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Long-term Water Absorption Behaviour of Polypropylene/Wood Flour/Organoclay Hybrid Nanocomposite

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ABSTRACT

Recently, to improve the properties of wood plastic composite (WPC), incorporation of nanofiller has been considered. In this study, hybrid composite of polypropylene/wood flour/nanoclay with different concentrations of nanoclay and maleated polypropylene (MAPP) as compatibilizer were fabricated in an internal mixer. The long-term water absorption of the composites was evaluated by their immersion in water at room temperature for several weeks (up to 3000 h). Water diffusion coefficients were evaluated. The results indicate that water absorption decreases with increase in clay loading. The morphology of nanoclay was determined by X-ray diffraction (XRD) and transmission electron microscope and the effect of morphology on water absorption is discussed. Due to inadequate compatibilizer, exfoliated morphology of nanoclay is not obtained but the intercalation has occurred. The order of intercalation for samples containing 3 phc is higher than that of 6 phc at the same MAPP content due to some agglomerations of organoclay. The effect of compatibilizer has been positive in terms of enhancing the dimensional stability of the composites and mechanical properties. The maximum elastic modulus may be related to 3 phc of nanoclay and 4 phc of MAPP. The maximum water absorption and diffusion coefficients are decreased by increasing the clay and MAPP contents. The mechanism of water absorption of the composites under study followed the kinetics of a Fickian diffusion process.

Key Words:

hybrid composite;
nanoclay;
wood flour;
water absorption;
diffusion coefficient.

INTRODUCTION

In recent years, the use of natural fibres as reinforcers and/or fillers in the manufacture of fibre thermoplastic composites has been of great interest, particularly in structural and automotive industry [1-4].

New applications and end uses of wood plastic composites (WPCs) for decking, flooring and outdoor facilities, window frames, various construction materials and bathroom parts for example, and their exposure to atmosphere or contact with aqueous media have made it necessary to evaluate the water uptake characteristics of these materials. Water absorption is one of the most important characteristics of WPCs exposed to environmental conditions that determine their end use applications. Therefore, as a limiting parameter, water absorption has to be taken into account in the design of WPCs for final applications [5-7].

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Generally, water absorption in WPCs is governed by two significant mechanisms: the hygroscopic nature of natural fillers/fibres and the penetration of water into the composites (diffusivity) via gaps and flaws at the interfaces between fibres and plastics [8-11].

Poor resistance of the fibres to water absorption can have undesirable effects on mechanical properties and dimensional stability and in long-term, embrittlement linked to the degradation of the macromolecular skeleton by hydrolysis [12]. Therefore, it is important to study in detail the water absorption behaviour in order to estimate not only the consequences that the water absorbed may have, but also how this water uptake can be minimized in practice. A number of attempts have been made to reduce water absorption of WPCs [13-16].

The impressive enhancement of material properties was achieved with the inclusion of submicron-size fillers in plastics and has stimulated active research in polymer composites. Clay nanocomposites, especially nanoclay/polymer composites, exhibit dramatic increases in modulus, strength, barrier properties, flammability resistance, heat resistance, and hygroscopic (water absorption, thickness swelling) properties compared with conventional composites [17-21].

The use of nanoscale fillers in WPCs has been reported in literature. The focus has been mainly on the effect of nanofiller incorporation on the mechanical properties [22-24], gas permeability [25], and flammability [26] of the WPCs. Hetzer et al. used blending high and low molecular weight maleated polyethylenes (MAPE) in order to maximize their compatibilization effects on WPC/clay nanocomposites. Their results showed that the addition of organically modified montmorillonite (OMMT) to a wood/polymer composite in the presence of MAPE reduces its linear coefficient of thermal expansion and increases the heat deflection temperature without affecting the processability [27,28]. Using carbon nanotube (CNT) in WPC based on PVC has been reported by Faruk et al. The results indicated that rigid PVC/wood-flour composites with properties similar to solid wood can be achieved by using CNT reinforced PVC as a matrix. The CNT reinforced PVC did not influence the electrical and thermal conductivity of the PVC/wood-flour composites [29].

The aim of this study was to investigate the effect of nanoscale filler on the long-term water absorption behaviour of polypropylene/wood flour composite.

