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Mechanical and Water Absorption Properties of Sawdust—Low Density Polyethylene Nanocomposite

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ABSTRACT: In this research, effect of nanoclay (Cloisite10A), coupling agent (MAPE), spruce sawdust and electron beam irradiation dose on mechanical and water absorption properties of sawdust-low density polyethylene nanocomposite are investigated. Design of the experiments (DOE) is performed by the statistical Taguchi method. The XRD analysis depicts partially intercalated/exfoliated nanocomposites. The findings reveal that increasing cloisite10A concentration from 2.5 to 7.5 wt % has improved the tensile and bending strengths and modulus also water diffusion coefficient is reduced. Increase the sawdust content from 40 to 60 wt % not only markedly increases the tensile and flexural properties but also increases water diffusion coefficient and reduces toughness significantly. Electron beam irradiation dose of 60 kGy improves the tensile and flexural properties and decreases water diffusion coefficient. The SEM micrographs confirm a suitable coherence between lignocelluloses filler phase and low density polyethylene matrix. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: wood plastic composite; mechanical properties; electron beam irradiation; nanoclay; water diffusion coefficient

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INTRODUCTION

During the last decade, the acceptance of wood derived fillers in the plastic industry has been growing because of their biodegradability, renewability, low cost, and satisfactorily processability. One of the common wood-derived fillers is spruce sawdust which is cheap, readily available, and renewable.

According to different affinity between the hydrophilic sawdust and hydrophobic polyethylene (PE), it is necessary to impart hydrophobicity to wood fillers by suitable treatments. The selection of proper coupling agents is one way to improve filler–matrix adhesion.[1] Maleic anhydride grafted polymers, such as maleated polyethylene (MAPE) and maleated polypropylene (MAPP), are widely used as coupling agents to develop composites with better mechanical properties.

Another approach for improving the wood plastic composites (WPCs) properties is the use of electron beam (EB) irradiation. The ionizing radiation is a clean process capable to modify the properties of a material. When thermoplastic materials are subjected to ionizing radiation, they undergo structural changes accompanied by molecular cross linking, grafting and chain scission reaction.[2] Cross linking reaction dominates chain scission in PE matrix up to 450 kGy dose of EB irradiation.[2] Youssef et al. investigated the effect of preirradiation of PE on the properties of uncoupled bagasse fiber-PE composites. According to their results, EB irradiation is more effective on LDPE than HDPE. It is due to the more amorphous phase present in LDPE.[2] Other investigators studied the effect of EB irradiation on molded composites with or without coupling agents.[1,3–5] The interfacial adhesions between wood filler and PE under irradiation process are significantly improved as a result of the formation of free radical molecules of the composite components.[6]

Enhancement of material properties achieved with montmorillonite (MMT) clay has stimulated active research in polymer composites. Faruk and Matuana examined two different methods of introducing nanoclays into HDPE-based WPCs. The melt blending process, in which nanoclay/HDPE nanocomposite was used as matrix, appeared to be a better approach of incorporating nanoclay in WPC than direct dry blending process. The results also showed that cloisite 10A was more effective than other types of nanoclays (i.e., cloisite15A, 20A, 25A, and 30B) because it was the only nanoclay to enhance both flexural and tensile properties of HDPE. To advance the interaction between PE chains and the organically modified montmorillonite (OMMT), MAPE is often introduced.[7] Han et al. reported

Table I. L9 Orthogonal Array of the Taguchi Method, Design of the Nine Compounds and Variable Factors

Compound no.	OMMT (wt %)	MAPE (wt %)	Spruce sawdust (wt %)	Irradiation dose (kGy)
1	2.5	1	40	0
2	2.5	3	50	30
3	2.5	5	60	60
4	5	1	50	60
5	5	3	60	0
6	5	5	40	30
7	7.5	1	60	30
8	7.5	3	40	60
9	7.5	5	50	0

that adding MAPE compensated the negative effect of pine flour on intercalation of HDPE molecular chains.[8]

Exposure of natural fiber–thermoplastic composites to the atmosphere or their contact with aqueous media has made it necessary to evaluate their water-uptake characteristics. Water absorption is known to have adverse effects on the mechanical properties of polymers and their composites. The absorption of water by the wood component of the composite has led to a degradation of the interface quality and resulted in a decrease in the composite strength.[9] Transport phenomena in composites under wet conditions can be modeled with Fick's law of diffusion, which is the simplest model for the diffusion of a solvent into a solid.[9]

This investigation aims to study the effect of nanoclay content, the amount of MAPE coupling agent, sawdust content, and irradiation dose on mechanical and water absorption properties of sawdust-LDPE nanocomposite. To achieve this aim, three levels for each of the four factors were chosen. Statistical Taguchi method was employed in the design of experiments. According to Taguchi's L9 orthogonal array, nine compounds were melt compounded twice using a twin screw extruder. Tensile and flexural test specimens were injection molded and water absorption test specimens were prepared by compression molding process.

