if, this interaction does not dominate the sorption process of water in the nanocomposites.

3.5. Influence of water on mechanical properties

The evaluation of the mechanical properties in terms of bending test showed that an increase in both modulus and strength occurred in the dry con-

dition, however, the tests under wet condition are performed on samples that are immediately removed immersion test.

Figure 9 illustrates the retention of the flexural strength of PA6 and that of PA6/organoclay nanocomposites as function of immersion time and at different immersion temperature. It is noticed a sharp decrease in the flexural strength as well as in the flexural modulus (not reported in this paper). This decrease levels off within about 25 h in the case for all investigated temperature which clearly shows the sensitivity of the PA6 towards water content. Nevertheless the presence of the organoclay may retain higher flexural strength as seen in Figure 9b (magnification of Figure 9a) it is observed that the neat PA6 has the lowest retention of the flexural strength as compared to the filled.

It is known that the absorbed moisture decreases T_g of PA6 and other polyamides because the water molecules interfere with the hydrogen bonds between the polymer chains and this increases the chain mobility. The reduced T_g in the presence of water results in a strong reduction of the amorphous modulus in the temperature range around T_g, which leads to a decrease of the modulus of the semi-crystalline polymer. Because of the reduction of the matrix modulus, also polyamide nanocomposites suffer from a modulus reduction after moisture conditioning. In addition, the increased mobility reduces the yield stress and increases the ductility and elongation at break.

The loss of mechanical performance i.e. the decrease in the flexural modulus occurs early in the diffusion process with the maximum loss realized much in advance of saturation. Initial uptake of water results in plasticization of the polymer matrix such that further ingression of water into the void spaces within the sample does not significantly alter the mechanical performance. The initial loss of performance, prior to the plateau, may be associated with the diffusion front progression through the sample. Further weight gain after this point may be attributed to the continued filling of voids spaces with water.

When the samples are moisture conditioned, the modulus of PA6 and the nanocomposites is significantly reduced. The reduction of the modulus in the presence of water is common to all polyamides to a certain degree, and it is caused by the plasticizing action of water molecules in polyamides [32] PA6
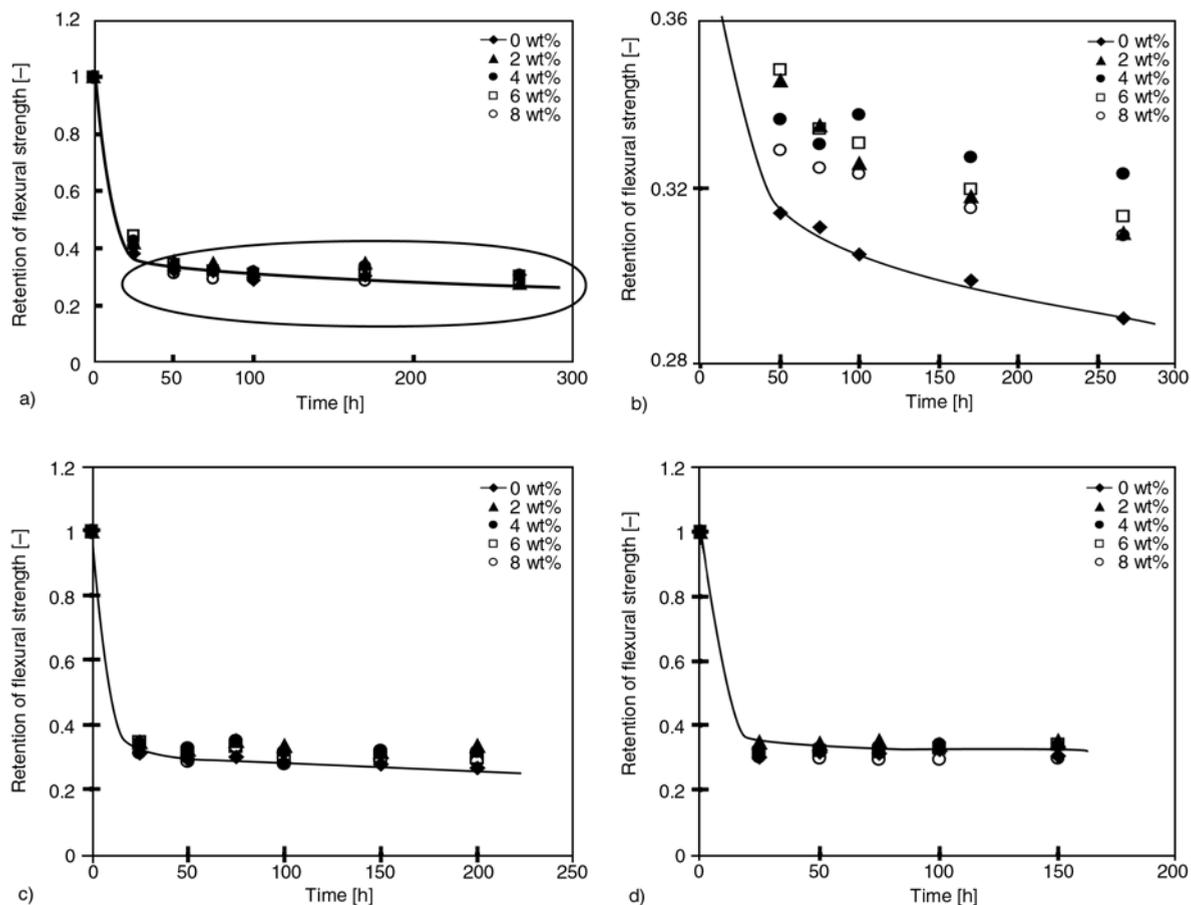
Figure 9. Retention of flexural strength of PA6/organoclay nanocomposites – wet condition – as function of immersion time at: a) and b) 40°C, c) 50°C and (d) 60°C

has a glass transition temperature around 60°C in dry conditions, but in moisture conditioned samples this can decrease to room temperature and below [33].

4. Conclusions

The investigation of the formation of a nanocomposites structure of the dispersed organoclay within PA6 matrix was done in addition to the study of the behavior of the diffusion of water within these nanocomposites materials. It was found that the organoclay was fully exfoliated and well dispersed within PA6 matrix for all the investigated organoclay content. An enhancement of the mechanical performance as function of organoclay content was obtained in terms of bending test where an increase of both flexural strength and flexural modulus were obtained. The immersion into water revealed that lower maximum weight change is obtained when immersed into water and that the diffusion coefficient of water is decreased by a half at some condition however the weight change was found to

increase as function of organoclay content but remains lower than the neat resin. Better mechanical properties were achieved with the addition of organoclay and despite the sharp decrease in the mechanical properties of the immersed sample, the nanocomposites ones showed higher retention compared to the neat PA6.

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