

EFFECT OF WEATHERING ON PHYSICAL AND MECHANICAL PROPERTIES OF HYBRID NANOCOMPOSITE BASED ON POLYETHYLENE, WOODFLOUR AND NANOCLAY

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ABSTRACT

Wood plastic composites have received increasing attention during the last decades, because of many advantages related to their use. However the durability of Wood plastic composites after ultraviolet exposure has become a concern. In this research, hybrid nanocomposites of polyethylene and woodflour with different concentrations of nanoclay were fabricated using melt compounding followed by injection molding. Specimens were exposed for 2000 h to ultraviolet radiation and moisture cycling in a laboratory weathering device to simulate the effects of exposure to sunlight and rain. Physical and mechanical properties of the nanocomposites were evaluated, before and after weathering. The results indicated that the water absorption of wood plastic composites increased after weathering but nanoclay reduced the intensity of weathering to some extent, through decreasing of water absorption. Also results showed that weathering decreased modulus of elasticity values, however good dispersion of clay layers resulted in fewer drop of modulus of elasticity values. Fourier transform infrared spectroscopy showed that lowest carbonyl index is related to the nano wood plastic composites with 2wt% nanoclay. Also X-Ray diffraction patterns revealed that intercalation morphology has been formed for nano particles.

Keywords: Carbonyl index, Fourier transform infrared spectroscopy, modulus of elasticity, *Populus deltoides*, water absorption, wood plastic composites, X-Ray diffraction.

INTRODUCTION

Using lignocellulosics as fillers and reinforcements in thermoplastics has been gaining acceptance in commodity plastics applications in the past few years. The advantages of using a bio based component in thermoplastic composites is non abrasive, low in cost, widely available, sustainable, high filling levels possible, high specific properties, lower density per weight of raw material, flexible and recyclable (Khonsari *et al.* 2015). However cellulosic fibers have some disadvantages, such as lower processing temperature, and incompatibility between the hydrophilic fibers and hydrophobic polymers. Also, moisture absorption of the cellulosic fibers has undesirable effects on the properties of composites (Belgacem *et al.* 1994). Therefore the use of composites by the construction industry has resulted in concern about the durability of these products when exposed to outdoor environments. On the one hand, the durability of WPC after ultraviolet exposure is very important (Stark and Matuana 2004). The weathering resistance of WPCs is generally less than other polymer based composites, and dimensional changes caused by outdoor exposure are major problems for their use outdoors (Stark *et al.* 2003). Some researchers studied accelerated weathering of WPCs with combinative ultraviolet radiation and water spray. They concluded that water absorption and thickness swelling of the composites were increased after accelerated weathering (Adhikary *et al.* 2009). On the other hand, weathering causes WPCs lose their mechanical properties. Moisture penetration into the WPC degrades the wood-polymer interface, which in turn causes loss of strength as the stress transfer from matrix to fiber becomes less efficient.

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Scientists exposed high density polyethylene (HDPE) composites filled with 40wt% wood fiber to a water bath for 2000 h. They concluded that WPCs experienced 22% decrease in flexural strength (Stark 2001). In the last years, the addition of materials at a nanometric scale into polymer matrices has increased in a remarkable way. Many researches of nanoparticles have been focused on modified nanoclays. These are composed of organic modified laminar silicate structures which allow obtaining a hybrid organic-inorganic structure. Montmorillonite based clays (MMT) offer high interest from an industrial point of view since the use of small amounts of them is enough to improve the overall properties of a polymer matrix at a relatively low cost (Pascual *et al.* 2009). These improvements include high moduli; increased tensile strength and thermal stability; decreased gas permeability, improved flammability properties, decrease in water absorbance and increased biodegradability of polymers (Ashori and Nourbakhsh 2009). However it seems that nanoparticles have an accelerating effect acting as catalysts to HDPE photo-oxidation. Scientists studied different series of HDPE nanocomposites which prepared by melt mixing, containing 2,5 wt% of multiwall carbon nanotubes, pristine and modified montmorillonite, and SiO₂ nanoparticles. From FTIR study it was found that SiO₂ and organically modified montmorillonite cause a serious effect on HDPE during UV degradation and new chemical compounds containing carbonyl, vinyl and hydroxyl groups were formed meaning that nanoparticles may accelerate the photo-oxidation of HDPE (Grigoriadou *et al.* 2011). The objective of this work is to investigate the influence of nanoclay loading level on mechanical property and water resistance of the nanocomposites before and after weathering. To interpret these properties the morphology of the nanoparticles was evaluated.

