MECHANICAL PROPERTIES AND WATER UPTAKE OF NANOCLAY/WOOD FLOUR/LDPE COMPOSITES AFTER FIBER SURFACE MERCERIZATION

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The purpose of this study is to evaluate the effect of nanoclay and alkali treatment of wood flour on the engineering properties of the wood plastic composite made from low-density polyethylene (LDPE) and beech flour. Thus, to conduct the study, the wood flour was chemically treated with 2% alkaline and then was mixed with LDPE at 40% weight ratio. To improve the properties of the composites, nanoclay particles (Cloisite 15 A) with the weight percentage of 0, 3 and 6% were selected for the study. In all samples, maleic anhydride grafted polyethylene (MAPE) was used in a weight proportion of 3%. The materials were mixed in an internal mixer (HAAKE) and then the samples were made using an injecting molding instrument. The physical properties, such as water absorption, and mechanical properties, such as tensile and impact strength, were measured. The physical testing results showed that by increasing the nanoclay content and alkaline treatment application, the water absorption rate was reduced. The tensile strength improved by increasing the nanoclay content, as well as using the chemical treatments. Also, the impact strength witnessed a 3% increase by increasing the nanoclay content and then reduced. The overall results suggest that the chemical treatments will increase the impact strength.

Keywords: wood plastic composite, nanoclay, chemical treatment, engineering properties

INTRODUCTION

Improving the adhesion in the interface region in fiber-plastic composites is one of the most important factors affecting the engineering properties of the resulting composites.[1] Wood plastic composites (WPCs) are a new group of substances that have attracted the attention of many researchers in recent years and have become a major part of the industry.[2] In fabricating these composites, a wide range of thermoplastic polymers, such as polypropylene, polyethylene, polyvinyl chloride, polystyrene and polyester, along with lignocellulosic materials or agricultural wastes, including wood flour, sawdust, bark, paper, paperboard, sawmill waste, rice straw, cotton, hemp and others are used. Lignocellulosic materials, compared to their competitors and other reinforcement agents, such as glass fibers and mineral fillers, have many advantages, including lower density, strength and higher specific modulus, low relative friction and fiber surface modification, as well as wide availability. These fibers are more cost-effective than the synthetic fibers and can be used as an alternative to synthetic fibers in the materials, where cost saving is preferable to the product strength properties.[3] The main shortcomings of natural fibers in composites are lower acceptable temperature for processing, difficult dispersion and spread of these fillers in polymeric materials. Also, natural hydrophilic fibers are incompatible with hydrophobic polymers, which may induce the possibility of moisture and water absorption by the fibers, which would result in the composites water absorption.[4] Today, with the advent of nanotechnology in materials science, reinforced polymers with nano-fillers have attracted the industrial and scientific communities' attention and have opened a new direction of scientific research in the intermediate and interdisciplinary studies at the micro-scale. Therefore, it is necessary to prioritize and understand the materials' behavior and interaction in the nanotechnology research field. From an industrial point of view, these materials are worthy of attention as they have significantly improved composite properties. Thus, the nanocomposites develop a new class of polymeric composite, with a structure that can be filled and loaded with nano-scale particles, such as nanoclay, thus improving the polymer composites properties, due to specific dimensions and aspect ratio, in comparison with other small-scale fillers.[5]

Therefore, in recent years, using modified clay as a nano-filler in making polymeric nanocomposites has received a lot of attention and attested major growth in application, since applying a small amount would yield into an increase in the modulus, strength, heat resistance, gas permeability reduction, flammability resistance and improved physical properties.[6-10] Moreover, these improved properties in most cases do not reduce product properties.[11-13] Thus, regarding the importance of the issue and the global approach to nanocomposites and their unidentified mechanism and structure, many studies aimed at identifying the properties of polymeric nanoclay composites and contributing to their pertinent and applicable development in recent years.[12] For example, Han *et al.*[14] studied the effect of nanoclay and coupling agent on the mechanical and thermal properties of produced composites from bamboo fibers and high density polyethylene (HDPE). Their study showed that the addition of 1% nanoclay increased the flexural modulus, dynamic elasticity modulus and crystallized temperature, while the impact strength of the samples decreased. Wang *et al.*[15] stated that the effect of nanoclay particle filler on the properties of composite depends on the form, size, aspect ratio, type, amount and quality of dispersed particles and their adhesion in the interface region. Also, they found out that the addition of small amounts of nanoclay particles improved the mechanical and thermal properties of the composites and provided the composites dimensional stability.

