NANOFILLER REINFORCEMENT EFFECTS ON THE THERMAL, DYNAMIC MECHANICAL, AND MORPHOLOGICAL BEHAVIOR OF HDPE/RICE HUSK FLOUR COMPOSITES

Behzad Kord [a,*]

Polymer nanocomposites reinforced with lower volume fractions of nanofiller have recently attracted steadily growing interest due to their peculiar and fascinating properties as well as their unique applications in commercial sectors. In this study, composites based on high density polyethylene and rice husk flour with different loading of nanoclay were fabricated in an internal mixer. The influence of nanofiller at four levels (0, 2, 4, and 6 per hundred compounds (phc)) on the thermal and rheological behavior was studied. The morphology of nanoclay was determined by X-ray diffraction (XRD), and the effect of morphology on the thermal and dynamic mechanical properties were considered. Results indicated that the crystallization temperature, crystallization enthalpy, and crystallinity level increased with increase of nanoclay up to 2 phc and then decreased. Also, the dynamic mechanical behavior of composites was improved by the addition of nanofiller. X-ray diffraction patterns (XRD) revealed that the nanocomposites formed were intercalated. Morphological findings showed that samples containing 2 phc of nanoclay had higher order of intercalation and better dispersion. It seems that the thermal and dynamic mechanical properties of the HDPE/rice husk flour composites were improved by increasing addition of coupling agent.

Keywords: Reinforcement; Nanofiller; Thermal Behavior; Rheological Property; X-ray Diffraction

Contact information: a: Assistant Professor, Department of Wood Science and Paper Technology, Islamic Azad University, Chalous Branch, P.O. Box: 46615/397, Mazandaran, Iran.
**Corresponding author: behzad_k8498@yahoo.com*

INTRODUCTION

Fillers play important roles in modifying the desirable properties of polymers and reducing the cost of their composites. In conventional polymer composites, many inorganic filers with dimensions in the micrometer range, e.g. calcium carbonate, glass beads, and talc have been used extensively to enhance the mechanical properties of polymers. Such properties can indeed be tailored by changing the volume fraction, shape, and size of the filler particles (Tjong 2006; Utracki 2007). A further improvement of the mechanical properties can be achieved by using filler materials with a larger aspect ratio, such as short glass fibers (Viswanathan et al. 2006). It is logical to anticipate that the dispersion of fillers with dimensions in the nanometer level having very large aspect ratio and stiffness in a polymer matrix could lead to even higher mechanical performances (Alexandre and Dubois 2000).

Recently, polymer nanocomposites have attracted great interest, both in industry and in academia, because they often exhibit remarkable improvements in materials properties when compared with virgin polymer or conventional micro- and macro-composites. Among the many types of nanocomposites studied and applied in industry, the most promising are polymer nanocomposites prepared with platelet nanofillers, most frequently with montmorillonite (Ray and Okamoto 2003). Montmorillonite (MMT) is the most commonly used layered silicate because of its natural occurrences and beneficial properties (high cationic exchange capacity, high surface area, and large aspect ratio) (Tjong 2006; Utracki 2007). Essential improvements of physical and mechanical properties including tensile modulus and strength, flexural modulus and strength, thermal stability, flame resistance, and barrier resistance have been observed for various thermoplastic and thermoset nanocomposites at low silicate content (Koo et al. 2002; Wu et al. 2007; Lei et al. 2007; Chen 2007; Samal et al. 2008; Kord et al. 2010).

Many efforts have been made in the formation of wood polymer composite (WPC), to improve such properties so as to meet specific end-use requirements. Both thermoplastic and thermosetting systems have been used and have achieved certain improvements in wood properties, but both showed limitations (Hetzer and Kee 2008; Han et al. 2008). Nanotechnological preparation of WPCs could represent a promising new approach to obtain better products. Few attempts, however, have been made in this regard. The main objective of this study is to evaluate the effect of nanoclay on the thermal, dynamic mechanical, and morphological behavior of polymer composite based on high density polyethylene and rice husk flour.