MATERIALS AND METHODS

Materials

HDPE with a density of 0,952 g/ml and MFR (190°C/2,16kg) of 18 g/10min as polymer matrix, poplar (*Populus deltoides*) as cellulosic material (80 mesh), maleic anhydride grafted polyethylene (MAPE) with a density of 0,965 g/cm³ (MFI 7 g/10min, grafted maleic anhydride 1 wt%) as coupling agent and natural montmorillonite modified with dimethyl-dehydrogenated tallow-ammonium chloride salt (cloisite 15A with d spacing of 31,5Å and modifier concentration of 125 meq/100g clay) as reinforcement were used.

Method

Sample Preparation

Before sample preparation, woodflour was dried in an oven at (70±5)°C for 24 h. Then HDPE, woodflour, nanoclay and MAPE 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 150°C and 60 rpm. First the HDPE was fed into mixing chamber, after melting of HDPE, nanoclay and coupling agent were added. After mixing for 5 min, the woodflour was fed into the system. The total mixing time was 10 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 105°C for 24 h. Test specimens were prepared by an injection molding machine (Imen Machine, IRAN) at 190°C. The specimens were stored under controlled conditions (50% relative humidity and 23°C) for at least 40 h prior to testing.

Table 1. Composition of the studied formulations.

Sample Code	HDPE (wt%)	Woodflour (wt%)	Nanoclay (wt%)	MAPE (wt%)
30W	67	30	0	3
30W2N	65	30	2	3
30W4N	63	30	4	3

Testing and analysis

Weathering

Composite specimens were weathered using an Atlas Electric Devices (xenon-arc type light exposure apparatus) according to ASTM D 2565. Specimens were rotated by the weatherometer at 1 rpm around a spray nozzle and UV source. The device was set to provide 102 min of light followed by 18 min of light and water spray, exposing one side of the specimens to direct light and water spray while subjecting both sides to high levels of humidity. The irradiance was maintained at $41,5 \pm 2,5$ (W/m²). The black panel temperature was maintained at $63 \pm 2^\circ\text{C}$. Specimens were placed on racks without backing and at the end of 2000 h selected specimens were removed for testing.

Fourier transform infrared spectroscopy

FTIR spectroscopy was conducted on a BRUKER Vertex-89 spectrometer to provide knowledge of functional groups present at the composite surface before and after weathering. For each sample, 16 scans were recorded in absorbance units from 4000 to 600 cm⁻¹. Spectra were obtained using attenuated total reflectance (ATR). Carbonyl index was calculated using the following equations:

$$\text{Carbonyl Index} = \frac{I_{1715}}{I_{2916}} \times 100 \quad (1)$$

where I represents the peak intensity. The peak intensities at 1715 cm⁻¹ corresponds to carbonyl groups that were normalized using the peak at 2916 cm⁻¹, which corresponds to alkane CH stretching vibrations of the methylene groups. This peak was chosen as a reference peak because it changed the least during weathering.

X-Ray Diffraction

The degrees of clay intercalation in WPCs were evaluated by X-ray diffraction (XRD) analysis. XRD measurements were carried out in a Philips diffractometer (Xpert MPD, Holland) using CuK_α ($\lambda=1,78\text{Å}$; 40 kV, 30 mA) radiation at a scanning rate of 1°/min with an angle ranging from 1° to 10°.