Chowdhury *et al.*[16] concluded that the highest flexural strength of reinforced polymeric composites with nanoclay particles was obtained when using 2% of the filler and the results of the dynamic-mechanical analysis indicate improved mechanical-thermal properties of the composites filled with nanoclay fillers. Liu *et al.*[17] concluded that nanoclay filler particles increase the composite strength, due to the proper coupling with the polymeric matrix and resin systems development, and increase the released tensed energy by the polymer. They also stated that the nano-filler utilization significantly reduced the water absorption in composites. The hydrophilic nature of wood fibers in WPCs causes the incompatibility with hydrophobic thermoplastic. The physical and mechanical properties of such a composite heavily depend on the connected components in the interface region. The given properties would be improved by increasing the adhesion and the coupling of the two phases in the interface region.[18] The chemical treatment, the alkaline treatment in particular, is considered as one of the most important techniques in improving the mechanical properties, improving the adhesion in the interface region.[19]

Some of the studies conducted on the specified issue have revealed important findings on the effect of the chemical treatment on the improvement of the WPCs engineering properties. For example, Mohanty *et al.*[20] used biodegradable polymer of polyesteramide and jute fibers to produce composites. The results of the performed chemical treatments showed that the mechanical strengths were increased, while alkali treatment and adding cyanoethyl to the fibers established further improvement in the flexural and tensile strengths. The addition of fibers treated with alkali to polyesteramide increased the strength by 40%. Mishra *et al.*[21] used three types of chemical treatments (alkaline, cyanoethyl and acetylation) of fibers in the manufacture of hybrid composites from polyester/glass fiber/sisal and polyester/glass fiber/pineapple fiber. Due to reducing the gaps and cavities between fiber and matrix and thus making possible a good adhesion in the interface regions, the chemical treatments determined a dramatic increase in the tensile and impact strengths. Farsi[19] and Ghasemi and Farsi[23] used different chemical treatments to improve adhesion in the interface region. The results showed an improved tensile strength using the alkaline treatment. Kokot and Stewart[24] reported that alkaline treatment enhanced the crystalline structure of cellulose, removed the natural and artificial impurities, and made the fiber surface rough.

The main rationale and motivation for this study is to evaluate the effect of nanoclay and alkaline treatment on the mechanical properties of the WPC from wood flour and low-density polyethylene (LDPE). In order to assess the resulted WPC engineering properties, the tensile strength, impact resistance and short-time water absorption were evaluated.

EXPERIMENTAL

Materials

Low-density polyethylene (LDPE) supplied by Bandar Emam Petrochemical Industries, Iran, with a melt flow index (MFI) of 2 g/10 min (ASTM D1238) and a density of 0.92 g/cm^3, was used as matrix in this experiment. Of the maleic anhydride grafted polyethylene (MAPE), supplied by Kimia Javid Sepahan Company, Iran, grafted maleic anhydride was 1 wt%. Wood flour (WF) was received from saw mill in the north of Iran. The composition of the wood flour was determined by standard methods of the Technical Association of the Pulp and Paper Industry (TAPPI) (T264 om-88, T211 om-85, T222 om-88). Based on the chemical analysis of the raw material, WF contained 41% cellulose, 30% hemicelloluse, 25% lignin and 3.6% ash. Nanoclay, with the trade name Cloisite 15 A, which is montmorillonite modified with a dimethyl-dehydrogenated tallow, quaternary ammonium with a CEC 125 meq/100 g clay, density 1.66 g/cc, and d-spacing d_{001} = 31.5 nm, was obtained from Southern Clay Products Co, USA. Sodium hydroxide was supplied by Merck, Germany. The polymers, nanoclay and sodium hydroxide were used as received. The wood floor was dried at 100 °C in an air-circulating oven for 24 h prior to use. The moisture content of the wood flour was less than 1 wt%.

Methods

Preparation of fiber

Treatment with sodium hydroxide

WF was immersed in a 2% solution of NaOH for half an hour and then washed with distilled water containing a few percent of acetic acid to remove the residual alkali. The washed fiber was then dried in the oven at 80 °C for 24 h.