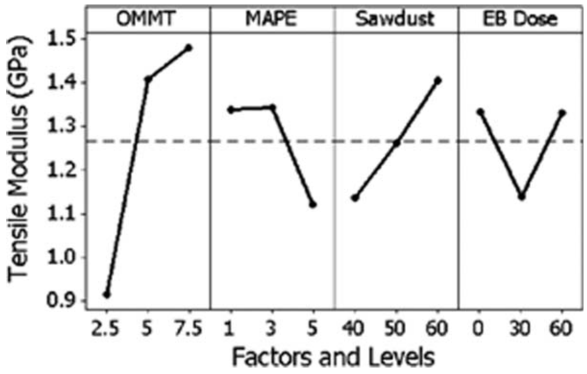

Figure 2. Effect of four factors at three levels on the tensile modulus.

EXPERIMENTAL

Materials

The film grade low density polyethylene (LDPE) with MFI (190°C, 2.16 kg) of 2 g/10 min was supplied by Bandar Imam Petrochemical Complex, Iran. The organoclay was Cloisite10A obtained from Southern Clay Products, USA. It is a natural montmorillonite modified with 125 meq of dimethyl, benzyl, hydrogenated tallow, quaternary ammonium per 100 g clay. Polyethylene grafted with maleic anhydride (MAPE) used as coupling agent was provided by Chemtura, Australia with MFI (190°C, 2.16 kg) of 3–6 g/10 min. Spruce sawdust with density of 0.4–0.7 g cm^{-3} was purchased from Alvar Plast Sepahan, Iran as the lignocelluloses filler.

Sample Preparation and Methods of Investigation

Design of the experiments (DOE) was performed by the statistical Taguchi method with Minitab 15 software. Four factors (Cloisite10A, MAPE, spruce sawdust and irradiation dose) in three levels were chosen, and the effects of each factor on mechanical properties and water absorption were studied. Nine compounds were prepared according to a L9 Taguchi orthogonal array which has nine combinations of levels. Table I shows the formulation of the compounds and variable factors. Results were statistically analyzed by 95% confidence with Qualitek 4 software.

Spruce sawdust was dried before mixing in a vacuum oven at 100°C for 24 h. All components were weighed according to design (Table I). In the first step, weighted LDPE, MAPE, and

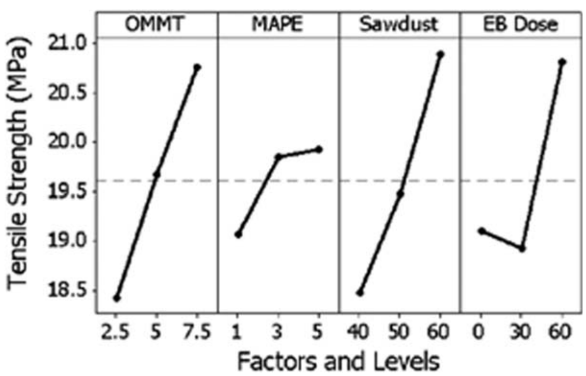

Figure 1. Effect of four factors at three levels on the tensile strength.

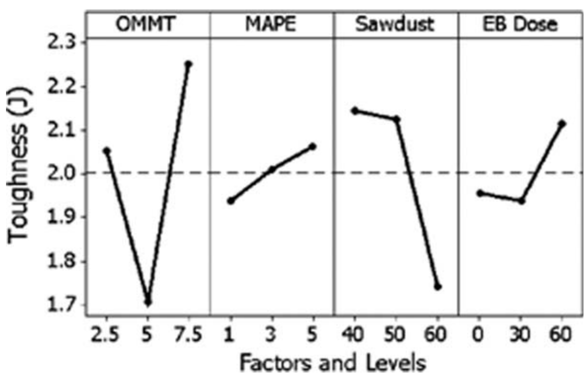

Figure 3. Effect of four factors at three levels on the toughness.