Water absorption

Water absorption tests were carried out according to ASTM D 7031-04. Three specimens for each formulation were dried in an oven ($102 \pm 2^\circ\text{C}$ for 24 h). The samples were weighed prior to immersion in the water. Afterwards, the dried specimens were placed in distilled water and kept at room temperature. The weight of the immersed samples was determined after 30 days. Water absorption of the samples was determined based on the following equation:

$$WA_t = \frac{W_t - W_0}{W_0} \times 100 \quad (2)$$

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.

Modulus of Elasticity

The tensile modulus tests were measured according to the ASTM D638, using an Instron machine (Model 1186, England). The tests were performed at crosshead speeds of 5 mm/min. For each treatment level, three replications were tested.

Statistics

To determine the effect of weathering on the physical and mechanical properties, student's two-tailed t-tests were carried out at $\alpha=0,05$ for each sample, testing the data for significant differences due to weathering.

RESULTS AND DISCUSSION

Water Absorption

The results of water absorption (after 30 days immersion) for WPCs with different percentages of nanoclay were shown in Figure 1. Generally the hydrophilic nature of woodflour is responsible for the water absorption of the composites. The water absorption of composites decreased with incorporation of nanoclay. The higher the amount of nanoclay, the lower was the water absorption (Samariha *et al.* 2015). Organically modified clay increases the tortuous path for water transport and as a result water diffusivity will decrease (Alexandre *et al.* 2006). Barrier property of nanocomposite was studied and it was stated that nanoclay hinders the permeation of water through the composite (Kord *et al.* 2011). Moreover, the void spaces in the woodflour were occupied by the polymer and nanoclay. Hence the available space for water absorption will decrease. The higher the nanoclay, the lower is the available space to hold the water. Both the tortuous path and reduction in void space decrease the water absorption capacity of WPC. Hence, nanoWPCs showed lower water absorption compared to WPCs. As can be seen from Figure 1, the water absorption of all samples increased after weathering. Comparing the water absorption values before and after weathering it can be seen that, WPCs increased 26,1% while nanoWPCs with 2 and 4wt% nanoclay increased 24,1% and 19,9%; respectively. These results imply that weathering affected the water absorption of WPCs more than that of nanoWPCs. The published papers revealed that weathering increases the wettability of the composites (Colom *et al.* 2003) and also showed that photo-degradation of HDPE can be accelerated by metal ions which can be found in nanoparticles and finally resulted in more increasing of water absorption of composites (Grigoriadou *et al.* 2011). Therefore, it is expected that UV exposure of WPCs containing nanoclay resulted in more severe weathering than WPCs and subsequently further increasing of water absorption. But our results indicated that increase of water absorption of nanoWPCs containing 4wt% nanoclay caused by weathering, is less than that of WPCs. This is consistent with the results of other researchers. They also stated that the nanoclay plays a greater role in decreasing water absorption than in increasing weathering (Eshraghi *et al.* 2013).

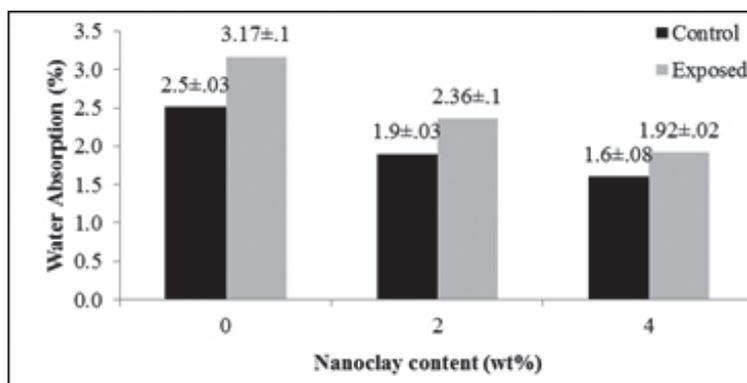


Figure 1. Effect of nanoclay on water absorption (30 days) of exposed and control composites.

