

# Water uptake behavior of layered silicate/starch–polycaprolactone blend nanocomposites

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**Abstract:** The water uptake behavior of biodegradable layered silicate/starch–polycaprolactone blend nanocomposites was evaluated. Three different commercial layered silicates (Cloisite Na<sup>+</sup>, Cloisite 30B and Cloisite 10A) were used as reinforcement nanofillers. Tests were carried out in two different environments: 60 and 90% relative humidity using glycerol solutions. The clay/starch–polycaprolactone blend nanocomposites were obtained by melt intercalation and characterized by gravimetric measurements and tensile tests. The intercalated structure (determined by wide-angle X-ray diffraction) showed a decrease in water absorption as a function of clay content probably due to the decrease of the mean free path of water molecules. The diffusion coefficient decreased with clay incorporation but a further increase in the clay content did not show an important effect on this parameter. Elongation at break increased with exposure showing matrix plasticization. Mechanical properties of the nanocomposites deteriorated after exposure whereas they remained almost constant in the case of the neat matrix. © 2007 Society of Chemical Industry

**Keywords:** water uptake; mechanical properties; clay nanocomposites; starch; polycaprolactone; biodegradable polymers; diffusion coefficients

## INTRODUCTION

In recent years, organic–inorganic nanoscale composites have attracted great interest since they frequently exhibit unexpected hybrid properties synergistically derived from both components.<sup>1–6</sup> Because of their nanoscale structure, nanocomposites have unique properties, i.e. better properties compared with those of traditional composites and they represent interesting opportunities to develop new technologies.

In order to achieve higher aspect ratios, a clay must be intercalated or exfoliated into a polymeric matrix. Silicate-based clays are hydrophilic and lack affinity with hydrophobic organic polymers, especially thermoplastics. For this reason, natural clays have been treated with organic molecules to transform them from hydrophilic to organophilic materials.<sup>7,8</sup>

MaterBi-Z is a commercial biodegradable blend of poly( $\epsilon$ -caprolactone) (PCL) and starch and has been used in the packaging industry since it was introduced onto the market.<sup>9</sup> How to produce a reduction in the water absorption of such a material is an important task to be studied. Polymer/clay nanocomposites have recently been prepared and

mostly exhibit low water absorption and excellent barrier properties due to their long delaminated clay layers.<sup>6,7,10–18</sup> Most authors have reported that the water absorption mechanism of clay/polymeric matrix nanocomposites is influenced by two factors. The first is that the clay body itself is water rich, and so absorbs more water than most of the thermoplastic used as matrix, leading to an increase in the equilibrium water absorption with the clay content. The other factor is that clay layers dispersed in the nanometer scale in a matrix can decrease the mean free path of water molecules to pass through the nanocomposite network compared the pure matrix which leads to lower water absorption.<sup>12,13</sup> However, a small quantity of work has been done on starch/PCL blends as a composite matrix.<sup>9,19–22</sup> In particular, MaterBi-Z is a commercial blend of both materials: PCL (hydrophobic) and starch (hydrophilic). In the case of this polymer and natural fiber composites, the decrease of starch content could produce a decrease of the maximum water uptake due to the hydrophilic character of natural fibers and starch. As the fiber content increases, the composite becomes more hydrolytically stable probably due to the presence of a fiber–fiber physical network.<sup>19</sup> As a consequence,

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it is clear that water absorption is dependent on the precise nature of the components and composite morphology.

Very few studies have been done on biodegradable starch-based nanocomposites where the main challenge lies in fine-tuning starch and nanoclay architecture to achieve strong bonding between clay and polymer. Pandey and Singh<sup>21</sup> have studied nanocomposites of starch and clay prepared by different addition sequences of plasticizer and clay from solution. They optimized the method in order to obtain nanocomposites with the best properties. They found that the best sequence was the addition of clay to starch and then the addition of plasticizer. They measured moisture resistance during 50 h at 98% relative humidity (RH) and they showed that the water resistance can be improved more by dispersion of the clay than by the presence of moisture-sensitive groups.