EXPERIMENTAL

Materials

High density polyethylene (HDPE) with a melt flow index (MFI) of 11 g/ 10min, and a density of 0.954 g/cm^3 was supplied by Arak Petrochemical Industries, Iran. Rice husk flour (RF) was used as the reinforcing fiber material was from Cellulose Aria Co. (Iran). Maleic anhydride polyethylene (MAPE) provided by Merck Co. (purchased from Arak Petrochemical Industries), was used as coupling agent (wherein the grafting rate of the maleic anhydride was 0.1 wt. %). Montmorillonite (MMT) modified with a quaternary ammonium salt (trimethylammonium chloride) of bis-2-hydroxyethyl tallow as an organic modifier, having a Cationic Exchange Capacity (CEC) of 90 meq/100g clay, a density of 1.98 g/cc, and a d-spacing of d_{001}=18.5A^o was obtained from Southern Clay Products Co, USA, with the trade name Cloisite 30B.

Composite Preparation

Before preparation of samples, rice husk flour was dried in an oven at (65 ± 2) °C for 24 hours. Then high density polyethylene, rice husk flour, nanofiller, and coupling agent were weighed and bagged according to formulations given in Table 1. The mixing was carried out with a Hakee internal mixer (HBI System 90, USA). First the high density polyethylene was fed into the mixing chamber. After melting of the HDPE, the coupling agent and nanoclay were added. At the fifth minute, the rice husk flour was fed, 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 resulting granules were dried at 105°C for 4 hours. Test specimens were prepared by injection molding (Eman Machine, Iran). Finally, specimens were conditioned at a temperature of 23 °C and relative humidity of 50% for at least 40 h according to ASTM D618-99 prior to testing.

Table 1. Composition of the Studied Formulations

Timar	HDPE Content (Wt. %)	Rice Husk Flour Content (Wt. %)	Nanoclay Content (Phc)*	MAPE Content (Phc)
A	50	50	0	2
B	50	50	2	2
C	50	50	4	2
D	50	50	6	2

*Per hundred compound

Measurements

The crystallization behavior of the samples was measured using a differential scanning calorimeter (DSC 131, France). According to ASTM D 3418, the samples of 4 to 5 mg were placed in aluminum capsules and heated from 25 to 200 °C at the rate of 5 °C/min to eliminate the heat history before cooling at 10 °C/min. From the crystallization curves that were recorded by computer, crystallization temperature (T_c), crystallization enthalpy, and crystallinity level (X_c) can be obtained.

A Du Pont 983 DMA instrument was used to characterize the dynamical mechanical behavior of the material at different temperatures. The dynamic properties were studied in fixed frequency mode at a frequency of 1 Hz and strain amplitude of 0.2 mm. The samples were heated in the temperature range from - 40 to +160 °C at a heating rate of 10 °C/min.

The tensile tests were measured according to D638-03, using an Instron machine (Model 1186, England); the tests were performed at crosshead speeds of 2mm/min. A Zwick impact tester (Model 5102, Germany) was used for the Izod impact test. All the samples were notched on the center of one longitudinal side according to ASTM D256. For each treatment level, five replicate samples were tested.

Wide angle X-ray diffraction (XRD) analysis was carried out with a Seifert-3003 PTS (Germany) with CuKα radiation (λ=1.54 nm, 50kV, 50mA) at room temperature; the scanning rate was 1^o /min.

RESULTS AND DISCUSSION

Morphological Behavior

Characterization of the morphological state of the hybrid composite was accomplished using X-ray diffraction. The X-ray scattering intensities for composites with different levels of nanoclay at the 2phc MA concentration are listed in Table 2. This table shows that with increasing nanofiller content the order of intercalation decreased. In other words, formation of the intercalation morphology and better dispersion was shown at a 2phc concentration of nanoclay, because the peak of sample with 2phc concentration of nanoclay was shifted to a lower angle. It seems that this is because of the limited value of MAPE in the nanocomposites. It is well known, through the improvement of the compatibility between neat HDPE and clay (using MAPE), the polymer chains could be well diffused into the clay layers, and the basal spacing of clay layers might be increased (Zhao et al. 2006; Han et al. 2008; Kord et al. 2010). In the case of polymers containing polar functional groups, alkyl ammonium surfactant modified nanofiller is adequate to promote nanocomposite formation. However, in the case of high density polyethylene, it is frequently necessary to use a coupling agent, such as maleic anhydride polyethylene (MAPE). So, we expected that the MAPE in lower concentration of clay has higher efficiency to affect the d-spacing of the layers. Kord et al. (2010) found that with increasing of nanoclay to 6 phc, the size of dispersed nanoclay became larger or even aggregated in part, and the presence of coupling agent improved the dispersion of the nanoclay as the clay aggregates were broken down into smaller stacks.

