

Physical Properties of Polyethylene–Wood Fiber–Clay Nanocomposites

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ABSTRACT: In this study, nanocomposites based on polyethylene (PE), maleic anhydride grafted polyethylene (MAPE), recycled newsprint fibers, and organically modified montmorillonite (nanoclay) were made by injection molding. The effects of two variable factors, namely, the nanoclay and MAPE contents, on the composite physical properties were examined. All blends were made with a fiber-to-PE weight ratio of 30 : 70. The results show that the addition of MAPE and nanoclay in the nanocomposite formulation significantly improved both the stability and water absorption properties. The improving effect of

MAPE could be explained by the improvement in the quality of adhesion between the polymer and fibers. Nanocomposites containing 5 wt % MAPE and nanoclay exhibited minimum water absorption during the whole duration of immersion. The results of this research study show that wood–plastic composites treated with a coupling agent and nanoclay will be desirable as building materials for outdoor applications. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3255–3259, 2010

Key words: biofibers; clay; composites; fibers; fillers

INTRODUCTION

Wood–plastic composites (WPC) are multiphase materials consisting of two or more physically distinct components: a continuous (matrix) phase and a dispersed (filler or reinforcement) phase. WPCs containing small quantities (1–5 wt %) of nanometric scale fillers represent a new class of reinforced nanocomposites.^{1–3} The small size of the reinforcement leads to an enormous surface area and, thereby, increased interaction with the polymer matrix on the molecular level; this results in materials with new properties. This system exhibits a remarkable improvement in the materials properties compared with virgin plastic and conventional WPCs. These improvements can include greatly enhanced mechanical properties, thermal stability, gas permeability resistance, and fire retardancy.^{4–6} The main nanofillers used today are carbon nanotubes (synthetic) and nanoclay (natural product). Synthetic carbon nanotubes are very expensive. Nanoclays (layered silicates), in contrast, are especially interesting for their bulk applications because they are relatively inexpensive and commercially available, exhibit a layered morphology with a high aspect ratio and

large specific surface area, and cause an improvement in the mechanical and physical properties of polymers. Commonly used nanoclays include montmorillonite, hectorite, and saponite, all of which belong to the same general family of 2 : 1 layered silicates or phyllosilicates (Fig. 1). Montmorillonite-based clays offer high interest from an industrial point of view because the use of small amounts of these clays is enough to improve the overall properties of WPCs at a relatively low cost.⁷

The main groups of plastics that are used in WPCs are semicrystalline plastics such as polyethylene (PE) and polypropylene. Only thermoplastics that melt at temperatures below 200°C are commonly used in the making of WPCs because of the limited thermal stability of natural fibers. Currently, PE is the most attractive thermoplastic for making WPCs, which are mainly used as exterior building components. Composites made from polypropylene are used in automotive applications.⁸

In recent years, WPCs have attracted great attention both in industrial and scientific applications.⁹ However, several disadvantages of natural fibers, such as their high moisture absorption, low dimensional stability, and low thermal stability, greatly reduce the potential of WPCs. In building applications, the dimensional stability of WPCs is critical, especially for outdoor use. To improve the stability, understanding the water absorption (WA) behavior and impact of the absorbed water on the

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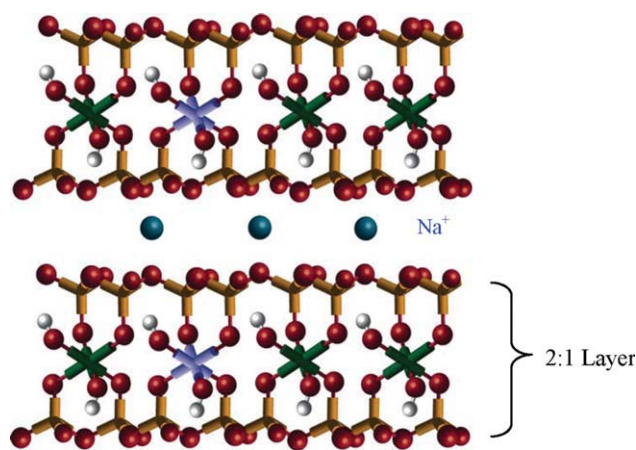


Figure 1 Structure of sodium montmorillonite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

dimensional change is important. The main objective of this study was to examine the effect of various nanoclay and coupling agent contents on the physical properties in terms of WA and dimensional stability.