Also, the effect of water uptake on the mechanical properties is very important.<sup>23,24</sup> Pérez *et al.*<sup>25</sup> have studied the effect of clay on the crystallization of MaterBi-Z. It has been demonstrated that these kinds of nanocomposite (MaterBi-Z/clay) show a near doubling of modulus for materials containing 5 wt% clay and the effect was improved when clay was organically modified.<sup>26</sup> A report was published by Kalambur and Rizvi,<sup>20</sup> who obtained starch-based nanocomposites by reactive extrusion processing. The addition of nanoclay produced an improvement in the mechanical properties. An immersion test showed that the sample with 6 wt% of clay retained the structural integrity.

As these biodegradable nanocomposites could be used for packaging, it will be important to know the effect of water uptake on the mechanical properties as well as the rate of water sorption and the equilibrium water content. This evaluation will permit us to compare modified clays under different humidities. Although work has been carried out in the field of water absorption of polymeric matrices/clay nanocomposites, there are not many results concerning two-component blends used as matrix in nanocomposites under two different humidities.

The aim of the work reported here was to analyze the effect of clay incorporation and content on the water uptake behavior of biodegradable starch/PCL blends, as well as the influence of the absorbed water on the mechanical properties.

## MATERIALS AND METHODS

### Matrix and reinforcements

A commercial starch/PCL blend called MaterBi-Z (MBZ), kindly supplied by Novamont, Novara, Italy, was used as a matrix. It consists of 18 wt% starch, 75 wt% PCL (the main component) and 7 wt% additives.<sup>22</sup> Three different clays were used as nanofillers. All of them were purchased from Southern Clay Products Inc., USA. The commercial names of

**Table 1.** Characteristic of the clays used

Material	Organic modifier
Cloisite Na <sup>+</sup> (MMT)	None
Cloisite 30B (C30B)	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\   \\ \text{H}_3\text{C}-\text{N}^+-\text{T} \\   \\ \text{CH}_2\text{CH}_2\text{OH} \end{array}$
Cloisite 10A (C10A)	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{N}^+-\text{C}-\text{C}_6\text{H}_5 \\   \quad   \\ \text{HT} \quad \text{H}_2 \end{array}$

the clays and the organic modifiers of each one are given in Table 1.

### Nanocomposite preparation

Nanocomposites were prepared by melt intercalation using an intensive mixer (Haake Rheomix 600). Filler content was in the range from 0 to 7.5 wt%. The mixing rate, temperature and time were fixed at 150 rpm, 100 °C and 10 min, respectively. The material obtained after mixing was compression molded in a hydraulic press for 10 min at 100 °C. A pressure of 50 kg cm<sup>-2</sup> was applied during 10 min. The samples obtained were plaques of 150 mm × 200 mm × 0.4 mm.

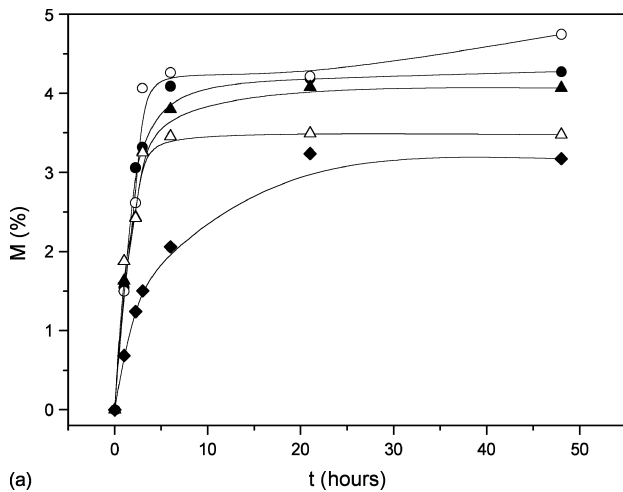
### Water absorption measurements

Matrix and nanocomposite samples cut from plaques (dumbbell-shaped) were placed in two different environments: (a) 60% RH prepared using a 72 wt% glycerol solution and (b) 90% RH prepared using a 34 wt% glycerol solution. Samples were removed from the environments at fixed times and were carefully dried with an absorbent paper. Weight change was determined by means of a microbalance calculated at 10 mg. Tests were carried out until constant weight was achieved. At least four specimens of each material were used. All the tests were carried out at room temperature. Before exposure, all samples were dried in a vacuum oven at 40 °C until constant weight was reached.

