EFFECT OF VIRGIN AND RECYCLED PLASTICS ON MOISTURE SORPTION OF NANOCOMPOSITES FROM NEWSPRINT FIBER AND ORGANOCLAY

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In this study the effect of virgin and recycled plastics on water absorption of nanocomposites from newsprint fiber and organoclay was studied. Newsprint fiber was mixed with either virgin or recycled polypropylene (PP) at 30% by weight fiber loading. The samples were made by melt compounding and then injection molding. The concentration was varied as 0, 2.5, and 5% for nanoclay. The amount of coupling agent was fixed at 10% for all formulations. The long-term water absorptions of samples were evaluated by immersing them in water at room temperature for several weeks, and water diffusion coefficients were also calculated by evaluating the water absorption isotherms. The results indicated that whether or not virgin plastic is used has a significant effect on the water absorption of composites. The water absorption of the newsprint fiber/recycled plastic composites was higher than those of virgin plastics. Furthermore, with addition of nanoclay content in composites, water absorption decreased. Water absorption of all formulations was proved to follow the kinetics of a Fickian diffusion process. Morphological findings showed the formation of intercalated morphology and better dispersion with 2.5% of nanoclay.

Keywords: Newsprint Fiber; Polypropylene; Virgin; Recycled; Organoclay; Moisture sorption

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INTRODUCTION

Composite materials based on cellulosic fibers, namely wood-plastic composite (WPC), demonstrate remarkable environmental and economical advantages, and they have, therefore, recently attracted much attention (Nourbakhsh et al. 2010).

In wood plastic composites manufacturing, virgin plastics such as high and low density polyethylene (HDPE and LDPE), PP, and PVC are commonly used. As for virgin plastics, any recycled plastic that melts and can be processed below the degradation temperature of wood is usually suitable for manufacturing wood-plastic composites. Plastic wastes are one of the major components of global municipal solid waste and present a promising raw material source for wood-plastic composites (thanks to their large amount of daily generation and low cost). For example, a city in a developing country with a population of 3 million inhabitants produces around 400 metric tons plastic waste per day with an annual increase of 25%. Hence, the development of new value-added products (WPC), with the aim of utilizing the wood waste (this means no need for additional wood resources) and low cost recycled plastics (which would otherwise be added to landfills), is assuming greater importance. The utilization of recycled plastic for the manufacture of wood-fiber-reinforced recycled plastic composites has been studied by a number of authors (Kazemi Najafi et al. 2006; Kazemi Najafi et al. 2007).

Water absorption and the consequent thickness swelling are the most important physical characteristics of wood-plastic composites exposed to environmental conditions and thus affecting their end-use applications. Water absorption can deteriorate both mechanical properties and dimensional stability in such composites. Therefore, hygroscopic characteristics have to be taken into account as limiting parameters in the design with regard to their final applications. Considerable research has been conducted on water absorption of WPCs made of virgin and/or recycled plastics (Merdas et al. 2001; Espert et al. 2004; Yang et al. 2006), and a number of attempts have been made to reduce water absorption of WPCs (Pothan and Thomas 2004; George et al. 2001).

On the other hand, nanoscience and nanotechnology have opened up a completely new way to develop WPCs (Tjong 2006; Utracki et al. 2007; Viswanathan et al. 2006). Nanotechnology is a very promising field for improving the properties of WPCs using nanosized fillers. 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 biodegradable polymers (Ashori and Nourbakhsh 2009). Using nanoclay filler in WPC composite has been reported in the literature (Zhao et al. 2006; Wu et al. 2007; Lei et al. 2007; Han et al. 2008; Hetzer and Kee 2008; Ghasemi and Kord 2009; Hemmasi et al. 2010; Kord et al. 2010; Kord 2010; Ashori and Nourbakhsh 2011, Nourbakhsh et al. 2011). Many efforts have been made in the formation of wood polymer composite to improve such properties so as to meet specific end-use requirements.

In order to improve the dimensional stability and to increase the potential applications, additional research is needed on wood plastic nanocomposites made from recycled plastics, especially mixed plastic waste, because separation of waste plastics imposes additional costs in practice. Therefore in this study, the effect of virgin and recycled plastics on water absorption of nanocomposites from newsprint fiber and organoclay has been considered.