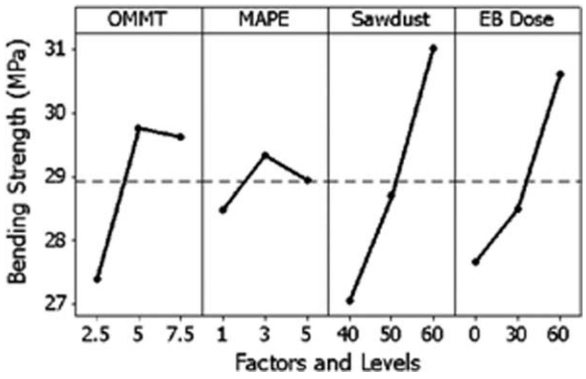

Figure 4. Effect of four factors at three levels on the bending strength.

cloisite10A for each compound were mixed manually. The compounds were loaded into a counter-rotating twin-screw extruder (Dr. Collin-ZK 25 S; *L/D* = 6; *D* = 25 mm) with a thermal profile of 140–150–155–160°C at a screw speed of 60 rpm. The extruded samples were cooled in water bath and pelletized. In the second step, spruce sawdust was physically mixed with the granulated samples and granulated by the same twin-screw extruder with the same processing conditions. To prevent water absorption, the extrudate were cooled in air and then ground in a Wieser mill. All compounds were finally exposed to different doses of electron beam (EB) irradiation according to Table I.

Tensile and bending tests were performed according to ASTM D638 and ASTM D790 (B method), respectively. Standard samples for these tests were prepared using injection molding machine with a thermal profile of 160–165–170°C at a screw speed of 60 rpm.

For each nanocomposite formulation two sheets with dimensions of 150 × 150 × 2 mm^3 were prepared at 170°C using compression molding method according to ASTM D 1037-100. All of the sheets were dried in a vacuum oven at 103°C and weighed with 0.01 g accuracy. Then sheets immersed horizontally in distilled water at room temperature. The weights of sheets were measured and recorded periodically for 305 days until they reached equilibrium.

X-ray diffractometery (XRD) method is used to characterize the dispersion of cloisite10A by estimating the distance between

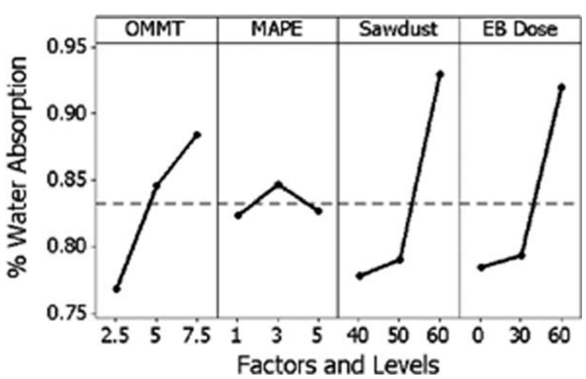

Figure 5. Effect of four factors at three levels on the water absorption.

Table II. Calculated *n* and *k* Values for the Samples

Compound	*n*	*k*	R^2
1	0.427 ± 0.002	0.068 ± 0.0009	0.996
2	0.451 ± 0.008	0.061 ± 0.0002	0.998
3	0.439 ± 0.024	0.061 ± 0.0072	0.997
4	0.455 ± 0.034	0.056 ± 0.0098	0.998
5	0.462 ± 0.020	0.052 ± 0.0046	0.998
6	0.439 ± 0.032	0.064 ± 0.0089	0.997
7	0.468 ± 0.017	0.054 ± 0.0024	0.998
8	0.461 ± 0.015	0.055 ± 0.0033	0.997
9	0.447 ± 0.003	0.0605 ± 0.0001	0.997

individual platelets of the nanoclay after being melt mixed into the polymer. The compounds 3, 7, and 9 were analyzed by a D8 ADVANCE (Bruker, Germany) XRD diffractometer with Cu Kα (λ = 1.5406°A) radiation in the 2θ range from 0.5 to 10°with step size of 0.04°, at room temperature.