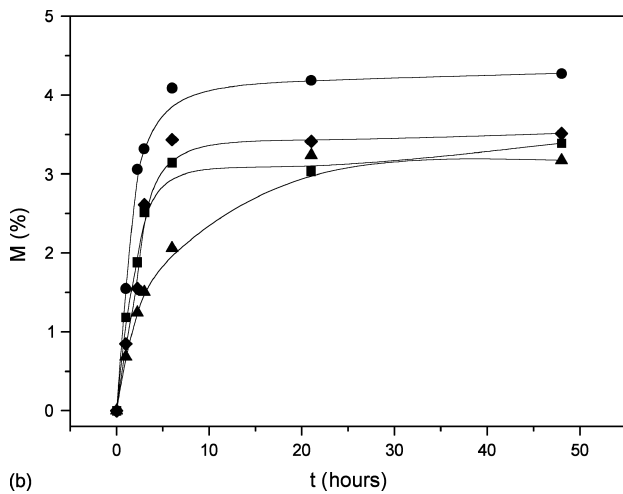
### Tensile tests

Tensile tests were carried out at room temperature using a universal testing machine (Instron 4467) at a crosshead speed of 1 mm min<sup>-1</sup>. Dumbbell-shaped specimens were used. The thickness was measured to an accuracy of 0.01 mm.

At least three specimens were tested for each condition. These tests were made at two different stages: (a) before exposure and (b) after constant weight was achieved. These measurements were carried out in order to analyze the effect of water uptake on the mechanical behavior of the neat matrix and the nanocomposites.



(a)



(b)

**Figure 1.** Curves of water content (%) as a function of exposure time for 60% RH environment. (a) Effect of clay content on the water uptake behavior of MBZ/MMT nanocomposites: (●) MBZ; (○) MBZ–1 wt% MMT; (▲) MBZ–2.5 wt% MMT; (△) MBZ–5 wt% MMT; (◆) MBZ–7.5 wt% MMT. (b) Effect of clay type on the water uptake behavior of 7.5 wt% clay/MBZ nanocomposites: (●) MBZ; (▲) MBZ–7.5 wt% MMT; (◆) MBZ–7.5 wt% C30B; (○) MBZ–7.5 wt% C10A.

## RESULTS AND DISCUSSION

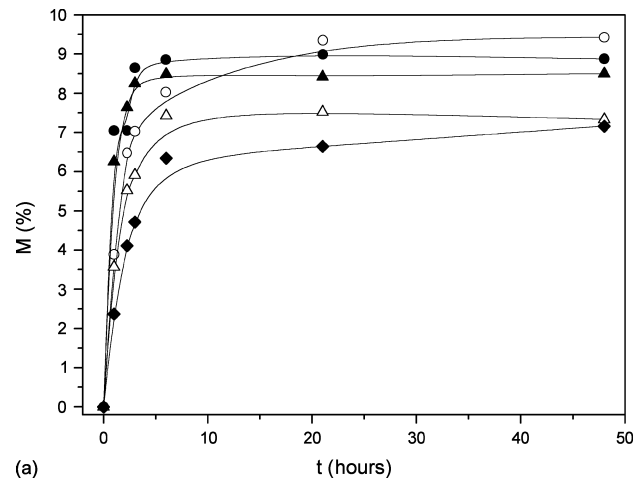
### Water absorption behavior

The weight change (wt%) during exposure to humid environments was determined using the following equation:

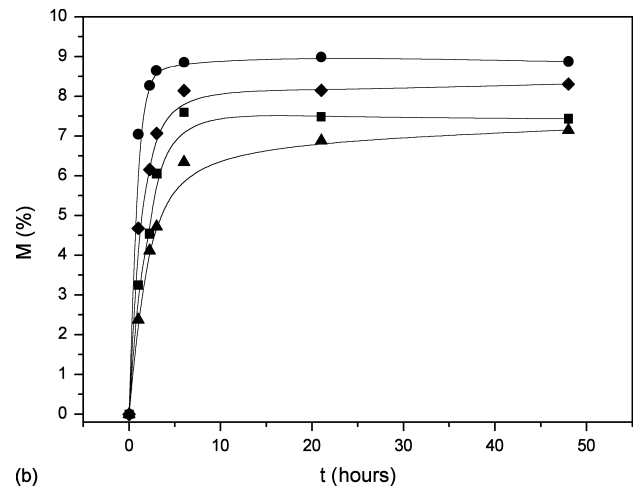
$$M(\%) = \frac{M_t - M_0}{M_0} \times 100 \quad (1)$$

where  $M_t$  is the mass of the sample at exposure time  $t$  and  $M_0$  is the weight of the dry sample. The weight changes of studied materials during exposure to the different environments are shown in Figs 1 and 2. It is clear that clay incorporation leads to a decrease in the amount of absorbed water.