Composite preparation

The composition of the composites used is shown in Table 1. The mixture was prepared by melt-blending the materials, using a high shear internal mixer (HBI System 90, USA) operating at 60 rpm, and was then discharged at 180 °C. First, the LDPE was fed into the mixing chamber, and, after melting of LDPE, coupling agent and nanoclay were added. After five minutes, the modified and unmodified WFs were fed, and the total mixing time was 13 min. The compounds were allowed to cool to room temperature and were palletized using a granulated grinder (Wieser, WGLS 200/200 Model). The granulates were then injection molded into tensile and impact test specimens at 180 °C, using an Injection molder (Eman Machine, Iran) equipped with a standard ASTM mold. Flexural specimens were also used as water absorption test specimens. Finally, specimens were conditioned at a temperature of 23 °C and relative humidity of 50% for at least 40 hours, according to ASTM D618-99, before testing.

Composite properties

Mechanical tests

The tensile strength tests were carried out according to the ASTM D 638, using an Instron machine (Model 1186, England), The tests were performed at crosshead speeds of 5 mm/min. A Zwick impact tester (Model 5102, Germany) was used for the Izod impact test. All the samples were notched in the center of one longitudinal side, according to the ASTM D256.

Water absorption

Treated and untreated LDPE/Nanoclay/WF samples of approximate dimensions (6.35×1.27×0.27 cm^3) were used for the measurement of water absorption. The samples were air-dried at 70 °C until a constant weight was reached, prior to the immersion in a static deionized water bath. The specimens were periodically taken out of the water, wiped with tissue paper to remove surface water, reweighed and dimensions remeasured and immediately put back into the water. At least three specimens for each sample were used.

Table 1
Composition of the studied composites

No	LDPE (%)	Wood flour (%)	NaOH (%)	MAPE (%)	Nanoclay (%)
1	60	40	0	3	0
2	60	40	2	3	0
3	60	40	0	3	3
4	60	40	2	3	3
5	60	40	0	3	6
6	60	40	2	3	6

Water absorption (WA) was calculated according to the following formula:

WA (%) = $(M_e - M_o)/M_o \times 100$

where M_e is the mass of the sample after immersion (g), and M_o is the mass of the sample before immersion (g).

Statistical analysis

For each treatment level, five replications were tested. SPSS for Windows (release 14.0, SPSS Inc.) was used for basic statistical analyses. Descriptive statistics are presented as mean ± SD values. ANOVA was used to assess the linear trend of variations in the three groups, and *post hoc* testing was undertaken using Duncan's multiple comparison test. Values of $P < 0.05$ were considered significant.

RESULTS AND DISCUSSION

Tensile strength

Fig. 1 shows the independent alkali treatment effect on the tensile strength of the samples. As can be seen from the figure, the alkaline treatment increased the tensile strength by 10.8%. The independent alkaline treatment effect on the tensile strength of LDPE/WF composites was significant at the 99% level, so that the tensile strength of the composites is classified and introduced in two separate groups, based on Duncan's classification. Fig. 2 shows the independent nanoclay effect on the tensile strength of LDPE/WF composites. As noted, by increasing the nanoclay amount to 3%, the tensile strength decreased, and then by increasing the nanoclay amount to 6%, there was a minor tensile strength increase, which is not statistically significant.

Fig. 3 illustrates the interactive effect of nanoclay and alkaline treatment on the tensile strength of LDPE/WF composites. As can be observed, by increasing the nanoclay amount in untreated samples, the tensile strength first decreased and then showed a minor increase, but with applying the alkaline treatment, the tensile strength increased significantly in untreated samples. Alkaline treatment of natural fibers removes the lignin and hemicelluloses from the fibers and causes the natural fibers to be separated into microfibrils, which leads to a more uniform distribution and dispersion of fibers in a polymeric matrix.[1] As a result, the alkaline treatment improves the tensile strength of WPCs made from the LDPE and WF.[22] Such a finding was also confirmed by Farsi,[19] Kokot and Stewart[24] and Mishra *et al*.[21]

Impact strength

Figures 4 and 5 shed light on the independent nanoclay and alkaline treatment effect on the impact strength of the samples made from LDPE and WF. As can be noted from Fig. 4, the alkaline treatment increased impact strength. The statistical results also reveal that the independent alkaline treatment effect on WPC impact strength was significant at the 99% level, so that the impact strengths of the composites are categorized and clustered in two separate groups, based on Duncan's classification. Fig. 5 shows the independent effect of nanoclay percentage on impact strength, the highest degree of impact strength being observed for the samples containing 3% of nanoclay, ranking (a) in Duncan's classification. By increasing the amount of nanoclay in the composite, the impact strength is reduced to a lower level, compared to that of the samples with no nanoclay.