EXPERIMENTAL

Materials

The fibrous raw material was recycled newsprint fiber. Virgin PE was obtained from Bandar Imam Petrochemical Co. (Mahshahr, Iran) as grade LF0450 with a melt flow index of 4–5 g/10 min (at 190°C and 2.16 kg). The coupling agent, maleic anhydride grafted polyethylene (MAPE), was obtained from Eastman Chemical Products, Inc. (Kingsport, USA). The material (Eastman G-2608) had a melt flow index of 8 g/10 min and an acid number of 8 mg of KOH/g. The modified nanoclay was obtained from Southern Clay Products, Inc., with the trade name Cloisite 20A. This nanoclay was a natural montmorillonite that was modified by a methyl tallow bis-2-hydroxy ethyl quaternary ammonium. It was supplied in a particulate form with sizes in the micrometer range (10% < 2 μm, 50% < 6 μm, and 90% < 13 μm).

Composite processing

The amount of fiber was fixed at 30 wt %; this value was selected because it is typical of many industrial formulations and represents an excellent balance between performance and cost. The concentration was varied from 0 to 5 wt % for the nanoclay and MAPE individually on the basis of the total weight of PE. The fiber, PE, MAPE, and nanoclay were premixed before they were fed into the first zone of the extruder. The blends were compounded in a corotating twin screw extruder (Ebersberg, Germany). The

barrel temperatures of the extruder were controlled at 165, 175, 185, and 190°C for zones 1, 2, 3, and 4, respectively, whereas the temperature of the die was held at 195°C. The screw speed was between 60 and 70 rpm. The extruded strand was passed through a water bath and pelletized. The resulting granules were subsequently injection-molded at 190°C to produce standard ASTM specimens.

Water immersion tests

The WA and thickness swelling (TS) tests were carried out according to ASTM D 570. The samples were immersed in distilled water at $23 \pm 1^\circ\text{C}$ for 24- and 2400-h intervals. Before testing, the weight and thickness of each sample were measured. Samples were removed at certain periods of time, wiped with tissue paper to remove the excess water on the surface, and immediately weighed and measured. WA was calculated according to the following formula:

$$\text{WA}(\%) = \frac{(m_t - m_0)}{m_0} \times 100 \quad (1)$$

where m_t is the mass of the sample after immersion (g) and m_0 is the mass of the sample before immersion (g). The value of absolute error for WA was $\pm 0.3\%$. In the water immersion tests, the thickness of each sample was also measured to determine TS with Eq. (2):

$$\text{TS}(\%) = \frac{(\delta_t - \delta_0)}{\delta_0} \times 100 \quad (2)$$

where δ_t and δ_0 are the sample thicknesses (mm) after and before the water immersion, respectively. The value of the absolute error bar for TS was $\pm 0.4\%$. The values obtained represented the averages of six samples for each formulation.

Scanning electron microscopy (SEM)

SEM model Phillips XL 30 (Ontario, Canada) with an accelerated voltage of 25.0 kV was used to observe the surface of the composites before and after the WA test. The samples were coated with a gold layer with a vacuum sputter coater.

RESULTS AND DISCUSSION

WA

One of the important properties that we evaluated for the WPCs was WA because it can limit their use. The fact that cellulosic fibers easily absorb water is actually one of the reasons for fiber surface treatments. The treated fibers may absorb less moisture and, thus, favor

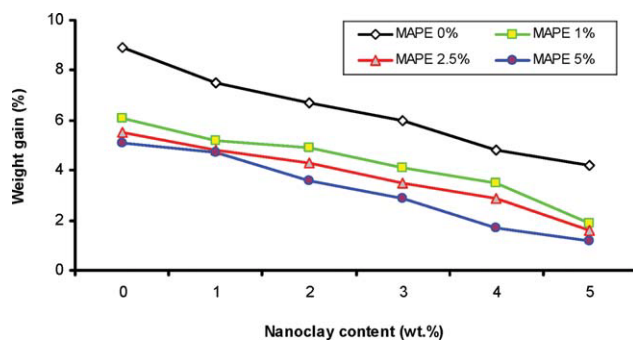


Figure 2 Weight gains (after 24 h) for the nanocomposites containing 30 wt % fiber based on various contents of coupling agent and nanoclay. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

adhesion with the polymer matrix and also present better performance in humid environments. The high WA of the WPCs may be indicative of difficulties during processing, such as incomplete curing of the thermoset matrix; the presence of voids or cracks; or even poor matrix–fiber adhesion.¹⁰

Figures 2 and 3 show the percentages of the water uptake for the nanocomposites at different periods of immersion, which varied depending on the nanoclay and coupling agent content. The WA of the pure PE, however, was very low ($\sim 0.5\%$) because of its hydrophobic nature. In general, polymers absorb very little moisture; when polymers do slightly absorb moisture, this indicates that moisture is being absorbed by the cellulosic material in the composite. The WA of the WPCs was due to the hydrogen bonding of the water molecules to the free hydroxyl groups present in the cellulosic cell wall materials and the diffusion of water molecules into the filler–matrix interface. Additionally, the large number of porous tubular structures present in the fiber accelerated the penetration of water by so-called capillary action [Fig. 6(a), shown later]. As shown in Figure 2, WA decreased sharply with increasing MAPE and nanoclay loading in the composites—a trend that was true for intervals of 24 and 2400 h. This may have been due to the presence of a better adhesion between the matrix and cellulosic material because there were fewer gaps in the interfacial region and also because more hydrophilic groups as hydroxyls were blocked by the coupling effect. Matuana et al.¹¹ reported that the addition of a coupling agent increased the ester linkages between the hydroxyl groups of the fiber and the anhydride part of MAPE. Therefore, the amount of free hydroxyl in the cellulose was reduced because some of them interacted with anhydride.