The structural changes of WPCs with and without nanoclay were investigated via FTIR spectroscopy before and during the weathering. The area that showed alterations corresponded to the carbonyl groups ($-C=O$, $1700-1800\text{ cm}^{-1}$) (Figure 2 a and b). WPC as well as nanoWPC gave expanded

peak in this area, indicating the oxidation of the materials. The intensity of this peak increased during ultraviolet radiation. Some reports stated that the intensity of carbonyl peak increases continuously with the increasing of illumination time. Moreover, it was observed that the band at 1700-1800 cm^{-1} broadened as the experiment was carried on. This is due to the appearance of multiple oxidation products as γ -lactones, esters, carboxylic acids and conjugated ketones (Vazquez *et al.* 2006, Roy *et al.* 2009). Comparing the carbonyl peak areas, it can be seen that after same exposure time the strongest carbonyl peak is related to nanoWPCs with 4wt% nanoclay, demonstrating that the use of 4wt% of nanoclay results in more weathered WPCs. Also it was found that after the same exposure time the carbonyl peak of nanoWPCs with 2wt% nanoclay content has grown less than other peaks meaning that less oxidation has occurred. It seems that this is due to intercalation morphology and good dispersion of clay layers and consequently lower water absorption (Figure 5). Some reports revealed the effect of morphology of nanoclay on water absorption. They stated that the water absorption affected by morphology of nanocomposite and also higher order of intercalation results in less water absorption (Ghasemi and Kord 2009). Also scientists noted that the presence of moisture (by accelerating the oxidation reactions) greatly contributes to more degradation of physical and mechanical properties of WPC during weathering (Stark 2006). Therefore it can be concluded that better dispersion of clay layers contribute to less water absorption and consequently less oxidation and finally less growing of carbonyl peak.

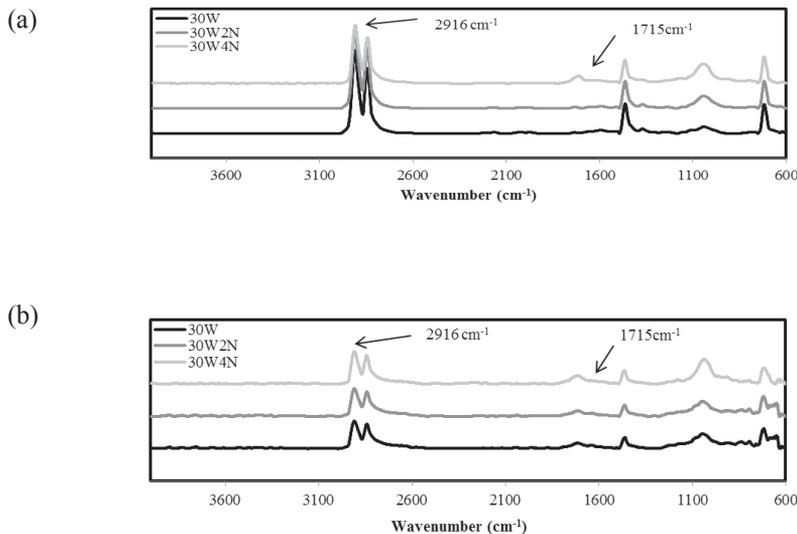


Figure 2. FTIR spectra of (a) control and (b) exposed composites with (2 and 4wt%) and without nanoclay.

Figure 3 shows that the carbonyl index of all samples increases upon exposure time and it can be observed that carbonyl index of the samples contain 2wt% nanoclay is less than that of the samples with 4wt% nanoclay after 2000 h of weathering. Also it can be seen that the carbonyl index of nanoWPCs (with 2wt% nanoclay) is less than WPCs during exposure time. Therefore, it can be concluded that addition of 2wt% of nanoclay to WPCs causes decreasing of carbonyl index significantly.

