DE GRUYTER DOI 10.1515/secm-2012-0091 — Sci Eng Compos Mater 2013; 20(1): 1–6

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Influence of nanoparticle on hygroscopic thickness swelling rate of composites from hemp fiber and recycled plastic

Abstract: In this study, the effect of nanoparticle on hygroscopic thickness swelling rate of composites from hemp fiber and recycled plastic was investigated. To meet this objective, hemp fiber was mixed with either virgin or recycled polypropylene (PP) at 50% by weight fiber loading. The samples were made by melt compounding and then injection molding. The concentration was varied as 0, 1, and 3 per hundred compounds (phc) for nanoclay. The amount of coupling agent was fixed at 2 phc for all formulations. The long-term thickness swelling rate of samples was evaluated by immersing them in water at room temperature for several weeks (up to 3000 h). The results indicated that whether or not virgin plastic is used has a significant effect on the thickness swelling of composites. The thickness swelling of the hemp fiber/recycled plastic composites was higher than those of virgin plastics. Furthermore, with the addition of nanoclay content in composites, thickness swelling decreased. The swelling rate parameter (K_{SR}) of the composites was influenced by plastics virginity and nanoclay. The minimum K_{SR} values were observed in composites made of 50VPP/50F/2C/3N. Morphological findings showed that samples containing 1 phc of nanoclay had higher order of intercalation and better dispersion.

Keywords: dispersion; hemp fiber; nanoparticle; plastics virginity; thickness swelling.

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1 Introduction

Wood-plastic composites (WPCs) are a new type of material used for housewares, car interiors (dashboards and rigid panel components) and various construction materials. They combine the favorable performance and low-cost attributes of wood and plastics [1]. The convenience of these composites lies in the fact that one of their ingredients (i.e., wood, a lignocellulosic material) can be easily obtained from natural resources and they can be made relatively easily [2]. They offer the possibility of resolving various environmental problems and fabricating products with a variety of properties and effective functions. The utilization of lignocellulosic materials would contribute to the sustainability of based resources. The substitution of the inorganic substances and synthetic fibers generally used as reinforcing fillers in plastics with lignocellulosic materials would contribute to the environmental protection. The benefits offered by lignocellulosic materials include making the final product lighter and decreasing the wear of the machinery used in the production process. Moreover, unlike traditional inorganic materials, the lignocellulosic materials are low cost and biodegradable [3]. In addition, these materials also help various agrowastes to be appropriately recycled. As a result, composites using lignocellulosic materials as reinforcing fillers have come to be used extensively in the automotive industry and as interior finishing materials, such as window frames and wood decks. In the past decades, wood composites have been extended to flooring, instrument grips, and pallet areas [2].

The market of natural-fiber-reinforced composites is one of the world's largest and fastest growing markets, which is in part due to the public desire to consume environmentally compatible products. Therefore, various sectors of industry are looking for novel materials having such properties [3]. Hemp production is easy to achieve organically; therefore, many of the ecological problems in chemical farming of other fibers are obviated. Hemp has been produced for thousands of years as a source of fiber for paper, cloth, sails/canvas, and construction materials. Furthermore, using hemp fiber to make composites can introduce a more effective application for this material [4].

In WPC manufacturing, virgin plastics such as high- and low-density polyethylene, polypropylene (PP), and polyvinyl chloride 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 WPCs. Plastic wastes are one of the major components of global municipal solid waste and present a promising raw material source for WPCs (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 of plastic waste per day with an annual increase of 25%. Hence, the development of new value-added products (WPCs), with the aim of utilizing the wood waste (thus eliminating the 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 [5, 6].

Nanoscience and nanotechnology have opened up a completely new way to develop WPCs [7, 8]. Nanotechnology is a very promising field for improving the properties of WPCs using nanosized fillers. These improvements include high mechanical strength and thermal stability, decreased gas permeability, improved flammability properties, decrease in water absorbance, and increased biodegradability of biodegradable polymers [9]. Using nanoclay filler in WPCs has been reported in the literature [10–18]. Many efforts have been made in the formation of wood-polymer composite to improve such properties so as to meet specific end-use requirements.