EXPERIMENTAL

Materials

Polypropylene, with trade name V30S (MFI: 18 g/10 min, density: 0.92 g/cm^3) was supplied by Arak Petrochemical Co. (Iran). Beech wood-flour (WF) was from Cellulose Aria Co. (Iran). The particle size of wood flour was 100 mesh. Maleic anhydride grafted polypropylene (MAPP) provided by Solvay with trade name of Priex 20070 (MFI: 64 g/min, grafted maleic anhydride, 0.1 wt%) used as coupling agent. Montmorillonite modified with a methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium (CEC = 90 meq/100 g clay, doo_1 = 18.5 A^0) was obtained from Southern Clay Products Co., USA, with trade name of Cloisite 30B.

Method

Sample Preparation

Before sample preparation, wood flour was dried in an oven at (65 ± 2)ºC for 24 h. Then polypropylene, wood flour, and nanoclay were weighed and bagged according to formulations given in Table 1. Mixing was carried out in a Haake internal mixer (sys 90, USA) equipped with cam blade at 180ºC and 60 rpm. First the polypropylene was fed to mixing chamber, after melting of PP, coupling agent and nanofiller was added. After mixing for 5 min, the wood flour was fed into the system. The total mixing time was 13 min. The compounded materials were then grinded to prepare the granules using a pilot scale grinder (WIESER, WGLS 200/200 model). The resulting granules were dried at 105ºC for 4 h. Test specimens were prepared by an injection moulding machine (Imen Machine, IRAN) at 190ºC. The compounded materials were then grinded using a pilot scale grinder (WIESER, WGLS 200/200 Model). The resulting granules were dried at 105°C for 4 h. Test specimens were prepared by injection moulding (Imen Machine, Iran) according to standard ASTM D638.

Table 1. Composition of the studied formulations.

Sample code	Polypropylene content (wt%)	Wood flour content (wt%)	Nanoclay content (phc*)	PP-*g*-MA (phc)
50W50P	50	50	0	0
50W50P2M	50	50	0	2
50W50P4M	50	50	0	4
50W50P3N	50	50	3	0
50W50P2M3N	50	50	3	2
50W50P4M3N	50	50	3	4
50W50P6N	50	50	6	0
50W50P2M6N	50	50	6	2
50W50P4M6N	50	50	6	4

(*) phc: per hundred compounds

The specimens were stored under controlled conditions (50% relative humidity and 23ºC) for at least 40 h prior to testing.

Measurements

Water absorption tests were carried out according to ASTM D-7031-04. Five specimens of each formulation (25.4×7.62×3.2 mm) were selected and dried in an oven for 24 h at 102±3ºC. The weight and thickness of dried specimens were measured to a precision of 0.001 g and 0.001 mm, respectively. The specimens were then placed in distilled water and kept at room temperature. For each measurement, specimens were removed from the water and the surface water was wiped off using blotting paper. Weight and thicknesses of the specimens were measured at different time intervals during the long-time immersion. The measurements were terminated after the equilibrium thicknesses of the specimens were reached. The values of the water absorption in percentage were calculated using the following equation:

$$WA(t) = \frac{W(t) - W_0}{W_0} \times 100 \qquad (1)$$

where WA(t) is the water absorption at time t, W_0 is the oven dried weight, and W(t) is the weight of specimen at a given immersion time t.

Wide angle X-ray diffraction (XRD) analysis was carried out with a Seifert-3003 PTS (Germany) with CuKα radiation (λ = 1.54 nm, 50 kV, 50 mA) at room temperature, scanning rate was 1º/min. The morphology structure of the nanocomposites was investigated by a Philips (Model EM 208, Netherland) transmission electron microscope (TEM) with an acceleration voltage of 100 kV. The ultrathin slides were obtained by a Leica Ultracut UCT (Germany).

RESULTS AND DISCUSSION

Morphology of Hybrid Composite

It is useful to start by expressing the morphology of nanocomposite. Characterization of the morphological state of the hybrid composite has been accomplished using X-ray diffraction and TEM. The X-ray scattering intensities for modified organoclay and hybrid composites with different levels of nanoclay at 2 phc MAPP concentration are demonstrated in Figure 1. In this figure, 2θ = 4.76º is related to neat clay with basal spacing of 18.5 nm. In the sample with 3 phc concentration of clay, the peak was shifted to a lower angle (2θ = 4.48º, d-spacing = 19.70 nm) which implies the formation of the intercalation morphology. The (001) peak of 6 phc nanoclay was appeared at 2θ = 4.54º, d-spacing = 19.44 nm. These data show that the order of intercalation is higher for 3 phc of nanocaly than 6 phc of nanoclay concentration. It seems this is because of the finite value of MAPP in the nanocomposites. It is well known, through the improvement of the compatibility between neat PP and clay (using MAPP), the polymer chains could be