Scanning electron microscopy (SEM) micrographs were obtained on a Philips XL30 scanning electron microscope. Injection molded Samples of compounds 3, 6, and 9 with dimensions of 80 × 10 × 3 mm^3 were broken in liquid nitrogen. A thin coating of gold was applied on the surface of the samples in order to avoid any static charges.

RESULTS AND DISCUSSION

Tensile Strength

Figure 1 shows the effects of the four factors at three levels on the tensile strength of the samples. Increasing the nanoclay content increased the tensile strength of the samples. This may be pointed to the formation of intercalated/exfoliated nanocomposite structures. An increase in the level of MAPE from 1 to 3 wt % caused an increase in the tensile strength. Additional content had no significant effect on this property, so it is expected that 3 wt % MAPE would be optimum value for improvement the interface property. Tensile strength enhanced 13% by increasing the amount of sawdust from 40 to 60 wt % in the matrix. Some researchers have reported the decrease of this property with increasing the wood filler content. They reached that it is due to the weak adhesion between the polymer and lignocelluloses filler and using proper amount of coupling agent can improve the interface adhesion and enhance the strength of the matrix.[10,11] Irradiation dose of 60 kGy caused an increase in the tensile strength of the compound. Ibrahim et al. explained this phenomenon by cross linking of the polymer matrix and adhesion improvement between polymer and fibers.[5]

Tensile Modulus

The effects of each one of four factors on the tensile modulus are depicted in Figure 2. The change in the level of nanoclay from 2.5 to 5 wt % increased the tensile modulus by 54%, but increasing the clay content to 7.5 wt % caused 5.3% more enhancement. Generally, high clay content in composites can lead to the reduction of interfacial adhesion and increase the agglomeration possibility,[12–14] so 5 wt % nanoclay would be more suitable. Increasing the MAPE content to 3 wt % had no

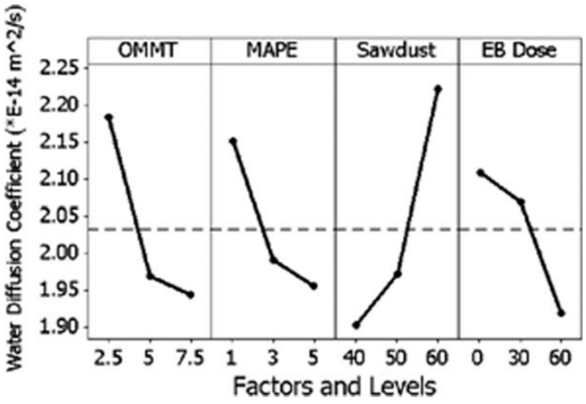

Figure 6. Effect of four factors at three levels on the water diffusion coefficient.

significant effect on the tensile modulus and additional amounts of the coupling agent decreased this property. It may be due to lower molecular weight of MAPE.[8] Tensile modulus increased 23.4% when the sawdust content increased from 40 to 60 wt %. The tensile modulus of wood (1–8 GPa) is much more than that of polyethylene (0.1–0.3 GPa), so it is supposed that increasing the amount of sawdust improve the tensile modulus of wood plastic composites (WPCs).[15] Irradiation dose of 30 kGy decreased the tensile modulus but 60 kGy doses retrieve this property. Contest between cross linking and cellulose degradation phenomena is the reason of this observation.[15]

Toughness

The effect of each four factors on the toughness was investigated. Statistical analyses showed that MAPE concentration and EB irradiation dose had no significant effect on the toughness. EB irradiation results the cross linking of the matrix which reduce the toughness. It also improves the interface adhesion and decreases the cavities. So these two elements neutralize each other effects. As shown in Figure 3, increasing the clay content from 2.5 to 5 wt % caused a 16% reduction in toughness. This may be cause of micro cavities formation through the separation of clay layers from polymer matrix.[14] With 7.5 wt % nanoclay, toughness increased 31% compared with the sample containing 5 wt % clay. The toughness of the samples decreased with increasing the sawdust content. Yihua Cui et al. showed the same results for HDPE WPCs. This phenomenon may be explicated by the fact that the presence of wood fiber ends can cause crack initiation[16]; therewith increasing the amount of sawdust meant the lower level of tough polyethylene.[17]

Bending Strength

Figure 4 shows the effect of the four factors at three levels on bending strength. With 5 wt % nanoclay, a significant increase in bending strength was observed. Increasing the clay content to 7.5 wt % decreased this property which may be as a result of clay agglomeration in the polymer matrix. Agglomeration raises the stress concentration possibility and reduces the homogeneity of the system.[12,14] MAPE concentration had no significant effect on the bending strength statistically. Increasing the sawdust concentration enhanced the bending strength just like the tensile strength. Increasing the irradiation dose enhanced the bending strength because increasing the irradiation dose can raise the chemical bond formation. Similar results were reported for polyethylene/wood flour composites.[6] Behavior of the modulus of elasticity of the samples was similar to the bending strength.