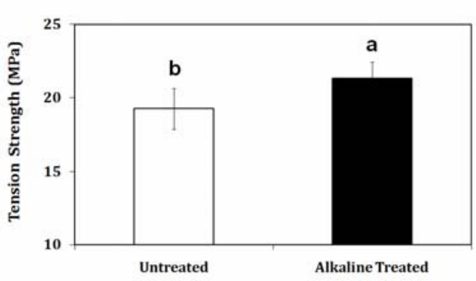

Figure 1: Tensile strengths of LDPE/WF composites treated with alkaline

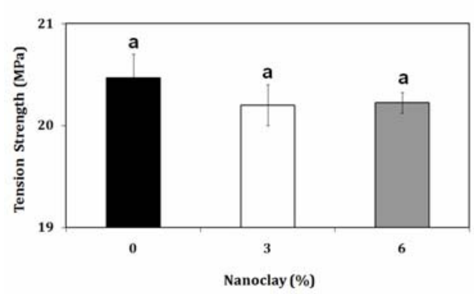

Figure 2: Tensile strengths of LDPE/WF composites containing different loading of nanoclay

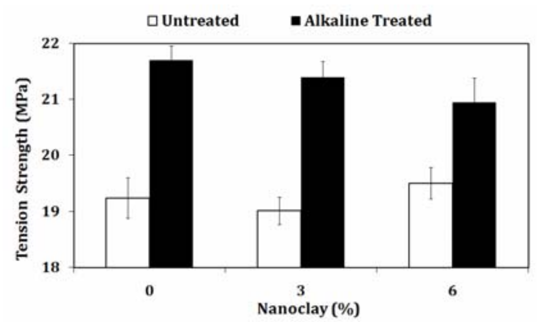

Figure 3: Tensile strengths of LDPE/WF composites treated with alkaline and containing different loading of nanoclay

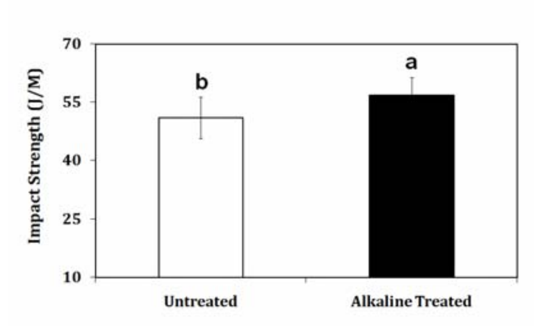

Figure 4: Impact strengths of LDPE/WF composites treated with alkaline

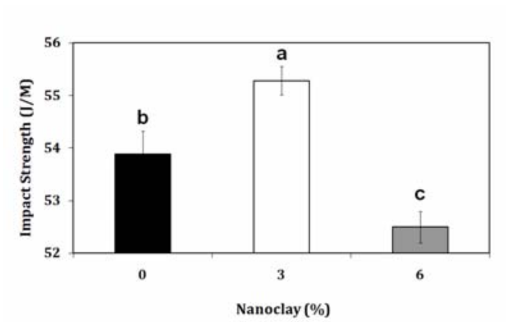

Figure 5: Impact strengths of LDPE/WF composites containing different loading of nanoclay

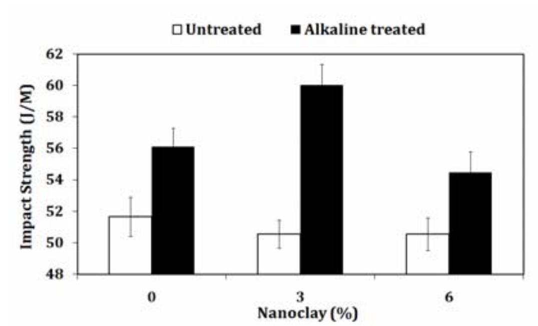

Figure 6: Impact strengths of LDPE/WF composites treated with alkaline and containing different loading of nanoclay