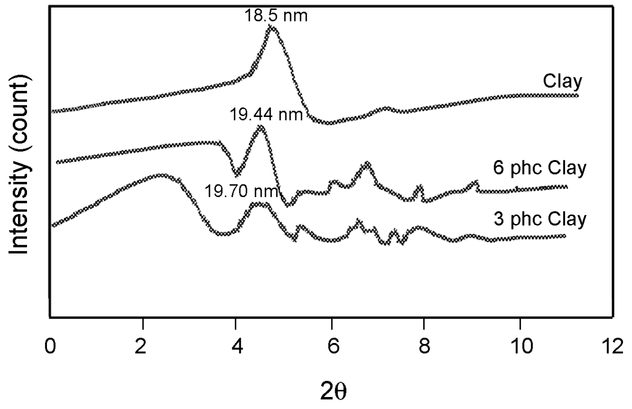

Figure 1. X-Ray scattering intensities for modified organoclay and hybrid composites with different levels of nanoclay at 2 phc MAPP concentration.

well diffused into the clay layers and the basal spacing of clay layers might be increased. In other words, the MAPP in lower concentration of clay has higher efficiency to d-spacing of the layers. The same trend was observed in Figure 2 which shows the X-ray diffraction of samples with different levels of MAPP at the same concentration of nanoclay. As can be seen with increase of MAPP in the composite, the d_{001} is increased. Because of the strong interaction between clay layers and coupling agent, MAPP molecules could enter and penetrate the gallery between the clay layers when clay was mixed with 4 phc of MAPP.

Figure 3 shows the dispersion state of the nanocomposites observed by TEM. The dark line represents the intersection of the silicate layers while

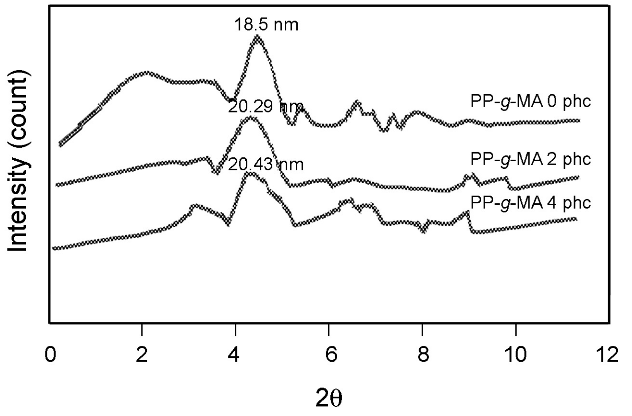

Figure 2. X-Ray diffraction of samples with different levels of MAPP at the same concentration of nanoclay 3 phc.