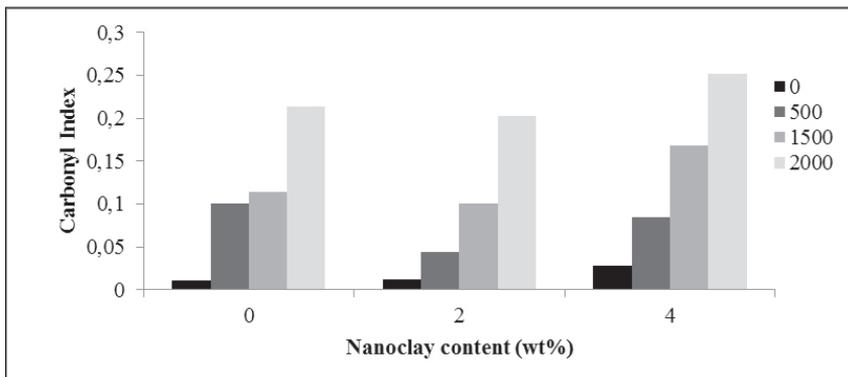


Figure 3. Effect of nanoclay on the carbonyl index during 500, 1500 and 2000 h of exposure.

Modulus of Elasticity

Figure 4 shows that the addition of nanoclay increases MOE values of the WPCs. MOE values increased with nanoclay loading up to 2 wt%, beyond that the values decreased. The observed higher values might be due to the higher dispersion of silicate layers of nanoclay in the polymer matrix. Besides the nanoclay contained some hydrocarbon portions which facilitated the interaction between woodflour and polymer matrix. All these suggested an improvement in adhesion between polymer, wood and clay. The nanoWPCs thus exhibited better properties over WPCs. The inclusion of organoclay resulted in the improvement in mechanical properties which were reported by other investigators (Lee and Kim 2009). The decrease in MOE values of nanoWPC with 4wt% nanoclay might be attributed to the migration of clay to the interface between woodflour and polymer. The presence of high amount of fibre and its interface with polymer might have reduced the reinforcement effect of clay. Similar observation was reported by other researchers (Candan and Akbulut 2015). Another reason for decrease in MOE could be related to the dispersion and homogeneity of the media (Samariha *et al.* 2015). Also Figure 4 shows the drop in MOE values after 2000 h of weathering for all WPCs with and without nanoclay content, however the loss in MOE values was 10,4% for the WPCs and 9,7% and 8,5% for nanoWPCs with 2 and 4wt% nanoclay content, respectively. Clearly it is observed that after weathering, the MOE values of nanoWPCs dropped less than that of WPCs. As mentioned above, metal ions in nanoparticles accelerate photo-degradation of HDPE (Grigoriadou *et al.* 2011). Also it has been observed that weathering has an adverse effect on both physical and mechanical properties of polymers and lignocellulosics (Lundin *et al.* 2004). Therefore it is expected that the mechanical properties of nanoWPCs degraded more than WPCs. However it should be noted that the negative effect of nanoclay on weathering is balanced by two phenomena. Dispersion of nanoclay as a positive effect could enhance the MOE (Hemmasi *et al.* 2010), and also barrier properties of nanoclay decrease the water penetration into nanocomposite materials (Ashori and Nourbakhsh 2011) and then less drop of MOE occurs by decreasing of water absorption. Scientists stated that the mechanical properties of woodflour filled polymer composites are negatively affected by moisture (Stark *et al.* 2003). Therefore it can be concluded that the negative effect of weathering that is accelerated by nanoclay can be neutralized by good dispersion and barrier property of nanoclay.

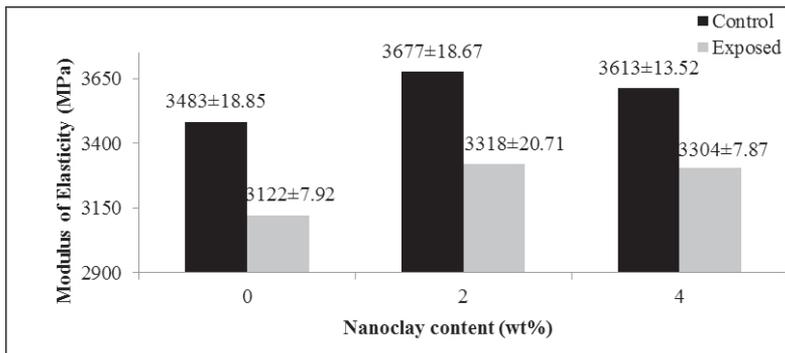


Figure 4. Effect of nanoclay on modulus of elasticity of exposed and control composites.