The weight continuously increased with immersion time until a plateau was reached. The equilibrium water uptake,  $M_\infty$ , was taken as the maximum value of these curves. The obtained values are reported in Table 2. In general, water uptake did not change with clay incorporation (content up to 1 wt%) but then



(a)



(b)

**Figure 2.** Curves of water content (%) as a function of exposure time for 90% RH environment. (a) Effect of clay content on the water uptake behavior of MBZ/MMT nanocomposites: (●) MBZ; (○) MBZ–1 wt% MMT; (▲) MBZ–2.5 wt% MMT; (△) MBZ–5 wt% MMT; (◆) MBZ–7.5 wt% MMT. (b) Effect of clay type on the water uptake behavior of 7.5 wt% clay/MBZ nanocomposites: (●) MBZ; (▲) MBZ–7.5 wt% MMT; (◆) MBZ–7.5 wt% C30B; (○) MBZ–7.5 wt% C10A.

**Table 2.**  $M_{\max}$  for different RH of matrix and nanocomposites as a function of clay content

Clay content (wt%)	MMT		C10A		C30B	
	60% RH	90% RH	60% RH	90% RH	60% RH	90% RH
0.0	4.5	9.0	4.5	9.0	4.5	9.0
1.0	4.7	9.4	4.8	8.9	4.7	9.4
2.5	4.1	8.5	4.0	7.6	4.3	8.8
5.0	3.5	7.3	3.6	7.8	4.3	8.6
7.5	3.2	7.1	3.4	7.4	3.5	8.3

decreased as the filler content was increased,<sup>12</sup> being the differences higher in the 90% RH environment. One reason could be that the clay immobilizes the polymer. It was reported previously that the degree of crystallinity (around 35%) was similar for matrix and nanocomposites,<sup>25</sup> and as a consequence the clay should be in the amorphous phase and produce a

**Table 3.** Calculation of theoretical water content for 98% RH

Material	$M_{\max}$ (%)
PCL	4
Starch	35
0 (18% starch–75%PCL)	9.3
1.0	9.2
2.5	8.8
5.0	8.6
7.5	8.1
Clay	5

network or intricate path for water diffusion into the center of a sample.

In the case of the matrix, the water absorption is mainly due to starch: starch absorbs around 35% of water<sup>21</sup> whereas PCL absorbs around 4% of water.<sup>27</sup> The starch absorption depends on its nature, and if the starch is a modified one the hydrophilic character is less than that of the native starch, as was found before.<sup>28</sup> It is important to point out that, at the early stages studied in the actual work, no starch dissolution took place. For higher clay contents, MaterBi-Z/clay nanocomposites exhibit lower water absorption than that of the neat matrix. The amount of water uptake decreased as a function of clay content.

Taking into account these values (starch and PCL absorptions at 98% RH) the theoretical values of maximum water uptake were calculated and the results are shown in Table 3.

These values are similar to the experimental ones for nanocomposites with C30B. The effect of the additives content on MaterBi-Z was not taken into account and it can produce some differences. The water uptake values for C10A clay are lower than the theoretical ones, which could be due to the higher degree of dispersion and more tortuous paths of water in the presence of clay platelets. So, in the case of C30B, the decrease in the water absorption can be related to the smaller starch content whereas for C10A an additional effect based on clay dispersion takes place.

MaterBi-Z/clay nanocomposites exhibit an intercalated structure.<sup>26</sup> In the case of unmodified montmorillonite, clays are intercalated into the polymer chains. For composites prepared with Cloisite 30B, the intensity of the  $d_{001}$  peak and its position in the DRX spectrum indicates that further increase in  $d$ -spacing due to the melt blending had not taken place. However, for nanocomposites with C10A, modifier incorporation and clay–polymer intercalation leads to a higher degree of intercalation.