EXPERIMENTAL

Materials

Virgin polypropylene (PP) and recycled PP were used as plastic matrix in newsprint fiber/organoclay nanocomposites. Virgin PP was purchased from Arak Petrochemical Company with a melt flow index of 18 g/10 min with the trade name V30S. Recycled PP was obtained from waste spindle with a melt flow index of 31.5 g/10 min. PP-g-MA provided by Solvay with trade name of Priex 20070 (MFI=64 gr/10min, grafted maleic anhydride 0.1 Wt. %) was used as compatibilizer. Newsprint fiber used as the reinforcing fiber material was from Mazandaran Wood and Paper Industry.

Montmorillonite (MMT) based nanoclay Cloisite 15A was a product of Southern Clay Products Inc. It is supplied in a particulate form with sizes in the micrometer scale range (10% less than 2 μm, 50% less than 6 μm, and 90% less than 13 μm). Cloisite 15A is a natural montmorillonite modified with a quaternary ammonium salt (dimethyl ammonium chloride) of dehydrogenated tallow as an organic modifier. It has a cationic exchange capacity (CEC) of 125 meq/100 g clay, a density of 1.66 g/cc, and a d-spacing of $d_{001} = 31.5$Å.

Composite Preparation

Before preparation of samples, newsprint fiber was dried in an oven at 65 ± 2 °C for 24 hours. Then polypropylene, newsprint fiber, nanoclay, and compatibilizer were weighed and bagged according to formulations given in Table 1. The mixing was carried out with a Hakke internal mixer (HBI System 90, USA). First the PP was fed to the mixing chamber; after it was melted, the nanoclay and compatibilizer was added. At the fifth minute, newsprint fiber was added, and the total mixing time was 13 min. The compounded materials were then ground using a pilot scale grinder (Wieser, WGLS 200/200 Model). The resulted granules were dried at 105 °C for 4 hours. Test specimens were prepared by injection molding (Eman machine, Iran). The specimens were stored under controlled conditions (50% relative humidity and 23 °C) for at least 40 hours prior to testing.

Table 1. Compositions of the Studied Formulations

Sample Code	Polypropylene (wt%)		Newsprint Fiber (wt%)	Compatibilizer (wt%)	Nanoclay (wt%)
	Virgin	Recycled			
60VPP/30NF/10C	60	-	30	10	0
57.5VPP/30NF/10C/2.5N	57.5	-	30	10	2.5
55VPP/30NF/10C/5N	55	-	30	10	5
60RPP/30NF/10C	-	60	30	10	0
57.5RPP/30NF/10C/2.5N	-	57.5	30	10	2.5
55RPP/30NF/10C/5N	-	55	30	10	5

Measurements

Water absorption tests were carried out according to ASTM D7031 specification. Five specimens of each formulation were selected and dried in an oven for 24 hours at 102 ± 3 °C. 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 Eq. 1,

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

where WA (t) is the water absorption at time t, W_o 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 device (Germany) with CuKα radiation (λ=1.54 nm, 50 kV, 50 mA) at room temperature; the scanning rate was 1^o/min.

RESULTS AND DISCUSSION

Water absorption curves of different composites are illustrated in Fig. 1, where the percentage of water absorption is plotted against time for all samples. As can be clearly seen, generally water absorption increased with immersion time, reaching a certain value at a saturation point, beyond which no more water was absorbed and the composites water content remained constant. Figure 1 also shows that the maximum water absorption of composites was not the same for all formulations. The 55VPP/30NF/10C/5N and 60RPP/30NF/10C composites showed minimum (3.99%) and maximum (5.37%) water absorptions, respectively. In composites, the maximum water absorption increased with the increase of recycled plastic loading.