Table 2. Summary of XRD Data of Nanofiller Dispersion in the HDPE/Rice Husk Flour Composites

Sample	2θ (^{o})	d-spacing (nm)
Pure nanoclay	4.76	18.5
Composite + 2 phc nanoclay	4.35	20.26
Composite + 4 phc nanoclay	4.46	19.80
Composite + 6 phc nanoclay	4.57	19.33

Thermal Properties

The effects of nanofiller content on the thermal behavior of the HDPE/rice husk flour composites are listed in Table 3. The crystallization temperature, crystallization enthalpy, and crystallinity level increased with increase of nanoclay up to 2 phc and then decreased. Crystallization behavior of polymers with nanoclay has been studied extensively. Many studies have shown a nucleating effect of nanoclay for different polymers (Kodgire et al. 2001; Maiti et al. 2002; Ma et al. 2002). This effect can be used to enhance the thermal behavior of the polymer. These increases indicated the nucleating effect of the nanofiller in the crystallization of the HDPE/rice husk composite. On the other hand, the nucleation efficiency and the crystallinity of composite can be improved by the presence of the nanofiller as a nucleating agent.

Table 3. Effect of Nanofiller on the Thermal Properties of the HDPE/Rice Husk Flour Composites

Nanoclay Content (Phc)	Crystallization Temperature (^{0}C)	Crystallization Enthalpy (J/g)	Crystallinity Level (%)
0	115.89	159.39	52.43
2	117.07	172.26	58.08
4	116.67	167.75	56.65
6	116.24	165.81	55.33

Generally the loading level, the dispersion, the surface chemistry of nanofillers, and the viscosity of composites can be expected to affect the thermal behavior (Mishra et al 2005). Also, it has been reported that clay, especially exfoliated clay, can increase the crystallization temperature and act as a nucleating agent (Lei et al 2007). In our research, the increase in thermal properties may also be attributed to the formation of intercalated nanocomposite structures formed at these loadings of clay. At higher weight loading, decreasing thermal properties may be attributed to the formation of agglomerated clay tactoids (Koo et al. 2002; Chen et al. 2007; Mohanty and Nayak 2007; Samal et al. 2008; Kord et al. 2010). Another reason is that the chain mobility of HDPE might be reduced by the addition of nanoclay (Lei et al 2007). It was believed that reduction effect of chain mobility on crystallization temperature overwhelmed that of the nucleation, resulting in lowered crystallization temperature and crystallization rate.

The crystallization rate of the polymer matrix has been shown to have an inverse effect on the intercalation and exfoliation of the polymer chains into the clay gallery spacing. The interlayer spacing of the clay gallery increases with the crystallization temperature. A higher interlayer spacing of nanoclay occurs in a high-temperature region. At high crystallization temperature, the crystallization rate is sufficiently slow and the polymer chains have sufficient time to intercalate inside the silicate galleries. With an increase of crystallization temperature and a decrease of clay content in nanocomposites, more and more chains find themselves within the silicate galleries, giving rise to higher intercalated species. The extent of intercalation strongly depends on the time the clay is exposed to the molten matrix (Hetzer and Kee 2008).