As it is known, alkylammonium ion exchange enables the conversion of the interior clay surface from hydrophilic to hydrophobic and increases the layer distance as well.<sup>29</sup> Remembering the factors that influence the water uptake in the case of nanocomposites,<sup>7</sup> it is possible that the decrease of the mean free path of water molecules became predominant leading to the lower water uptake.

In the case of C10A there exists a greater compatibility between clay modifier and the polymer matrix which are both hydrophobic (the polymer is mainly composed of PCL). The difference in the dispersion, reflected in the initial mechanical properties,<sup>26</sup> could be a consequence of the organic groups of the clay. The benzyl group of 10A clay has more surface space than the hydroxyethyl substituents.

As a consequence, the reduced amount of water molecules diffusing into the composite results from the longer and more tortuous pathway for water molecules, i.e. the stacking layers can act as barrier to water diffusion into the polymer film.<sup>6,14</sup>

### Diffusion coefficient

In order to use Fick's law, several considerations must be taken into account: the material is considered homogeneous, no chemical interaction exists between the material and water, diffusion is the only mechanism for sorption and the material structure change is negligible.

The present material does not meet these conditions because: (i) the material is non-homogeneous, (ii) there is a chemical interaction between the hydrophilic part of the matrix and the water, (iii) the interphase could be not good and, as a consequence, capillarity could be another mechanism, (iv) some soluble material could be extracted from the specimen and the specimen weight is a consequence of two effects, water absorption and soluble extraction, and (v) the dimension of the specimen could change during the absorption process.

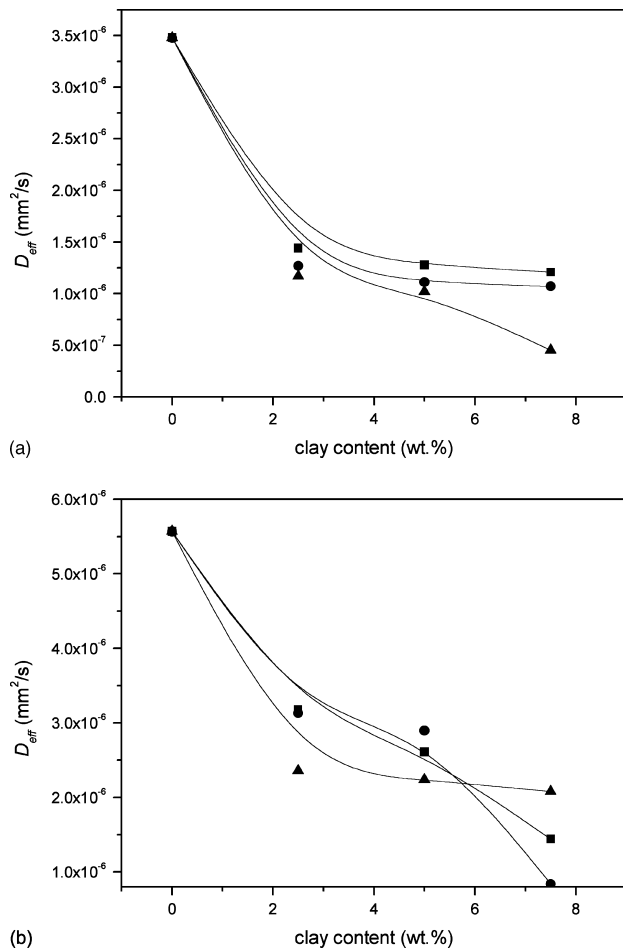
As a consequence, the Fick's second law can be applied avoiding some of the previous hypotheses, if we take into account only the increase of weight of the specimen, considering that no extraction of soluble material was produced before (during the time of the experiment) and defining a maximum increase of weight in the specimen ( $M_{\max}$ ) instead of an equilibrium value ( $M_{\infty}$ ). On this basis, we define an effective diffusion coefficient,  $D_{\text{eff}}$ , that considers all the mechanisms involved in the water absorption process like a diffusion process. In this way, we can compare similar material by the value of the effective diffusion coefficient, it being related to the neat velocity of the global water uptake process.<sup>30,31</sup> Water uptake has been modeled by Fick's second law for several materials:<sup>32</sup>

$$\frac{dc}{dt} = D_{\text{eff}} \frac{d^2c}{dx^2} \quad (2)$$

where  $c$  is the water concentration,  $t$  is the time of immersion and  $x$  is the flux direction.