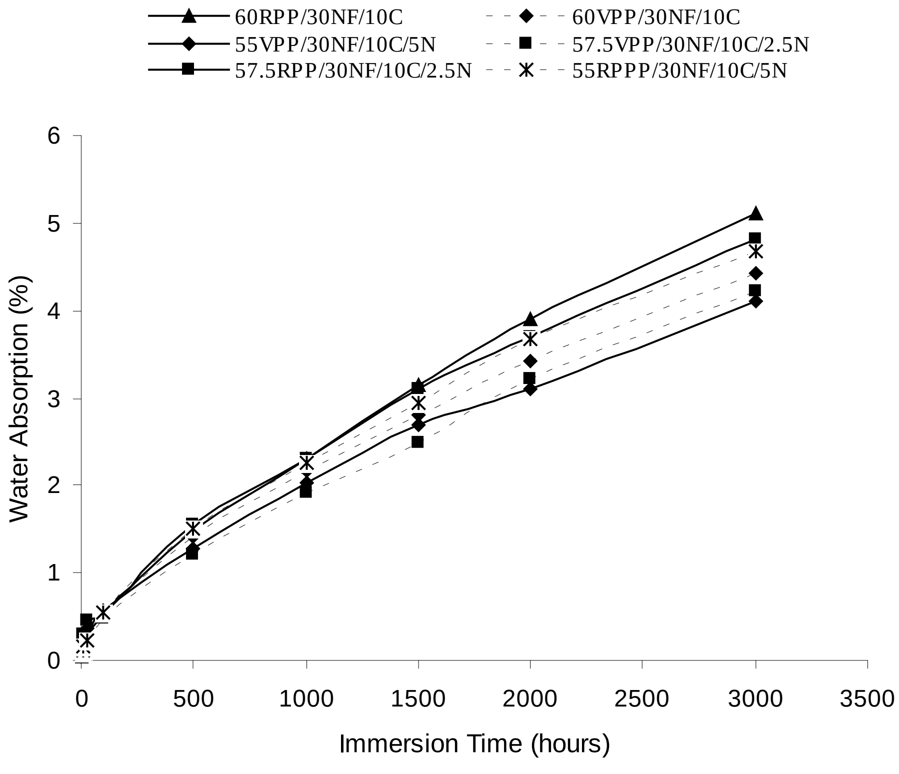

Fig. 1. Effect of plastics virginity and the presence of nanoclay on water absorption of composites from newsprint fiber and organoclay

The hydrophilic nature of wood flour was responsible for the water absorption in manufactured WPCs (the plastics have negligible water absorption). Because of constant newsprint fiber content (30%) in all formulations, the different water absorption between all manufactured composites can be attributed to the virginity of plastics. The possible reason is that the chemical impurities would interfere with interfacial adhesion, as well as compositional differences (MFI and crystallinity) between virgin and recycled plastics. Therefore, the water absorption of the newsprint fiber/RPP composites was higher than those of virgin plastics.

Another interesting result in Fig. 1 is that water absorption decreased with increase of nanoclay loading. It seems that the barrier properties of nanoclay fillers inhibit the water permeation in the polymer matrix. Two mechanisms have been reported in attempts to explain this phenomenon. The first is based on the hydrophilic nature of the clay surface that tends to immobilize some of the moisture (Rana et al. 2005); second, surfactant-covered clay platelets form a tortuous path for water transport (Alexandre et al. 2006; Bharadwaj et al. 2002). The latter barrier property hinders water from going into the inner part of the nanocomposite. It seems that both of the aforesaid mechanisms could be more efficient when the morphology is exfoliated. In other words, in the exfoliated morphology there is more available surface area of organoclay (with hydrophilic nature) and surfactant-covered clay platelets (tortuous path), so the water transport goes down under the severe conditions. Another reason for less water uptake could be ability of nanoclay to act as a nucleating agent (Ghasemi and Kord 2009). Due to such nucleation, the crystallinity of the hybrid composite can be improved by the presence of the nanofiller as a nucleating agent. As the crystalline regions are impermeable, the water absorption is less in the composites.

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 flour, and polymer-filler interfacial adhesion. These cases can be distinguished theoretically by the shape of the sorption curve represented by the following equation (Adhikary et al. 2008; Ghasemi and Kord 2009),

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

where M_t is the water absorption at time t; M_∞ is the water absorption at the saturation point, and k and n are constants. The amount of the n is different for the following cases: in Fickian diffusion $n = 0.5$, in relaxation $n > 0.5$, and in the anomalous transport mechanism $0.5 < n < 1$.

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 55VPP/30NF/10C/5N is given in Fig. 2, 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 approached the Fickian diffusion case.

Table 2. Diffusion Case Selection Parameter for all Samples

Sample Code	*n*	*K* (h^2)
60VPP/30NF/10C	0.46	0.008698
57.5VPP/30NF/10C/2.5N	0.43	0.007398
55VPP/30NF/10C/5N	0.41	0.006464
60RPP/30NF/10C	0.49	0.009985
57.5RPP/30NF/10C/2.5N	0.46	0.008849
55RPP/30NF/10C/5N	0.44	0.007575