Dynamic Mechanical Study

The effects of nanofiller content on the dynamic mechanical behavior of the HDPE/rice husk flour composite are listed in Table 4. The storage and loss modulus values were increased with increase of the nanoclay loading. The dynamic mechanical behavior of the nanocomposite materials is related to the properties of the components, the morphology of the system, and the nature of the interface between the nanofiller and polymer matrix. When nanoclay is added to a matrix to form a polymer nanocomposite, an interphase is created. This interphase is very sensitive to the surface modification of nanofiller, such as the compatibility between the nanoclay and the matrix (Mishra et al 2005). Based on the results of this study, we can see that the storage and loss modulus was improved considerably. This improvement was, however, more obvious for the surface modified layered silicate (OMMT). Wang et al. (2001) reported that the addition of 1% nanoclay to a HDPE matrix resulted in a storage modulus increase of two percent at low frequency.

Table 4. Effect of Nanofiller on the Dynamic Mechanical Behavior of the HDPE/Rice Husk Flour Composites

Nanoclay Content (Phc)	Storage Modulus (GPa)	Loss Modulus (GPa)
0	1.75	0.15
2	1.84	0.16
4	1.87	0.17
6	1.90	0.18

Mechanical Properties

The effects of nanofiller content on the mechanical properties of the HDPE/rice husk flour composite are listed in Table 5. The tensile strength and modulus increased with increase of nanoclay up to 2 phc and then decreased. At low weight of nanoclay loadings the enhancement of properties is attributed to the lower percolation points created by the high aspect ratio nanoclays. The increase in properties may also be attributed to the formation of intercalated and exfoliated nanocomposite structures formed at these loadings of clay (Wang et al. 2001; Lei et al. 2007; Wu et al. 2007; Han et al. 2008). At higher weight loading, decreasing mechanical properties may be attributed to the formation of agglomerated clay tactoids (Koo et al. 2002; Chen et al. 2007; Mohanty and Nayak SK 2007; Samal et al. 2008).

As can be seen, the impact strength of the composites decreased with increasing nanoclay loading (Table 5). The decrease in impact strength at higher nanoclay content levels is probably due to the formation of clay agglomeration and the presence of un-exfoliated aggregates and voids (Zhao et al. 2006; Hetzer and Kee 2008).

Table 5. Effect of Nanofiller on the Mechanical Properties of the HDPE/Rice Husk Flour Composites

Nanoclay Content (Phc)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Impact Strength (MPa)
0	25.64 ± 0.09	2567.12 ± 10.45	18.39 ± 0.05
2	29.83 ± 0.13	3209.64 ± 12.63	17.82 ± 0.03
4	28.45 ± 0.11	3128.47 ± 11.74	17.16 ± 0.02
6	27.71± 0.11	3075.53 ± 11.52	16.89 ± 0.02

CONCLUSIONS

The following conclusions could be drawn from the results of the present study:

1. The crystallization temperature, crystallization enthalpy, and crystallinity level increased with increase of nanoclay up to 2 phc and then decreased.

2. The storage and loss modulus of composite were improved by addition of nanofiller.

3. X-ray diffraction patterns (XRD) revealed that the nanocomposites formed were intercalated. Also, morphological findings showed that samples containing 2phc of nanoclay had higher order of intercalation and better dispersion.

4. It seems that with increase of coupling agent a fully exfoliation morphology could be obtained. Therefore, the thermal and rheological properties of the HDPE/rice husk flour composites were improved by increasing MAPE content.

REFERENCES CITED

Alexandre, M., and Dubois, P. (2000). "Polymer-layered silicate nanocomposites: Preperation, properties and use of a new class of materials. A review," *Journal of Material Science and Engineering* 28, 1-63.

Chen, H., Wang, M., Lin, Y., Chan, C. M., and Wu, J. (2007). "Morphological and mechanical property of binary polypropylene nanocomposites with nanoclay particles," *Journal of Applied Polymer Science* 103, 4451-4458.

Han, G., Lei, Y., Wu, Q., Kojima, Y., and Suzuki, S. (2008). "Bamboo–fiber filled high density polyethylene composites. Effect of coupling treatmentand nanoclay," *Journal of Polymer Enviroment* 21, 1567-1582.

Hetzer, M., and Kee, D. (2008). "Wood/polymer/nanoclay composites, environmentally friendly sustainable technology. A review," *Journal of Chemical Engineering* 16, 1016-1027.