Figure 3 clearly illustrates that the long-term WA of the nanocomposites treated with 5 wt % MAPE significantly increased in the initial stage and thereafter

remained almost constant. It was also clear that the water uptake of all of the composites increased with increasing immersion time and reached a certain value at the saturation point, where no more water was absorbed and the composites' water content remained constant. According to Das et al.,¹² initially, water saturates the cell wall (via porous tubular and lumens) of the fibers, and next, water occupies the void spaces. Because composite voids and the lumens of the fibers are filled with nanoclay, this prevents the penetration of water by capillary action into the deeper parts of composite.³ This suggests that WA occurred in the surface layer. As shown in Figure 3, there was a significant difference in the amount of WA when the nanoclay loading was increased. In other words, the composites made with 5 wt % nanoclay showed the lowest percentage WA compared to the other formulations. Additionally, the use of 5 wt % MAPE led to better interaction, decreased WA, and slow moisture penetration in the composite systems.

Dimensional stability

TS is an important property, which represents the stability performance of the composite. Generally, the swelling rates for polymer matrix composites are low during the initial stages of moisture absorption because of the viscoelasticity of the polymer matrix. In addition, any pores or voids that are present after fabrication will help to accommodate some of the swelling of the added wood fiber.¹³ As mentioned earlier, the poor absorption resistance of cellulosic material is mainly due to the presence of polar groups, which attract water molecules through hydrogen bonding. This phenomenon leads to moisture buildup in the fiber cell wall (fiber swelling) and also in the fiber–matrix interface. This is responsible for the changes in the dimension of WPCs, particularly in

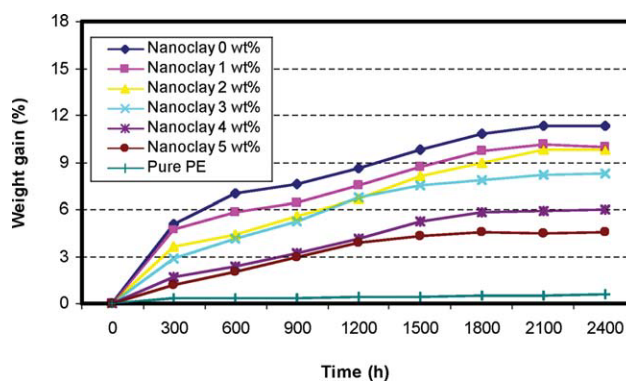


Figure 3 Long-term WA of the treated nanocomposites containing 30 wt % fiber and 5 wt % MAPE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

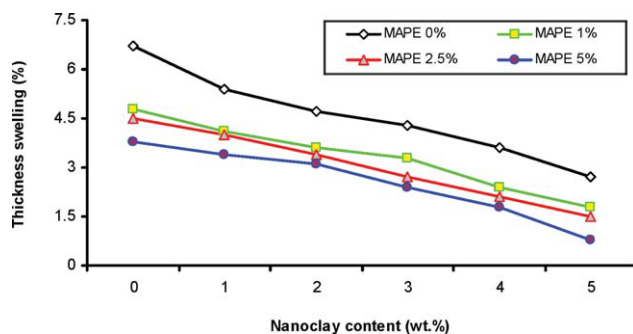


Figure 4 TS (after 24 h) for the nanocomposites containing 30 wt % fiber on the basis of various contents of coupling agent and nanoclay. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the thickness and linear expansion because of reversible and irreversible swelling of the composites.¹⁴

The effects of the coupling agent and nanoclay on TS of the nanocomposites are presented in Figures 4 and 5. TS of the nanocomposites increased with WA and, thus, showed a trend similar to that of WA. The TS values for the 24-h water immersion varied from 1.2 to 8.9%, and these values increased after the 2400-h immersion, varying from 0.3 to 11.3%. Furthermore, TS decreased with increasing nanoclay and MAPE contents. The samples made with 5 wt % MAPE had the lowest TS compared to all of the nanocomposites. This indicated that the flaws and gaps at the interface of the fiber and PE, which were the main factors for moisture diffusion in the composites, were reduced. In addition, the presence of coupling agent led to strong interactions between the polymer matrix and fibers; this promoted a restriction in the polymer chain displacement and movement.¹³