Water absorption and the consequent thickness swelling are the most important physical characteristics of WPCs exposed to environmental conditions and thus affect their end-use applications. Moisture 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 [19–21].

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 thickness swelling of composites from hemp fiber and nanoclay has been considered.

2 Materials and methods

2.1 Materials

The nanoparticle used in this study was natural montmorillonite modified with a quaternary ammonium salt (dimethyl ammonium chloride) of dehydrogenated tallow as an organic modifier, having a cationic exchange capacity of 125 meq/100 g clay, density of 1.66 g/cm^3, and a d-spacing of d_{001}=31.5 Å (trade name Cloisite 15 A, Southern Clay Products Co., TX, USA). Polypropylene, which is used as the polymer matrix, was obtained from Arak Petrochemical Company (Markazi Province, Iran) and has a density of 0.92 g/cm^3 and a melt flow index (MFI) of 18 g/10 min. Maleic anhydride grafted PP (PP-g-MA), provided by Solvay (Solvey International Chemical Group, Brussels, Belgium) with the trade name of Priex 20070 (MFI=64 g/min, grafted maleic anhydride 0.1 wt%) was used as coupling agent. Virgin PP and recycled PP were used as plastic matrix in newsprint fiber/organoclay nanocomposites. Virgin PP was purchased from Arak Petrochemical Company (trade name V30S) and has an MFI of 18 g/10 min. Recycled PP was obtained from waste spindle with an MFI of 31.5 g/10 min. Hemp, which is used as the reinforcing fiber material, was collected from a hemp field in Behshashr, a city in the southern region of Golestan province (Iran). Hemp fibers were separated from the hemp stalk through the warm water retting process; when the retting process is complete, the primary fibers are readily separated from the core. The hemp fibers averaged 100 mm in length.

2.2 Method

2.2.1 Composite preparation

Before the preparation of samples, hemp fiber was dried in an oven at 65±2°C for 24 h. Then, PP, hemp fiber, nanoclay, and coupling agent were weighed and bagged according to formulations given in Table 1. The mixing was carried out with a Haake internal mixer (HBI System

Sample code	Polypropylene (wt%)		Hemp fiber (wt%)	Coupling agent (phc)	Nanoclay (phc)
	Virgin	Recycled			
50VPP/50F/2C	50	–	50	2	0
50VPP/50F/2C/1N	50	–	50	2	1
50VPP/50F/2C/3N	50	–	50	2	3
50RPP/50F/2C	–	50	50	2	0
50RPP/50F/2C/1N	–	50	50	2	1
50RPP/50F/2C/3N	–	50	50	2	3

Table 1 Compositions of the studied formulations.
VPP, virgin polypropylene; RPP, recycled polypropylene; F, hemp fiber; C, coupling agent; phc, per hundred compounds.

90, CA, USA) at 180°C and 60 rpm. First, the PP was fed to the mixing chamber; after it was melted, the nanoclay and compatibilizer were added. At the fifth minute, hemp 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, Hamburg, Germany). The resulting granules were dried at 105°C for 4 h. Test specimens were injection-molded into ASTM standard by an injection molder at a molding temperature of 185°C and injection pressure of 3 MPa (Eman Machine, Tehran, Iran). Finally, the specimens were conditioned at a temperature of 23°C and relative humidity of 50% for at least 40 h according to ASTM D 618 prior to testing.

2.2.2 Measurements

Thickness swelling tests were carried out according to ASTM D 7031. Specimens with a dimension of 20 mm× 20 mm×20 mm were cut for the hygroscopic thickness swelling measurements. Five replicates were used for each sample code. To ensure the same moisture content for the specimens before each test, all the specimens were oven-dried at 102±3°C. The thickness of dried specimens was measured to a precision of 0.001 mm. 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 with blotting paper. Thicknesses of the specimens were measured at different times during the long-time immersion. The measurements were terminated after the equilibrium thicknesses of the specimens were reached. The values of the thickness swelling in percentage were calculated using Eq. (1),

$$TS(t)=\frac{T(t)\text{-}T_0}{T_0}\times 100 \tag{1}$$

where $TS(t)$ is the thickness swelling at time t, T_0 is the initial thickness of specimens, and $T(t)$ is the thickness at time t.