Water Absorption

Figure 5 shows the effect of four factors on the water absorption behavior of the WPCs sample. MAPE concentration had no significant effect on this property, statistically. Increasing the amount of nanoclay enhanced the water absorption after 24 h. This phenomenon may be cause of the water adsorption on the compressed composite surface which has lower intercalated and oriented nanoclay. Increasing sawdust content enhanced the water absorption of the WPCs. 60 kGy doses of irradiation increased the water absorption, whereas it supposed unlike that.[18] The reason of increasing the water absorption can be the surface oxidation.

Water molecules diffusion in polymer composites can occur by three mechanisms: Fickian diffusion, relaxation-controlled diffusion and non-Fickian or Anomalous. Mechanism of diffusion depends on polymer chemical structure, dimension and morphology of filler and polymer-filler adhesion.[12] The water absorption graph and eq. (1) can use to investigate the main mechanism of water diffusion in polymer composites.

$$\log\left(\frac{M_t}{M_{sat}}\right) = \log k + n \times \log t \tag{1}$$

where M_t is the water absorption at time t, M_{sat} is the saturated water absorption, k and n are constants. For Fickian diffusion n value is 0.5, for relaxation-controlled diffusion $n > 1$ and for Anomalous transferring, $0.5 < n < 1$. The constants n and k can be calculated from the Slope and intercept of the M_t/M_{sat}—t logarithmic graph.[9] The n and k values for all of the samples are reported in Table II. As can be seen, n values are near to $n = 0.5$ which indicates the Fickian diffusion of water molecules into the composites.

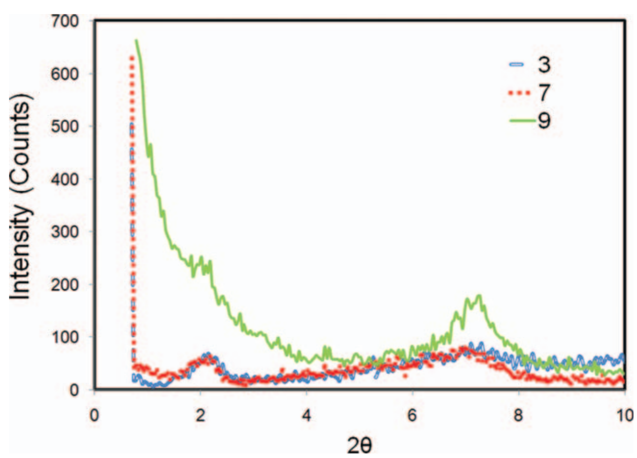

Figure 7. XRD patterns of the samples 3, 7 and 9. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