Experimentally, the *effective diffusion coefficient* can be obtained from the initial slope of  $M$  (percent water absorption) versus  $t^{1/2}$  (square root of immersion time) curve as follows:<sup>33</sup>

$$D_{\text{eff}} = \pi \left( \frac{h}{4M_{\max}} \right)^2 \left( \frac{dM}{d\sqrt{t}} \right)^2 \quad (3)$$



**Figure 3.** Effect of clay content on the effective diffusion coefficient for MBZ/clay nanocomposites. (a) 60% RH: (■) MBZ–MMT; (●) MBZ–C10A; (▲) MBZ–C30B. (b) 90% RH: (■) MBZ–MMT; (●) MBZ–C10A; (▲) MBZ–C30B.

where  $h$  is the specimen thickness and  $M_{\max}$  is the maximum relative water uptake until the linear relationship between  $M$  and  $t^{1/2}$  is verified.

Figure 3 shows the effective diffusion coefficient as a function of clay content. This parameter clearly decreased (2.5 times) with clay incorporation. The values are similar for all clay contents studied in this work. The presence of the nanoparticles leads to a lower rate at which water is absorbed. In our case it is clear that the decrease on the free path for the water molecules to pass through the nanocomposite network is the main factor for such behaviour. In addition to the immobilized phase, the presence of crystallites or other impermeable particles obviously also lowers the overall rate of water transport. It has also been suggested that impermeable phases increase the average diffusion path length.<sup>34</sup>

### Mechanical properties

The mechanical properties of dried materials were reported in a previous work.<sup>26</sup> Elongation at break and mechanical properties are shown in Tables 4 and 5, respectively.

Elongation at break decreased when clay was incorporated (Table 4).<sup>35</sup> There is no relationship

**Table 4.** Elongation at break of matrix and nanocomposites

Material	Elongation at break (%)		
	Initial	60% RH	90% RH
MBZ	13.0 ± 2.0	17.6 ± 1.0	14.6 ± 0.5
1.0% MMT	6.8 ± 1.5	7.5 ± 0.2	10.0 ± 1.0
2.5% MMT	6.5 ± 0.5	9.6 ± 1.5	11.2 ± 0.5
5.0% MMT	7.0 ± 0.5	7.8 ± 0.5	14.9 ± 2.0
7.5% MMT	5.5 ± 0.5	7.0 ± 0.2	12.0 ± 1.5
1.0% 10A	9.5 ± 0.5	11.0 ± 1.0	29.3 ± 9.0
2.5% 10A	11.5 ± 0.5	14.0 ± 2.0	16.6 ± 10.0
5.0% 10A	9.0 ± 2.0	8.4 ± 1.5	18.3 ± 11.0
7.5% 10A	10.0 ± 1.5	11.1 ± 2.0	14.2 ± 3.0
1.0% 30B	7.5 ± 1.0	9.2 ± 0.5	13.5 ± 2.0
2.5% 30B	6.5 ± 1.0	9.6 ± 0.2	10.1 ± 0.5
5.0% 30B	7.1 ± 1.5	11.6 ± 0.7	18.5 ± 2.0
7.5% 30B	7.5 ± 1.5	8.2 ± 1.6	10.2 ± 1.0

between clay content and elongation at break. It is also clear from this table that after exposure this property increased for both the matrix and the nanocomposites, which is an indication of matrix plasticization. It is probably due to the water–clay interaction and/or the difference in the morphology of the nanocomposites related to the intercalation (higher tortuosity). The effects are remarkable in the case of nanocomposites, especially for C10A where, after exposure to 90% RH environment, elongation at break became higher than that of the neat matrix.

From Table 5, it is evident that the loss of mechanical properties is negligible in the case of the matrix: properties remain almost constant after exposure to both environments. For nanocomposites, properties became poorer after exposure and the decrease was generally more significant in the case of tensile modulus.<sup>24</sup> The decrease in the mechanical properties can be related to void formation around nanoparticles and the deterioration of the particle/matrix interface, probably due to the possibility of hole formation. This behavior after water exposure is a common response of composites, especially the deterioration of the reinforcement/matrix interface.<sup>36–40</sup>

In all cases the differences are higher for the 90% RH environment because the equilibrium water content is higher. The higher the amount of water inside the composite the higher the void content and the lower the mechanical properties.