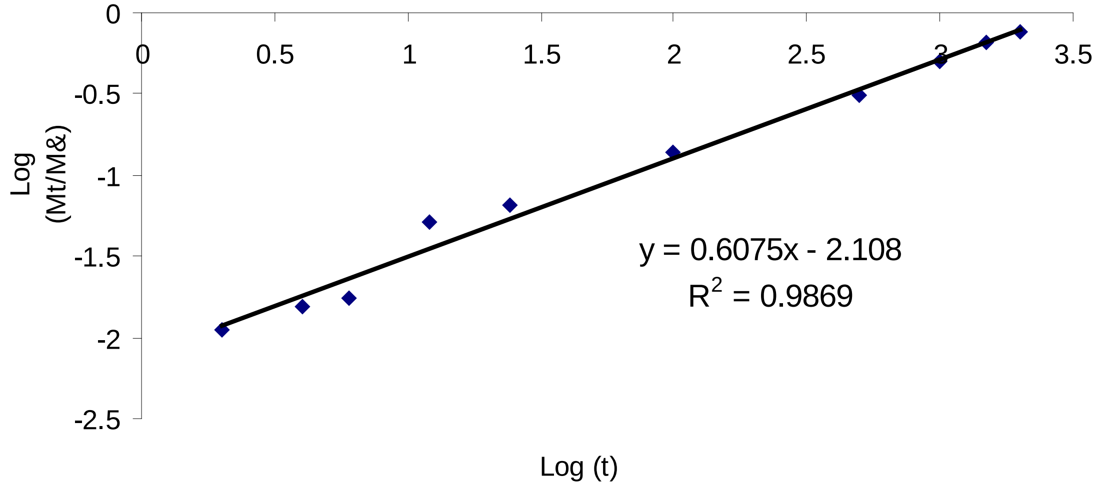

Fig. 2. Diffusion case fitting for 55VPP/30NF/10C/5N composites

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 (Adhikary et al. 2008; Ghasemi and Kord 2009),

$$M_t/M_\infty = 4t^{1/2}/ (D\,t /\pi L^2)^{1/2} \qquad (3)$$

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

The data were plotted as M_t/M_∞ against $t^{1/2}$ (Fig. 3), and the diffusion coefficients were obtained from the slopes of the linear part of the plots using the least-squares method. Table (3) shows the water diffusion coefficients for all formulations. The results show the water diffusion coefficients decreased with incorporation of coupling agent into polypropylene composite. The 55VPP/30NF/10C/5N composite exhibited the lowest diffusion coefficients.

Table 3. Maximum Water Absorption and Water Diffusion Coefficients for all Samples

Sample Code	Maximum Water Absorption (%)	Water Diffusion Coefficient ($\times 10^{-12}$ m^2s^{-1})
60VPP/30NF/10C	4.81	1.78
57.5VPP/30NF/10C/2.5N	4.20	1.62
55VPP/30NF/10C/5N	3.99	1.49
60RPP/30NF/10C	5.37	1.95
57.5RPP/30NF/10C/2.5N	4.85	1.86
55RPP/30NF/10C/5N	4.42	1.63

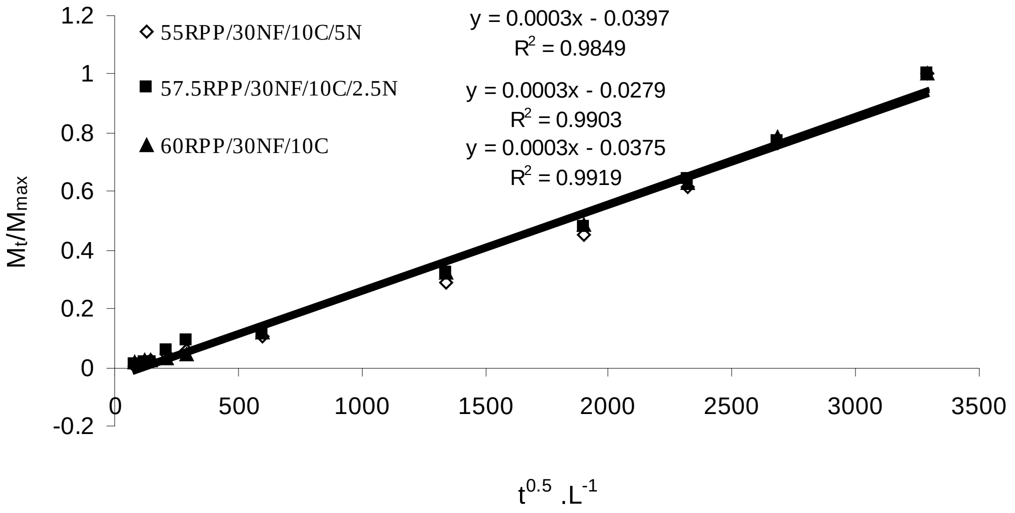

Fig. 3. Water uptake ratio (M_t/M_∞) versus time$^{1/2}$ for all formulations

Characterization of the morphological state of the polypropylene/newsprint fiber nanocomposites was accomplished using X-ray diffraction. To verify a homogeneous dispersion of nanoparticles (so-called intercalation and exfoliation) in a polymer matrix, the interlayer spacing in nanolayered silicates (Bragg's law) and the relative intercalation (RI) of the polymer in nanoclay were quantified using the following equations:

$$n\lambda = 2d\sin\theta \tag{4}$$

$$\mathrm{RI} = \frac{d - d_0}{d_0} \times 100 \tag{5}$$

where n is the integer number of wavelength (n = 1), λ is the wavelength of the X-ray beam, d is the interlayer or d-spacing of the clay in the nanocomposite, θ is half of the angle of diffraction, and d_0 is the the spacing of the clay layers in the pristine clay.

The X-ray scattering intensities for composites with different levels of nanoclay are listed in Table 4. This table shows that the order intercalation and relative intercalation of samples increased with increase of nanoclay content up to 2.5% and then decreased. The peaks appearing at 2.8° correspond to powdered nanoclay with d_{001} = 31.5 nm. In the sample with the addition of 2.5% nanoclay, the peak was shifted to a lower angle (2θ = 2.37°, d_{001} = 37.3 nm), which implies formation of the intercalated morphology. The increase of the interlayer distance and relative intercalation might result from the stronger shear during processing when the newsprint fiber introduced. These data show that the order of intercalation was higher for 2.5% of nanoclay. Also, the clay was not exfoliated, since the peak still obviously existed. In other words, formation of the intercalated morphology and better dispersion was shown at the 2.5% level of nanoclay, because the peak of that was shifted to a lower angle.

Table 4. Summary of XRD Data of Nanoclay Content in Polypropylene/Newsprint Fiber Composites

Nanoclay Content (%)	2θ (°)	d-spacing (nm)	Relative Intercalation (%)
Pure nanoclay	2.8	31.5	-
2.5	2.37	37.3	18.41
5	2.46	35.8	13.65

CONCLUSIONS

1. The extent to which virgin plastic is used has a significant effect on the water absorption of wood-plastic composites. The maximum water absorption increased with the increase of recycled plastic loading. The water absorption of the newsprint fiber/recycled plastic composites was higher than those prepared with virgin plastic.
2. With addition of nanoclay content in composite, water absorption decreased.
3. Water absorption of all formulations was proved to follow the kinetics of a Fickian diffusion process.
4. XRD data show the formation of the intercalation morphology and better dispersion with 2.5% of nanoclay.

REFERENCES CITED

Adhikary, K. B., Pang, S., and Staiger, M. P. (2008). "Long-term moisture absorption and thickness swelling behavior of recycled thermoplastics reinforced with *Pinus radiata* sawdust," *Chem. Eng. J.* 142, 190-198.

Alexandre, M., and Dubois, P. (2000). "Polymer-layered silicate nanocomposites: Preperation, properties and use of a new class of materials; A review," *J. Mater. Sci. Eng.* 28, 1-63.

Ashori, A., and Nourbakhsh, A. (2009). "Effects of nanoclay as a reinforcement filler on the physical and mechanical properties of wood based composite," *Compos. Mater.* 43(18), 1869-1875.

Ashori, A., and Nourbakhsh, A. (2011). "Preparation and characterization of polypropylene/wood flour/nanoclay composites," *European Journal of Wood and Wood Products*, DOI: 10.1007/s00107-010-0488-9.

Nourbakhsh, A., Foad Farhani Baghlani, F., and Ashori, A. (2011). “Nano-SiO_2 filled rice husk / polypropylene composites: Physico-mechanical properties,” *Industrial Crops and Products* 33(1), 183-187.

Bharadwaj, R. K., Mehrabi, A. R., Hamilton, C., Trujillo, C., Murga, M., Fan, R., Chavira, A., and Thompson, A. K. (2002). “Structural property relationship crosslinked polyester clay nanocomposites,” *Polym. J*. 43, 3699-3705.

Espert, A., Vilaplana, F., and Karlsson, S. (2004). “Comparison of water absorption in natural cellulosic fibers from wood and one-year crops in polypropylene composites and its influence on their mechanical properties,” *Compos Part A*, 35, 1267-1276.