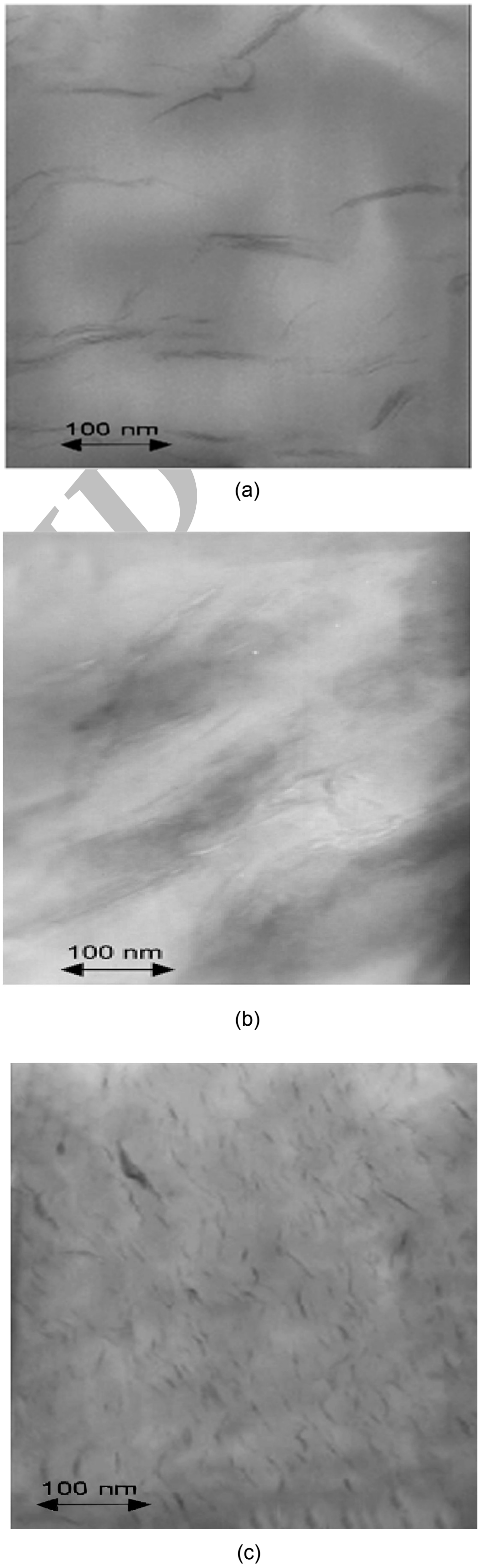

Figure 3. TEM micrographs of PP/WF/nanoclay hybrid composites: (a) 3 phc clay, (b) 6 phc clay and (c) 3 phc clay with 2% MAPP.

the white background corresponds to polypropylene matrix. When the loading level of nanoclay into the PP/WF composite is as low as 3 phc (Figure 3a), nanoclay exhibits better dispersion of the clay layers within the polymer matrix compared to 6 phc of nanoclay content (Figure 3b). Increasing the level of nanoclay to 6 phc, the size of dispersed nanoclay became larger or even aggregated in part (as confirmed by decreased d-spacing from XRD in Figure 1). It is also clear from the TEM images in Figure 3c that the presence of coupling agent improves the dispersion of the nanoclay as the clay aggregates have been broken down into smaller stacks. With increase of MAPP, the intergallery spacing of composite increased (as confirmed by increased d-spacing from XRD in Figure 2).

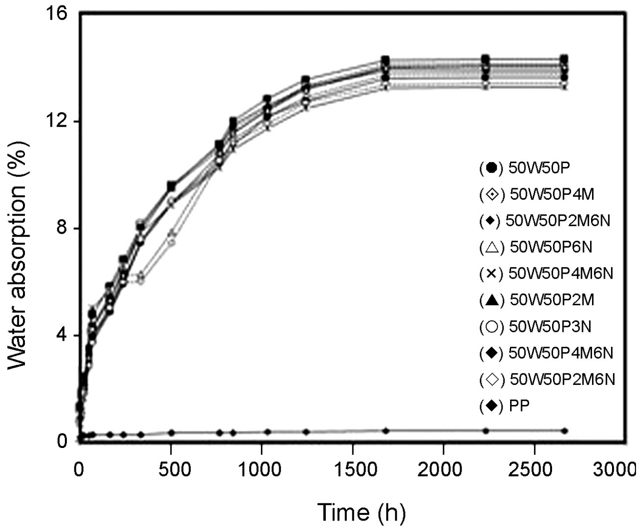

Figure 4. Water absorption of the samples.

Long Term Water Absorption Behaviour

Water absorption curve is illustrated in Figure 4 where the percentage of water absorption is plotted against time for all samples. As it is clearly seen, generally water absorption increases with immersion time, reaching a certain value at saturation point where no more water was absorbed and the composites water content remained constant. Time to reach the saturation point was not the same for all formulations. The 50W50P4M6N and 50W50P samples showed minimum (13.26%) and maximum (14.29%) water absorptions, respectively.

The hydrophilic nature of wood flour causes the water absorption in manufactured WPCs (the plastics have negligible water absorption). Because of constant wood flour content (50 wt%) in all formulations, the different water absorptions among all manufactured composites can be attributed to the role of coupling agent and nanoclay.

Figure 4 also shows that water absorption decreases by adding MAPP. This means that it is the interface region which influences the water absorption of the composite. Because the uncompatibilized wood flour composite has weak fibre/matrix adhesion in nature, at the presence of the compatibilizer the interface is enhanced. Generally it is necessary to use compatibilizers or coupling agents in order to improve the polymer/fibre bonding and in turn to enhance water resistance. The MAPP chemically bonds with the OH groups in the lignocellulosic filler and limits the water absorption of the composites. As a result, it is important to use coupling agents to improve the quality of adhesion between plastics and fibres, to reduce the gaps in interfacial region and to block the hydrophilic groups.