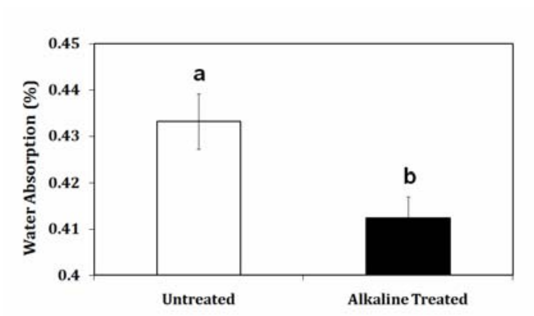

Figure 7: Water absorption of LDPE/WF composites treated with alkaline

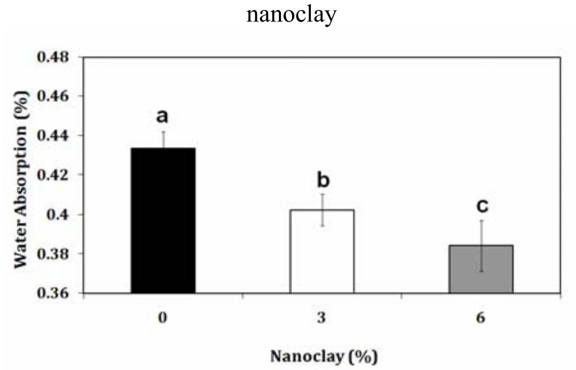

Figure 8: Water absorption of LDPE/WF composites containing different loading of nanoclay

Considering that the nanoclay particles generate the points of stress concentrations, by increasing the nanoclay amount, the impact strength of the composites undergoes a reduction. The nanoclay incidence increases the energy absorbed by the composites, for this reason, the increase of nanoclay amount creates areas that provide points of stress concentrations in the polymeric matrix, thus providing sites for crack initiation and potential composite failure. Consequently, the results show that increasing the amount of nanoclay will reduce the impact strength in WPCs.[13-14,21] The chemical treatments also improve the adhesion in the interface area and increase the impact strength, which is also confirmed by Ghasemi and Farsi.[23]

Water absorption

Figures 7 and 8 point out the independent nanoclay and alkaline treatment effects on 2-hour water absorption. Considering Fig. 7, the alkaline treatment reduces 2-hour water absorption by 31%. Fig. 8 presents the independent nanoclay effect on 2-hour water absorption. Based on this figure, by increasing the amount of nanoclay up to 6%, the 2-hour water absorption rates showed 4.5% and 6.2% decreases, respectively, and the maximum water absorption was related to the samples containing 6% of nanoclay (ranking c in Duncan's classification). The effect of nanoclay particles on the properties of composites depends on the form, size, aspect ratio, type, amount and quality of the dispersed particles and their adhesion in the interface area.[15] Nanoclay particles have significantly reduced the water absorption in composites due to the proper adhesion with the polymer matrix and to adhesion network development, which is congruent with the studies conducted by Liu *et al.*[17] and Kord *et al.*[25] Fig. 9 demonstrates the interactive effect of nanoclay and alkaline treatment on 2-hour water absorption. Accordingly, increasing the nanoclay amount in the treated samples, compared to untreated samples, showed a reduction in 2-hour water absorption and had a positive effect on reducing the short-time water absorption rate in WPCs.

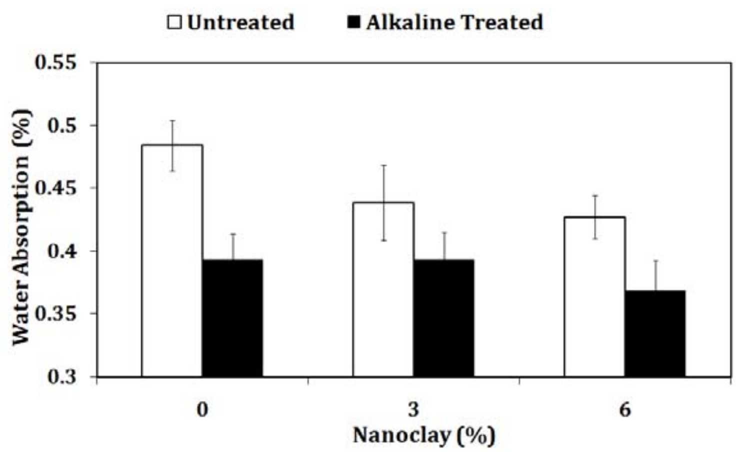

Figure 9: Water absorption of LDPE/WF composites treated with alkaline and containing different loading of nanoclay

CONCLUSION

1 – The alkaline treatment improves the tensile strength of WPCs made from LDPE and beech flour and by increasing the nanoclay content to 3% and 6%, the tensile strength slightly decreases.

2 – The presence of nanoclay decreased the impact strength of WPCs. The alkaline treatment increased the impact strength by improving the adhesion in the interface region.

3 – The results of physical tests showed that the water absorption rate decreased with increasing the nanoclay content. The alkali treatment also had a positive effect on short-time water absorption of WPCs.

The overall results of the study show the cumulative effects of the alkaline treatment and nanoclay in improving and developing the adhesion in the interface region and improving the engineering properties of the LDPE/ nanoclay/WF composites.

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