George, J., Sreekala, M. S., and Thomas, S. (2001). “A review on interface modification and characterization of natural fiber reinforced plastic composites,” *Polym. Eng. Sci.* 41(9), 1471-1485.

Ghasemi, I., and Kord, B. (2009). “Long-term water absorption behavior of polypropylene/ wood flour/organoclay hybrid nanocomposite,” *Irani Polym. J*. 18(9), 683-691.

Han, G., Lei, Y., Wu, Q., Kojima, Y., and Suzuki, S. (2008). “Bamboo-fiber filled high density polyethylene composites; Effect of coupling treatmentand nanoclay,” *J. Polym. Enviro*. 21, 1567-1582.

Hemmasi, A., Khademi-Eslam, H., Talaiepoor, M., Ghasemi, I., and Kord, B. (2010). “Effect of nanoclay on the mechanical and morphological properties of wood polymer nanocomposite,” *J. Reinf. Plas. Comp.* 29(7), 964-971.

Hetzer, M., and Kee, D. (2008). Wood/polymer/nanoclay composites, environmentally friendly sustainable technology; A review. *Chemi. Engineer J*. 16, 1016-1027.

Kazemi Najafi, S., Hamidinia, E., and Tajvidi, M. (2006). “Mechanical properties of composites from sawdust and, recycled plastics,” *J. Appl. Polym. Sci*. 100, 3641-3645.

Kazemi Najafi, S., Tajvidi, M., and Hamidina, E. (2007). “Effect of temperature, plastic type and virginity on the water uptake of sawdust/plastic composites,” *Holz Roh-Werkst* 65(5), 377-382.

Kord, B., Hemmasi, A., and Ghasemi, I. (2010). “Properties of PP/wood flour/ organomodified montmorillonite nanocomposite,” *Wood Sci Technol*. 45, 111-119.

Kord, B. (2010). “Effect of organo-modified layered silicates on flammability performance of HDPE/ Rice husk flour nanocomposite,” *J. Appl. Polym. Sci*. 120, 607-610.

Lei, Y., Wu, Q., Clemons, C. M., Yao, F., and Xu, Y. (2007). “Influence of nanoclay on properties of HDPE/wood composites,” *J. Appl. Polym. Sci*. 18, 1425-1433.

Merdas, I., Thominette, A., Tcharkhtchi, A., and Verdu, J. (2001). “Factors governing water absorption by composite matrices,” *Compos. Sci. Tech*. 62, 487-492.

Nourbakhsh, A., Ashori, A., Ziaei Tabari, H., and Rezaei, F. (2010). “Mechanical and thermo-chemical properties of wood-flour polypropylene blends,” *Polym. Bull*. 65(7), 691-700.

Pothan, L. A., and Thomas, S. (2004). “Effect of hybridization and chemical modification on the water absorption behavior of banana fiber-reinforced polyester composites,” *J. Appl. Polym. Sci*. 91, 3856-3865.

Rana, H. T., Gupta, R. K., Ganga Rao, H. V. S., and Sridhar, L. N. (2005). "Measurement of moisture diffusivity through layered-silicate nanocomposites," *AIChE J*. 51, 3249-3256.

Tjong, S. C. (2006). "Structural and mechanical properties of polymer nanocomposites; A review," *J. Mater. Sci. Eng.* 53, 73-197.

Utracki, L. A., Sepehr, M., and Boccaleri, E. (2007). "Synthetic layered nanoparticles for polymeric nanocomposites (PNCs); A review," *J. Polym. Adv. Technol.* 8, 1-37.

Viswanathan, V., Laha, T., Balani, K., Agarwal, A., and Seal, S. (2006). "Challenges and advances in nanocomposite processing techniques; A review," *J. Mater. Sci. Eng.* 54, 121-285.

Wu, Q., Lei, Y., Clemons, C. M., Yao, F., Xu, Y., and Lian, K. (2007). "Properties of HDPE/clay/wood nanocomposites," *J. Plast. Tech*. 27, 108-115.

Yang, H. S., Kim, H. J., Park, H. J., Lee, B. J., and Hwang, T. S. (2006). "Water absorption behavior and mechanical properties of lignocellulosic filler- polyolefin bio-composites," *Compos. Struct*. 72(4), 429-437.

Zhao, Y., Wang, K., Zhu, F., Xue, P., and Jia, M. (2006). "Properties of poly (vinylchloride)/ woodflour/montmorillonite composites: Effects of coupling agents and layered silicate," *J. Polym. Degrad. Stabil.* 91, 2874-2883.

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