Eq. (1) was applied to the thickness swelling data for all composites. We noticed that Shi and Gardner [21] tried to quantify the thickness swelling rate of WPCs for more convenient comparisons. They developed a swelling model describing the hygroscopic swelling process of wood-based composites. In this model, a swelling rate parameter K_{SR}, as determined using the test data, can be used to quantify the swelling rate. The swelling model is expressed in the following equation,

$$TS(t)=\left(\frac{T_\infty}{T_0+(T_\infty\text{-}T_0)e^{\text{-}K_{SR}t}}\text{-}1\right)\times 100 \tag{2}$$

where $TS(t)$ is the thickness swelling at time t. T_0 and T_∞ are the initial and equilibrium board thickness, respectively. K_{SR} is a constant referred to as the initial (or intrinsic) relative swelling rate. The values of K_{SR} in Eq. (1) depend on how fast the composites swell and also on their equilibrium thickness swelling.

Nonlinear curve fitting was used to find the swelling rate parameter K_{SR} that provided the best fit between the equation and the data. This algorithm seeks the parameter values that minimize the sum of the squared differences between the observed and predicted values of the dependent variable, as seen in Eq. (3),

$$SS=\sum_{i=1}^{n}(y_i\text{-}\hat{y}_i)^2 \tag{3}$$

where SS is the sum of squared differences, and y_i and $\hat{y}_i$ are the observed and predicted values of the dependent variable, respectively.

The degree of nanoparticle dispersion in PP/hemp fiber composites were characterized by X-ray diffraction (XRD) method. XRD measurements taken on powdered nanoclay and nanocomposites were carried out with a Seifert-3003 PTS (Germany) using CuKα radiation (λ=1.54 nm) at room temperature; the generator power was 50 kV and 50 mA. The scan mode was continuous with a scan rate of 1°/min in scan range from 0° to 12°.

3 Results and discussion

Thickness swelling curves of different composites are illustrated in Figure 1, where the percentage of thickness swelling is plotted against time for all samples. As can be clearly seen, generally thickness swelling increased with immersion time, reaching a certain value at a saturation point, beyond which no more water was absorbed and the composite's water content remained constant. Time to reach the saturation point was not the same for all formulations. The 50VPP/50F/2C/3N and 50RPP/50F/2C composites showed minimum (1.91%) and maximum (3.32%) thickness swelling, respectively. In composites, the maximum thickness swelling increased with the increase of recycled plastic loading. 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 (50%) in all formulations, the different thickness swelling between all manufactured composites can be attributed to the virginity of plastics. It seems that the quality of adhesion in interface phase,

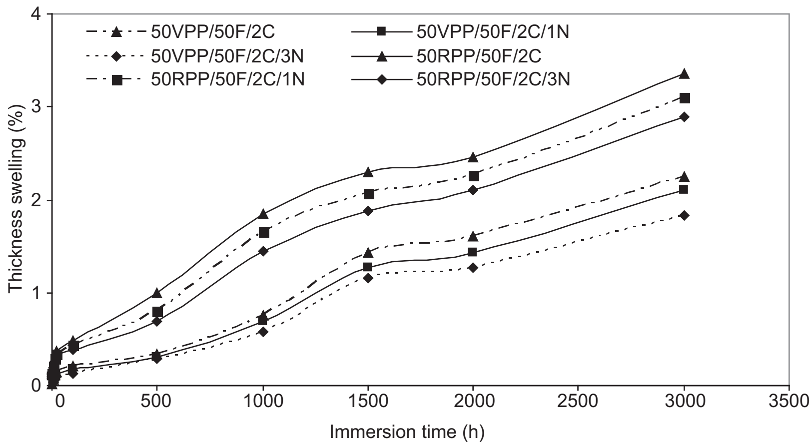

Figure 1 Effect of plastics virginity and the presence of nanoclay on thickness swelling of hemp fiber/PP composites.

different molecular and compositional differences (MFI and crystallinity) between virgin and recycled plastics which affected on the moisture sorption of composites. Therefore, the thickness swelling of the hemp fiber/recycled PP composites was higher than those of virgin plastics. Therefore, the thickness swelling of the hemp fiber/recycled PP composites was higher than those of virgin plastics.