Tensile modulus was evaluated to confirm the positive effect of coupling agent on the interfacial bonding between wood and plastic (Figure 5). As can be seen, the modulus is affected by PP-*g*-MA and nanoclay content. The modulus of nanocomposites increased with increase of MAPP at different levels of nanoclay which means the presence of the MAPP as coupling agent enhances the interface adhesion and brings better encapsulation of wood particles by the

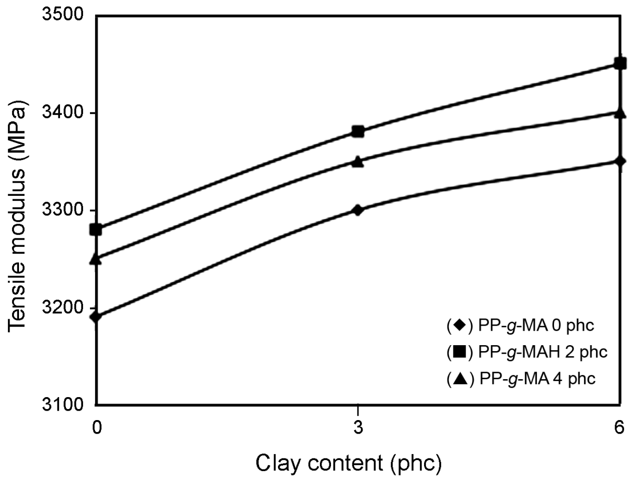

Figure 5. Tensile modulus of the samples.

plastic. A maximum tensile modulus of composite was observed at 3 phc of nanoclay content. The main reason for this behaviour may be due to the agglomeration of nanoparticles at 6 phc concentration of the nanoparticles.

Another reason for less water absorption could be the change in crystallinity of WPCs coupled by coupling agent and existence of nanoclay as a nucleating agent. It was reported that crystallinity of the WPCs is much greater than that of the corresponding WPCs without the MAPP modification [30]. On the other hand, the nucleation efficiency and the crystallinity of the hybrid composite can be improved at the presence of the nanofiller as a nucleating agent. As the crystalline regions are impermeable to penetration, the water absorption is reduced in the composites.

Another result in Figure 4 is that the composites containing clay have exhibited lower water absorption as compared with those made without clay. By increasing the clay content to 6%, the water absorption of composites has been reduced. It seems the barrier properties of nanoscale filler inhibit the water permeation in the polymer matrix. Two mechanisms have been reported for this phenomenon. The first is based on the hydrophilic nature of the clay surface that tends to immobilize some of the moisture [31], and the second, surfactant-covered clay platelets form a tortuous path for water transport [32,33]. This barrier property hinders water from going into the inner part of the nanocomposite. It seems both of aforesaid mechanisms could be more efficient when the morphology is exfoliated. In other words in exfoliated morphology, there is more available surface of organoclay (with hydrophilic nature) and surfactant (tortuous path), so the water transport goes down under the severe conditions.

Mechanisms of Water Transport

In general, there are three known mechanisms for water transport in polymer composites which are: Fickian diffusion, relaxation controlled, and non-Fickian or anomalous. The dominant mechanism depends on factors such as chemical structure of the polymer, dimensions and morphology of the wood filler and polymer-filler interfacial adhesion. These cases can be distinguished theoretically by the shape of the sorption curve represented by the following equation [34,35]:

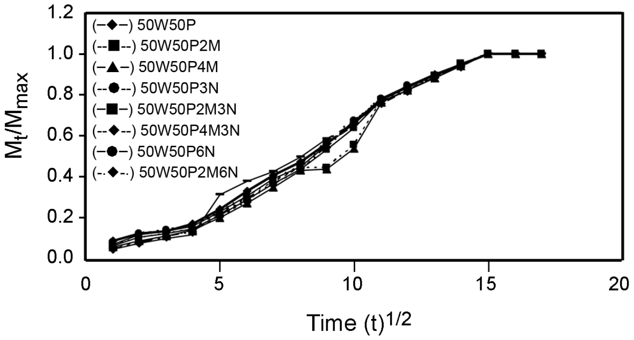

Figure 6. Diffusion case fitting for 50W50P3N and 50W50P2M3N nanocomposites.

$$\log(\frac{M_t}{M_\infty}) = \log(k) + n\log(t) \qquad (2)$$

In this equation M_t, M_∞, k, and n are the water absorption at time t, the water absorption at the saturation point, and constants, respectively. The value of n is different for the cases as follows: in Fickian diffusion n = 0.5, relaxation n > 0.5, and anomalous transport 0.5 < n < 1.