Kodgire, P., Kalgaonkar, R., Hambir, S., Bulakh, N., and Jog, J. P. (2001). "PP/clay nanocomposites: Effect of clay treatment on morphology and dynamic mechanical properties," *Journal of Applied Polymer Science* 81(7), 1786-1794.

Koo, C. M., Ham, H. T., Kim, S. O., Wang, K. H., and Chung, I. (2002). "The effect of crystallization on the structure and morphology of polypropylene/clay nanocomposites," *Macromolecules* 35, 5116-5130.

Kord, B., Hemmasi, A., Khademi-Eslam, H., Talaiepoor, M., and Ghasemi, I. (2010). "Effect of nanoclay on the mechanical and morphological properties of wood polymer nanocomposite," *Journal of Reinforced Plastics and Composites* 29(7), 964-971.

Lei, Y., Wu, Q., Clemons, C. M., Yao, F., and Xu, Y. (2007). "Influence of nanoclay on properties of HDPE/wood composites," *Journal of Applied Polymer Science* 18, 1425-1433.

Ma, J., Zhang, S., Qi, Z., Li, G., and Hu, Y. (2002). "Crystallization behaviors of polypropylene/montmorillonite nanocomposites," *Journal of Applied Polymer Science* 83, 1978-1985.

Maiti, P., Nam, P. H., Okamoto, M., Hasegawa, N., and Usuki, A. (2002). "Influence of crystallization on intercalation, morphology, and mechanical properties of polypropylene/clay nanocomposites," *Macromolecules* 35, 2042-2049.

Mishra, J. K., Hwang, K. J., and Ha, C. S. (2005). "Preparation, mechanical and rheological properties of thermoplastic polyolefin (TPO)/organoclay nanocomposites with reference to the effect maleic anhydride modified polypropylene as a compatibilizer," *Polymer* 46, 1995-2002.

Mohanty, S., and Nayak, S. K. (2007). "Effect of clay exfoliation and organic modification on morphological, dynamic mechanical and thermal behavior of melt compounding polyamide-6 nanocomposites," *Journal of Polymer Composite* 153-162.

Ray, S., and Okamoto, M. (2003). "Polymer/layered silicate nanocomposites. A review from preparation to processing," *Progress in Polymer Science* 28, 1539-1641.

Samal, S. K., Nayak, S., and Mohanty, S. (2008). "Polypropylene nanocomposites. Effect of organo-modified layered silicates on mechanical, thermal and morphological performance," *Journal of Thermoplastic Composite Material* 8, 243-263.
Tjong, S. C. (2006). "Structural and mechanical properties of polymer nanocomposites; A review," *Journal of Material Science and Engineering* 53, 73-197.
Utracki, L. A., Sepehr, M., and Boccaleri, E. (2007). "Synthetic layered nanoparticles for polymeric nanocomposites (PNCs); A review," *Journal of Polymer Advanced Technology* 18, 1-37.
Viswanathan, V., Laha, T., Balani, K., Agarwal, A., and Seal, S. (2006). "Challenges and advances in nanocomposite processing techniques; A review," *Journal of Material Science and Engineering* 54, 121-285.
Wang, K. H., Choi, M. H., Koo, C. M., Choi, Y. S., and Chung, I. J. (2001). "Synthesis and characterization of maleated polyethylene/clay nanocomposites," *Journal of Polymer* 42, 9819-9826.
Wu, Q., Lei, Y., Clemons, C. M., Yao, F., Xu, Y., and Lian, K. (2007). "Properties of HDPE/clay/wood nanocomposites," *Journal of Plastic Technology* 27, 108-115.
Zhao, Y., Wang, K., Zhu, F., Xue, P., and Jia, M. (2006). "Properties of poly(vinylchloride)/woodflour/montmorillonite composites: Effects of coupling agents and layeredsilicate," *Polymer Degradation and Stability* 91, 2874-2883.

Article submitted: December 8, 2010; Peer review completed: January 12, 2011; Peer review of revised version completed: March 4, 2011; Revised version received and accepted: March 5, 2011; Published: March 7, 2011.