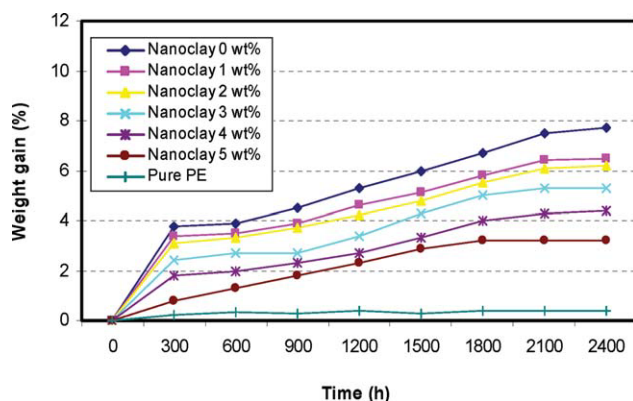


Figure 5 Long-term TS of the treated composites containing 30 wt % fiber and 5 wt % MAPE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

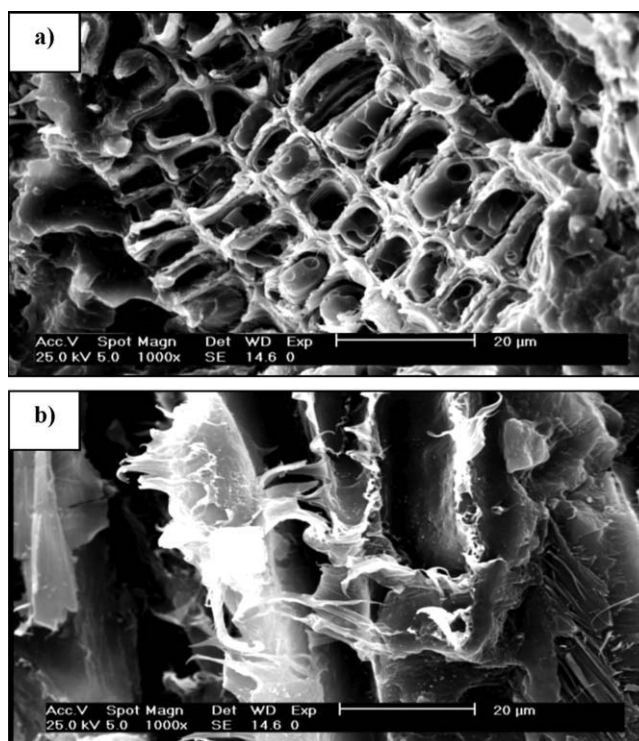


Figure 6 Surface of the untreated nanocomposite (a) before and (b) after WA.

Interestingly, the long-term TS also followed a similar trend to the WA behavior, increasing with immersion time until an equilibrium condition was attained. As time went on, water penetrated the interphase, and also, the loose cellulose network structure of the fiber resulted in a high water uptake. On the other hand, in untreated samples, because of the poor interaction between the matrix and fiber, water easily penetrated the nanocomposite initially. The long-term dimensional stability of the nanocomposites treated with 5 wt % MAPE is elucidated in Figure 5. As shown, the TS values of the composites increased with increasing water exposure time. The swelling of the fiber placed stress on the surrounding matrix and led to microcracking, which would have eventually caused the composite to fail catastrophically.¹⁴ As a result, the fiber–matrix adhesion was weak, and the dimensional stability of the composites, particularly for outdoor applications, was greatly affected.

Figure 6(a) shows the SEM image of the surface of the untreated fibers before WA. The figure shows that the uniform fiber lumened. Figure 6(b) illustrates the fracture surface after WA. This figure clearly shows the separation between the matrix and fiber after WA due to the nonhomogeneous swelling of the filler and matrix. Nonhomogeneous swelling created the tension between the fiber and the matrix. This tension helped to break the interaction bond between the filler and the matrix.

CONCLUSIONS

The main conclusions drawn from this study were as follows:

- The majority of WA/swelling occurred during the first 15 days. After that, the percentage of changes was negligible.
 - The dimensional stability and WA properties of the WPCs were improved by an increase in the nanoclay content or by the addition of the coupling agent.
 - Those nanocomposites treated with MAPE as a coupling agent absorbed less water compared with the untreated samples. The presence of the coupling agent improved the quality of adhesion between the polymer matrix and the cellulosic materials, reduced the gaps in the interfacial region, and blocked the hydrophilic groups.
 - In addition, MAPE acted as a bridge between the nonpolar PE polymer chains and the organic component of the clay to form interlock points at the structural level, which were responsible for the physical improvement. For this reason, the dimensional stability was improved.
- Because the composite voids and the lumens of the fibers were filled with nanoclay, this prevented the penetration of water by capillary action into the deeper parts of composite. Therefore, WA in the WPCs filled with nanoclay was significantly reduced.

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