Another interesting result in Figure 1 is that thickness swelling 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 hydrophobic nature of the clay surface that tends to immobilize some of the moisture [22]; second, surfactant-covered clay platelets form a tortuous path for water transport [23, 24]. 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 hydrophobic nature) and surfactant-covered clay platelets (tortuous path), so the water transport goes down under the severe conditions. Generally, when the nanoclay was well dispersed and formed exfoliation morphology in the composites the thickness swelling of samples decreased. The better dispersion of nanoclay by increasing of barrier property and tortuous path formation in samples caused a decrease in moisture absorption and thickness swelling. Furthermore, by increasing the agglomeration of clay into the samples the accessibility of moisture absorption decreased (a phenomenon called zigzag effect). Another reason for less water uptake could be the ability of nanoclay to act as a nucleating agent [15]. 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 moisture absorption and thickness swelling is less in the composites.

The swelling rate parameter K_{SR} of composites is given in Table 2. It can be seen that the composites containing 50RPP/50F/2C exhibited higher K_{SR} than those containing nanoclay. It is important to note that in the swelling model K_{SR} was obtained considering the whole thickness process until it was equilibrated; that is, it was dependent not only on the initial rate of swell but also on the equilibrium thickness swelling of the composites [21]. Table 2 shows that the K_{SR} of the composites was influenced by the chemical foaming agent and nanoclay. The

Sample code	W_0 (%)	W_∞ (%)	T_0 (mm)	T_∞ (mm)	TS (%)	K_{SR} ($\times 10^{-3}$ h^{-1})	R^2
50VPP/50F/2C	4.36	4.81	10.51	10.75	2.28	0.0073	0.85
50VPP/50F/2C/1N	3.88	4.20	10.63	10.86	2.16	0.0061	0.87
50VPP/50F/2C/3N	3.71	3.99	10.49	10.69	1.91	0.0054	0.90
50RPP/50F/2C	4.80	5.37	10.54	10.89	3.32	0.0096	0.82
50RPP/50F/2C/1N	4.42	4.85	10.61	10.94	3.11	0.0081	0.84
50RPP/50F/2C/3N	4.09	4.42	10.58	10.89	2.93	0.0069	0.93

Table 2 Thickness swelling values and swelling rate parameters for all formulations.
W_0, initial water absorption; W_∞, equilibrium water absorption; T_0, initial thickness; T_∞, equilibrium thickness; K_{SR}, swelling rate parameter.

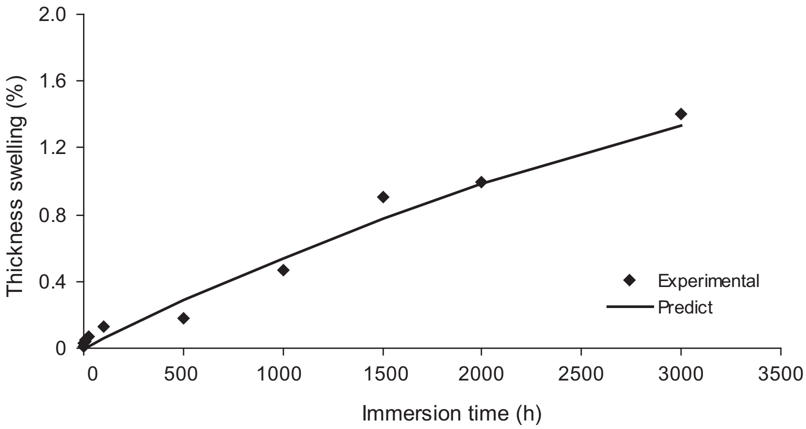

Figure 2 Experimental and prediction models for thickness swelling of 50VPP/50F/2C/3N composites.

minimum K_{SR} values were observed in composites made of 50VPP/50F/2C/3N.