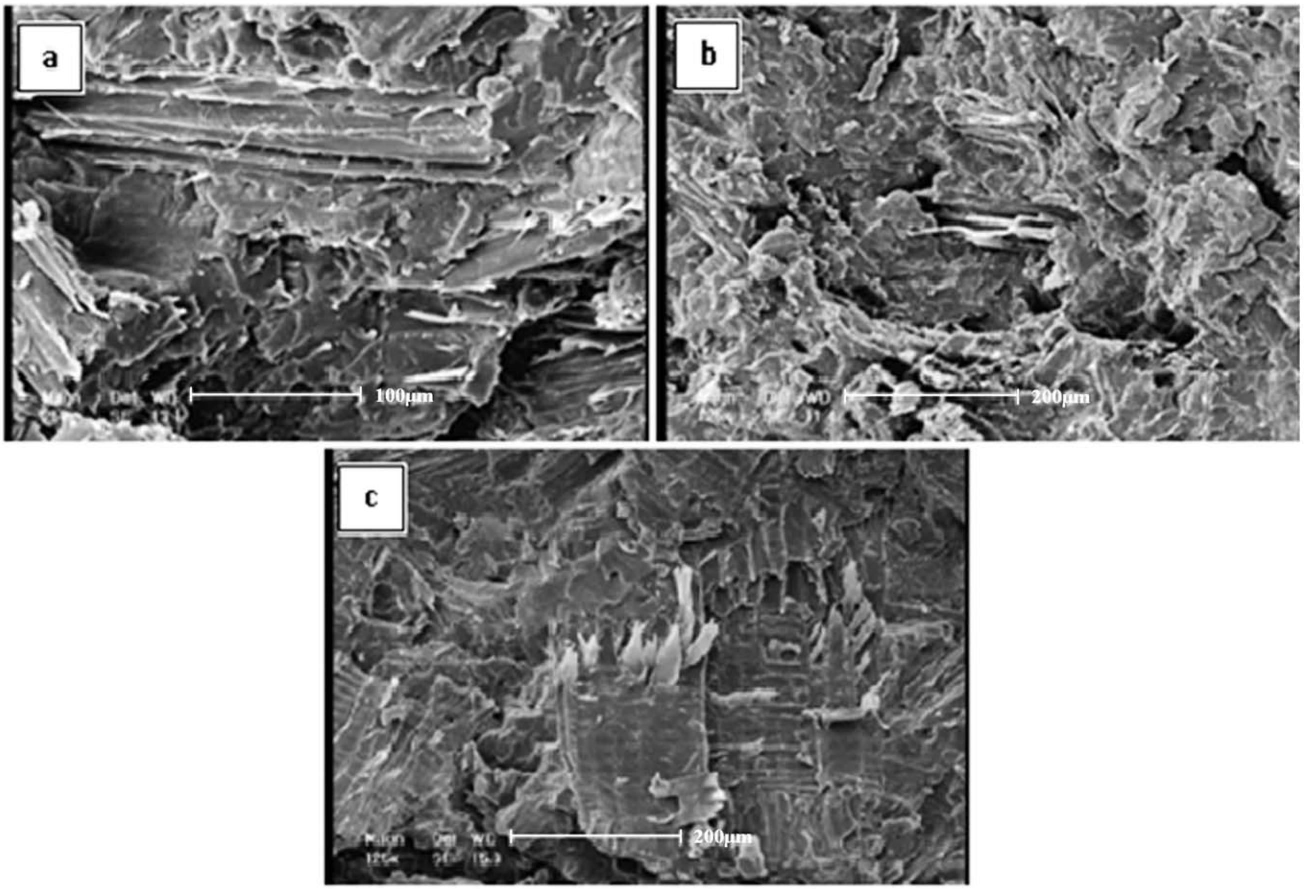

Figure 8. SEM micrograph of (a) compound 6 with 40 wt % sawdust, (b) compound 9 with 50 wt % sawdust, and (c) compound 3 with 60 wt % sawdust.

According to the Fick rule, at the beginning time, there is a linear relation between the weight percent of absorbed water and time square:

$$\%M = \left([4.\%M_{sat} \cdot \sqrt{D_A}]/(h.\sqrt{\pi})\right) \times \sqrt{t} \quad (2)$$

$\%M_{\mathrm{sat}}$ is the weight percent of water absorption in saturation state, h is the height of the sample and $\%M$ is the weight percent of absorbed water and calculates from eq. (3). D_A is the appearance diffusion coefficient which estimates from equ. (4).

$$M = [(M_{\mathrm{wet}} - M_{\mathrm{dry}})/M_{\mathrm{dry}}] \times 100 \quad (3)$$

where M_{dry} is the sample weight after drying before dipping and M_{wet} is the sample weight after immersing in water.

$$D_A = \pi\left[\frac{h^2}{16(M_{sat}\%)^2}\right][(M_2\% - M_1\%)/(\sqrt{t_2} - \sqrt{t_1})]^2 \quad (4)$$

where $\%M_1$ and $\%M_2$ are the weight increase percent at t_1 and t_2. The appearance diffusion coefficient calculated from eq. (4) is one dimensional, while diffusion occurs by edges too. To the reason the Edge Correction Factor has been used [eq. (5)].

$$ECF = \left(1 + \frac{h}{l} + \frac{h}{w}\right)^2 \quad (5)$$

where w, l, and h are the width, length, and height of the sample respectively and corrected diffusion coefficient is given by[9]:

$$D = D_A/ECF \quad (6)$$

Figure 6 depicts the water diffusion coefficient of the samples. Increasing the nanoclay content reduced the water diffusion coefficient. This can be explained by three effects; (i) immobilization the moisture because of the hydrophilic nature of the clay surface, (ii) a tortuous path formation through the clay platelets in the polymer matrix, and by (iii) improvement the crystallinity by the presence of the nanofiller as a nucleating agent.[12]