The X-ray patterns for modified organoclay and hybrid nanocomposites with different levels of nanoclay at 3 wt % MAPE are shown in Figure 5. The interlayer spacing was calculated according to Bragg’s law,

$$n\lambda = 2d \sin \theta \quad (3)$$

In this figure, $2\theta = 2,80^\circ$ is related to neat clay with basal spacing of $31,5 \text{ \AA}$. In the sample with 2wt% nanoclay, the peak was shifted to a lower angle ($2\theta = 2,25^\circ$; d-spacing = $39,18 \text{ \AA}$) which implies the formation of the intercalation morphology. The peak of 4wt% nanoclay was appeared at $2\theta = 2,35^\circ$; d-spacing = $37,6 \text{ \AA}$. These data show that the order of intercalation is higher for 2wt% of nanoclay than that of 4wt%. It seems this is because of the limited value of MAPE in the nanoWPCs. The shifting of the peak to lower angle indicated an increase in interlayer spacing of silicate layers. The polymer chains were intercalated into the silicate nanolayers. A shifting of diffraction peak to the lower angle for the clay based HDPE nanocomposite was reported in the literature (Faruk and Matuana 2008). The observed peak at 4wt% of nanoclay might be due to agglomeration of some clay. The shifting of the peak from higher diffraction angle to lower diffraction angle was reported by Lee and Kim (Lee and Kim 2009).

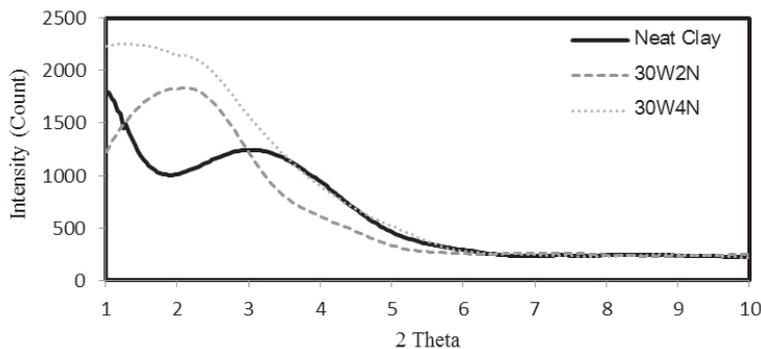


Figure 5. XRD patterns of nanoclay content at 1° to 10° .

CONCLUSIONS

The effect of weathering on the physical and mechanical properties of the WPC containing different nanoclay levels has been investigated. The main observations drawn from this study are summarized as follows:

The general trend of WPC weathering shows that surface oxidation increased after exposure. However after 500, 1500, and 2000 h of weathering the nanocomposites containing 2wt% of nanoclay showed less carbonyl index as compared to other samples.

The water absorption of control and weathered WPCs was increased after 30 days water exposure. Addition of nanoclay to the WPCs improved the water absorption. However water absorption of weathered nanoWPCs was less than that of weathered WPCs.

MOE values of WPCs were improved by the addition of nanoclay to the composite. However weathering decreased the MOE values of WPC and nanoWPC. Although weathering conditions can degrade the MOE of WPCs, good dispersion of nanoclay in the HDPE matrix to some extent can hide the negative effect of weathering.

FTIR spectroscopy also revealed that using of 2wt% of nanoclay decreased the forming of carbonyl groups meaning that less degradation has occurred.

XRD study indicated a better intercalation in WPC loaded with 2wt% nanoclay compared to WPC loaded with 4wt% nanoclay. The agglomeration of nanoclay might be responsible for this phenomenon.

The addition of nanoclay up to 2wt% can provide indirect protection against the deleterious effects of weathering and thereby less drop of MOE through decreasing of water absorption and its oxidative role has occurred.

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