### CONCLUSIONS

The effect of water uptake on the mechanical behavior of starch/PCL blends filled with different clays was studied.

In the case of the neat matrix, the water absorption is mainly due to starch (the most hydrophilic component). It was determined that maximum water uptake did not change for nanocomposites with 1 wt% clay but for higher clay content it decreased as the filler content was increased. It was established

**Table 5.** Residual mechanical properties (calculated using Eqn (4)) after exposure to humid environments

Material	Modulus, $E'$ (MPa)			Yield strength, $\sigma$ (MPa)		
	0% RH	60% RH	90% RH	0% RH	60% RH	90% RH
MBZ	162 ± 5	159 ± 3	143 ± 10	6.6 ± 0.5	7.3 ± 0.5	7.6 ± 0.3
1.0% MMT	211 ± 6	165 ± 4	130 ± 8	7.5 ± 0.2	7.1 ± 0.4	5.8 ± 0.5
2.5% MMT	228 ± 3	160 ± 3	135 ± 10	8.7 ± 0.3	7.1 ± 0.3	6.4 ± 0.3
5.0% MMT	264 ± 5	191 ± 12	202 ± 9	10.2 ± 0.5	7.5 ± 0.2	7.4 ± 0.3
7.5% MMT	298 ± 11	290 ± 12	183 ± 15	10.1 ± 0.4	9.8 ± 0.6	8.5 ± 0.8
1.0% 10A	256 ± 23	184 ± 17	161 ± 12	9.6 ± 0.03	8.6 ± 0.5	8.3 ± 0.4
2.5% 10A	301 ± 8	203 ± 18	181 ± 5	9.8 ± 0.3	9.4 ± 0.7	8.9 ± 0.2
5.0% 10A	330 ± 32	278 ± 10	266 ± 13	10.3 ± 0.3	9.5 ± 0.2	9 ± 0.5
7.5% 10A	580 ± 15	354 ± 17	328 ± 16	11.3 ± 1.1	10 ± 1	9.5 ± 0.3
1.0% 30B	162 ± 7	169 ± 13	130 ± 11	6.8 ± 0.7	6.4 ± 0.5	6.1 ± 0.2
2.5% 30B	210 ± 19	196 ± 19	179 ± 12	6.9 ± 0.3	8.6 ± 0.3	8.3 ± 0.2
5.0% 30B	253 ± 7	245 ± 10	206 ± 18	8.9 ± 0.4	8.4 ± 0.1	7.9 ± 0.3
7.5% 30B	281 ± 3	224 ± 13	193 ± 9	9.7 ± 0.8	8.3 ± 0.4	8.5 ± 0.4

that there are several factors that need to be taken into account: (i) the clay body itself is water rich (leading to higher water absorption), (ii) starch has a hydrophilic nature and it decreases when clay content increases and (iii) the clay layers being dispersed on a nanometer scale in the matrix can increase the mean free path of water molecules to pass through the network (leading to lower water uptake). As clay content increases the last factor became predominant. In the case of C30B, the decrease in the water absorption was related to starch content, whereas for C10A an additional dispersion effect was also considered.

Diffusion coefficient decreased with clay incorporation. This result was attributed to the immobilized phase and to the presence of crystallites or other impermeable particles that lower the overall rate of transport. The increase of clay content has only a small influence on this parameter.

Elongation at break showed a clear increase after exposure for both the matrix and the nanocomposites, indicating matrix plasticization. Also water could be interacting with clay and clay modifiers because the effects are marked in the case of nanocomposites, especially for C10A.

Loss of mechanical properties was low for PCL–starch blend but it was very important in the case of nanocomposites. The decrease was generally higher due to interfacial effects such as void formation around nanoparticles and the deterioration of the particle/matrix interface.

All studied parameters could be related to the different compatibilities between clay and the matrix. Cloisite 10A has the greatest compatibility with the matrix (due to the clay modifier) because they are both hydrophobic. The difference in the degree of dispersion, reflected in the initial mechanical properties, equilibrium water uptake and diffusion coefficient, could be a consequence of the organic groups of the clay. Benzyl group of C10A clay has more surface space than the hydroxyethyl substituents.

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