Increasing the amount of MAPE decreased the water diffusion coefficient. This is confirmed by the previous study on wood/HDPE composites.[9] It shows the efficiency of adhesion at the interface on water absorption in WPCs. Presence of MAPE reduced free volumes of the interface and blocks the hydrophilic groups. It's also reported that crystallinity of the WPCs containing MAPE is more than those without any coupling agent.[19] As the crystalline regions are impermeable, the water absorption is less in the composites. Reaction between anhydride groups of MAPE and hydroxyl groups on wood surface provides the appropriate sites for the moisture.[20] In addition the chemical bond between MAPE and wood particles is a barrier for water transfer.

As it can be seen in Figure 6 the water diffusion coefficient increased with increasing the sawdust content. At higher percent of lignocelluloses filler (sawdust), agglomeration is more possible which results an increase in water absorption.

The water diffusion coefficient of the sample at the irradiation dose of 60 kGy reduced by 8.9% compared with the sample with no irradiation. Cross linking as a result of irradiation is a good barrier against the water molecules diffusion. On the other hand increasing the irradiation dose reduces the mobility and free volumes of the system. Decrease in free volume can decrease the water transfer into system.

X-Ray Diffractometery Analysis

XRD analysis is used to characterize the distance between individual platelets of cloisite10A in the samples 3, 7, and 9. Figure 7 shows the XRD patterns of these compounds. Cloisite10A has a main reflection peak at $2\theta = 4.64°$ (d-spacing 19 °A).[7] As it can be seen in Figure 7 all of the samples showed a broad peak around this angle. Broadening of the clay diffraction peak is considered to be the result of partial exfoliation. Another peak was observed in all three samples around $2\theta = 7.1°$ which represents the distance between unmodified layers in montmorillonite. The presence of this peak demonstrates the degradation of clay modifier structure through the stress and thermal history.

The worst condition of nanoclay dispersion in this study can occur in compound no. 7 with highest level of nanoclay and sawdust and lowest amount of MAPE. As can be seen in Figure 7, this sample showed a peak at around $2\theta = 2.2°$, equivalent to an interlayer spacing of 40.125°A from Bragg's equation, $n\lambda = 2d \sin \theta$. Increase in d-spacing compared to cloisite10A (19°A) demonstrates the intercalated structure of the compound no. 7. Therefore a better dispersion of nanoclay is expected for the other samples.

The compound no. 9 containing higher amount of MAPE and lower loading of sawdust compared with compound no. 7 showed an intercalated/exfoliated structure. For Sample 3, a broad peak was observed at $2\theta = 2.1°$, corresponding to a d-spacing of 42.04° A. The Sample 9 with higher clay and lower sawdust demonstrated a larger interlayer spacing than Sample 3. It can be explained by two effects; the first one is the reaction between the hydroxyl groups on wood surface and MAPE and more consumption of MAPE in the presence of higher amounts of sawdust. Second, nanoclay particles migrate to the polymer-wood flour interface and more amounts of sawdust leads to more migration possibility. Clay d-spacing in compound no. 3 was more than Sample 7, because of the higher ratio of MAPE/clay.

Scanning Electron Microscopy Analysis

SEM micrographs were used to investigate the dispersion of the lignocelluloses filler in Compounds 3, 6, and 9. Figure 8 shows the SEM micrograph of these samples with magnification of ×125. SEM observations show that the fractured surface of the samples was highly porous, indicating a good adhesion between two phases (polymer and sawdust).

CONCLUSIONS

Cloisite10A increased the water absorption resistance, tensile, and bending properties of the WPCs. The optimum concentration of MAPE for improvement the interface property was 3 wt %. Increasing the sawdust content from 40 to 60 wt % enhanced the tensile and bending properties, but it also raised the water absorption resistance and reduced the toughness of the composites. Totally 60 kGy irradiation doses showed a positive effect on water absorption and mechanical properties. The XRD analysis depicted intercalated/exfoliated structure in nanocomposites. SEM micrographs indicated a good adhesion between spruce sawdust and LDPE.

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