The coefficients (n and k) are calculated from slope and intercept of the log plot of M_t/M_∞ versus time which can be drawn from experimental data.

An example of the fitting of the experimental data for 50W50P3N and 50W50P2M3N nanocomposites

Table 2. Diffusion case selection parameter for all formulations.

Sample code	Water absorption	
	n	K (h^2)
50W50P	0.3845	0.0594
50W50P2M	0.4132	0.0466
50W50P4M	0.4352	0.0397
50W50P3N	0.3912	0.0561
50W50P2M3N	0.4249	0.0445
50W50P4M3N	0.4632	0.0357
50W50P6N	0.3818	0.0546
50W50P2M6N	0.4688	0.0342
50W50P4M6N	0.4774	0.0348

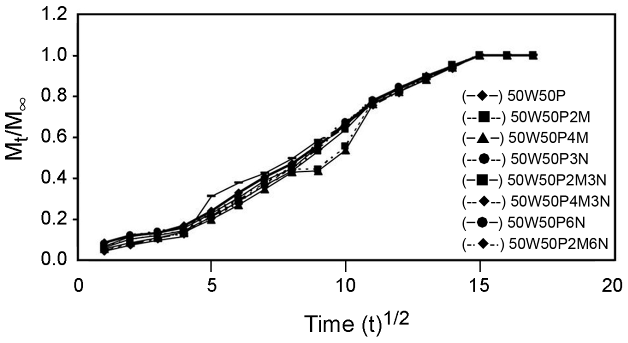

Figure 7. Water uptake ratio (M_t/M_∞) versus $t^{1/2}$ for all formulations.

is given in Figure 6 and the values of k and n resulting from the fitting of all formulations are shown in Table 2. The n values are similar for all formulations and close to n = 0.5. Therefore, it can be concluded that the water and moisture absorption of all formulations approach the Fickian diffusion case.

The diffusion coefficient is the most important parameter of the Fick`s model and shows the ability of water molecules to penetrate inside the composite structures. At early stages and small times (typically $M_t/M_\infty \leq 0.5$), the diffusion process is presented as follows [36]:

$$M_t / M_\infty = 4t^{1/2} / (Dt / \pi L^2)^{1/2} \tag{3}$$

where L is the thickness of the specimen and D is the diffusion coefficient.

Table 3. Maximum water absorption and water diffusion coefficients for all formulations.

Sample code	Maximum water absorption (%)	Water diffusion coefficient ($\times 10^{-12}$ m^2s^{-1})
50W50P	14.2861	3.9295
50W50P2M	14.0547	3.7667
50W50P4M	13.7526	3.2589
50W50P3N	14.1606	4.0159
50W50P2M3N	13.8785	4.1368
50W50P4M3N	13.6163	4.1589
50W50P6N	14.0224	4.0374
50W50P2M6N	13.4081	3.9933
50W50P4M6N	13.2577	3.8925

The data were plotted as M_t/M_∞ against $t^{1/2}$ (Figure 7), and the diffusion coefficients were obtained from the slopes of the linear part of the plots using the less-squares method. Table 3 shows the water diffusion coefficients for all formulations. The results show the water diffusion coefficients decrease with incorporation of MAPP into hybrid composite. The 50W50P4M composite exhibited the lowest diffusion coefficients.

CONCLUSION

The following conclusions could be drawn from the results of the present study:

- Water absorption of the hybrid composite increased with immersion time, reaching a certain value at saturation point and the composites water content remained constant.

- With increase of the MAPP and organoclay content in composite, water absorption decreased.

- The intercalation morphology was observed for hybrid nanocomposite. The order of intercalation for samples containing 3 phc was higher than that of 6 phc at the same MAPP content due to some agglomeration of organoclay.

- The mechanism of water transport in hybrid composite was Fickian diffusion and it seems, the water transport could be more restricted in exfoliated morphology through this mechanism.

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