Also, we predicted the thickness swelling curve of composites by nonlinear curve fitting. It is seen that the swelling model fits the experimental data well for most of the cases, as the R^2 values for all the model fits were above 0.80 (Table 2). For example, it can be seen from the Figure 2 that the model provides better prediction for the initial portion of the thickness swelling process of composites containing virgin plastic and 3% nanoclay. This phenomenon can be related to lower inner debonding or damage that could have occurred at higher swelling rates (higher water uptake). This could eventually lead to changes in the thickness swelling process and induce some error in the swelling model prediction. The relationships were established as:

50VPP/50F/2C/3N composites: $K_{SR}=0.071X+0.00186 \quad R^2=0.93$

Characterization of the morphological state of the composites was accomplished using XRD. 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:

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

$$\mathrm{RI}=[(d-d_0)\div d_0]\times 100 \tag{5}$$

where n is the integer number of wavelength (n=1), λ is the wavelength of X-ray, 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 d_0 of the clay in the pristine clay.

The X-ray scattering intensities for composites with different levels of nanoclay are listed in Figure 3. This figure shows that the order of intercalation and relative intercalation of samples increased with increase of nanoclay content up to 1 phc and then decreased. The peaks appearing at 2.8° correspond to powdered nanoclay with d_{001}=3.15 nm. In the sample with the addition of 1 phc nanoclay, the peak was shifted to a lower angle (2θ=2.30°, d_{001}=3.84 nm; RI=21.90), which implies formation of the intercalated morphology. By increasing the level of nanoclay to 3 phc, the d-spacing of nanoclay decreased (2θ=2.57°, d_{001}=3.43 nm; RI=8.89), and the size of dispersed nanoclay became larger or even aggregated in part. The increase of the interlayer distance and relative intercalation might result from the stronger shear during processing when the hemp fiber was introduced. These data show that the order of intercalation was higher for 1 phc of nanoclay. Also, the clay was not exfoliated, because the peak still obviously existed. In other words, formation of the intercalated morphology and better dispersion was shown at the 1 phc level of nanoclay, because the peak of that was shifted to a lower angle.

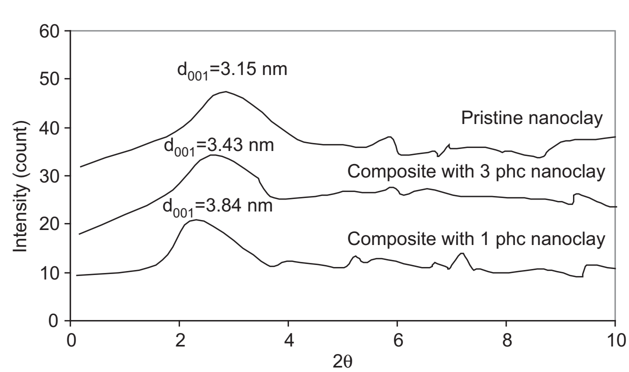

Figure 3 X-ray scattering intensities for PP/hemp fiber composites with different levels of nanoclay.

4 Conclusion

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

1. The extent to which virgin plastic is used has a significant effect on the thickness swelling of hemp fiber/PP composites. The maximum thickness swelling increased with the increase in recycled plastic loading. The thickness swelling of the hemp fiber/recycled plastic composites was higher than those prepared with virgin plastic.
2. The thickness swelling of the composite decreased with increase in nanoclay.
3. The K_{SR} of the composites was influenced by the plastics virginity agent and nanoclay. The minimum K_{SR} values were observed in composites made of 50VPP/50F/2C/3N.
4. The XRD tests clarify that the nanoclay in the hemp fiber/PP samples is not exfoliated, and the dispersion is in need of improvement. Also, morphological findings showed that samples containing 1 phc of nanoclay had higher order of intercalation and better dispersion.

Received August 26, 2012; accepted October 11, 2012; previously published online November 21, 2012

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