the water absorption

PREPARATION OF NANOCLAY REINFORCED HDPE/WOOD FLOUR FOAMES VIA INJECTION MOLDING

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Abstract

In present study, the effects of chemical blowing agent (CBA) and nanoclay (NC) on the physical, mechanical and morphological properties of composites based on high density polyethylene (HDPE) and wood flour were described. The amount of wood flour was fixed at 50 wt% for all samples. For NC (organomodified montmorillonite), and CBA (azodicarbonamide), different levels of 0, 2, 4, 6 per hundred resins (phr) and 0, 0.5, 1, 1.5 phr were considered respectively. Results indicate cell size and average cell density increased with rise of CBA content. However, by addition of NC, cell size and tensile modulus were declined whereas the cell density and the water absorption amplified. The optimal condition was attained by incorporating 0.5 phr blowing agent and 4 phr nanoclay in composite formulation.

1. Introduction

Global ecological concern has resulted in a renewed interest in natural materials such as natural organic fibers. These fibers have several advantages, such as high specific strength and modulus, low cost, low density, renewable nature, absence of associated health hazards, easy surface modification, wide availability, and relative non abrasiveness. Many scientists successfully have been developed thermoplastic/natural fibers composites, especially wood plastic composites (WPCs). These composites replaced natural wood in many fields, but their applications have been limited, because of weak modulus, low impact strength, low screwing- nailing ability, and relatively high

density, as well as their flammability [1]. The incorporation of nanoclay and foam structure into WPC has been studied to dramatically alleviate these drawbacks [2].

In recent years, an increasing interest in foamed wood polymer composites has been observed [3]. Foaming offers unique advantages such as decreasing weight and saving material cost [10-11]. Faruk et al. (2007) reported that the foaming of WPCs can improve their ability to withstand repeated nailing and screwing operations. In addition, the foaming of WPC results in material weight and cost reduction, better surface quality and sharper contours and corners than unfoamed profiles [4]. Matuana and Faruk (2010) were studied the effect of gas saturation conditions on the expansion ratio of microcellular poly (lactic acid)/wood-flour composites. They reported that the addition of wood flour into the PLA matrix significantly affected the expansion ratio of PLA/wood-flour composite foams [5].

Foams can be classified based on their cell density and cell size as shown in Table 1. It is well known that the physical and mechanical properties of foamed plastic composite are closely related to their cellular structures. Microcellular plastics typically exhibit higher impact strength (up to a five-fold increase over unfoamed plastic), higher toughness (up to a five-fold increase over unfoamed plastic), higher fatigue life (up to a fourteen-fold increase over unfoamed ones), higher heat-insulation property, higher sound-insulation property, and higher thermal stability [2, 5,7].

Foam Type	Cell Size	Cell Density
Conventional	> 300 μm	$< 10^6$ cell/cm^3
Fine-Celled	10-300 μm	10^6-10^9 cell/cm^3
Microcellular	< 10 μm	$> 10^9$ cell/cm^3

Table1. Foam Classification

Polymer nanocomposites form an emerging class of mineral filled plastics that contain relatively small amounts (usually 5 to 10 wt %) of nanometer-sized particles. Layered silicate clays, as in situ reinforcement, have been intensively investigated. Essential improvements of physical and mechanical properties, thermal stability, flame resistance, and barrier resistance have been observed for various thermoset and thermoplastic based nanocomposites, at low silicate content [8, 9]. Recently, nanoclay particles have also been used in the polymeric wood plastic foams [2]. Lee (2008) were investigated the foaming behaviors of thermoplastic-based wood flour/nanoclay composites using N2 as the blowing agent in an extrusion process. He found that the cell nucleation and growth behaviors of wood flour/polyolefin/clay composite foams were elucidated while varying the temperature, pressure, wood flour content, clay content and dispersion degrees.

All thermoplastic foams are blown using either chemical blowing agent (CBA) or physical blowing agent (PBA). CBA are better choice for foaming than PBA as they can easily incorporate in WPC blend through manufacturing process, while PBA need lateral expensive devices for gas injection and only can be used in extrusion foaming process. Therefore, the aim of this study was to investigate the influence of chemical foaming agent and nanoclay on the physical, mechanical and morphological properties of high density polyethylene/wood flour/organoclay nanocomposite.

2. Experimental

2.1 Materials

The polymer matrix used in this study was high density polyethylene (HDPE) with a melt flow index of 23 gr/10 min, and a density of 0.965 g/cm^3 (supplied by Maroon Petrochemical Industries, Iran). Wood flour (WF) which was used as the reinforcing material was supplied from Cellulose Aria Co (Iran); the average size of wood flour particles was about 425 micron. Maleic anhydride grafted polyethylene (PE-g-MA) provided by Kimia Javid Co, Iran (Grafted maleic anhydride was 1 wt %). It was used as coupling agent. Montmorillonite modified with a dimethyl-dehydrogenated tallow, quaternary ammonium with Cationic Exchange Capacity (CEC) of 125 meq/100 g clay, density of 1.66 g/cc, and a d-spacing of $d_{001}=31.5$ nm was obtained from Southern clay Products Co, USA, with trade name Cloisite 15 A. Azodicarbonamide (Yang Chang Co.), the exothermic chemical blowing agent, was used to foam wood plastic composites. As its decomposition temperature was 200 - 210 °C, Zinc oxide (Ajax Chemical Co, Netherland) was used as a catalyst (kicker) to decrease the decomposition temperature of blowing agent to 170°C (30 wt%). The main produced gas was Nitrogen and its yield was 300gr/cm^3.

3. Method

3.1 Composite Preparation

Nanocomposite formulations are given in Table 2. The nanoclay, HDPE and PE-g-MA were granulated by a counter-rotating intermeshing twin-screw extruder (Model EX1, 2002, Brabender Plastic Corder Co. Germany) having a barrel temperature profile ranging from 160 to 180 ^{0}C (the feeding zone to the die zone) at a screw speed of 60 rpm. Consequently, the resulting granules were mixed with wood flour and modified blowing agent in a counter-rotating intermeshing twin-screw extruder (Model T20, 1990, Dr.Collin GmbH, Germany) which its barrel temperature ranging from 140 to 160 ^{0}C at six zone, from feeding zone to the die zone, at a screw speed of 110 rpm. Resulting materials were grinded and then formed into experimental specimens, using an injection molding device (Model EM80, Aslanian Co., 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.

Code	HDPE (Wt. %)	Wood flour (Wt. %)	Foaming Agent (phr)*	Nanoclay (phr)	PE-g-MA (phr)
50WF/50HDPE/0F/0N/3M	50	50	0	0	3
50WF/50HDPE/0F/2N/3M	50	50	0	2	3
50WF/50HDPE/0F/4N/3M	50	50	0	4	3
50WF/50HDPE/0F/6N/3M	50	50	0	6	3
50WF/50HDPE/0.5F/0N/3M	50	50	0.5	0	3
50WF/50HDPE/0.5F/2N/3M	50	50	0.5	2	3
50WF/50HDPE/0.5F/4N/3M	50	50	0.5	4	3
50WF/50HDPE/0.5F/6N/3M	50	50	0.5	6	3
50WF/50HDPE/1F/0N/3M	50	50	1	0	3
50WF/50HDPE/1F/2N/3M	50	50	1	2	3
50WF/50HDPE/1F/4N/3M	50	50	1	4	3
50WF/50HDPE/1F/6N/3M	50	50	1	6	3
50WF/50HDPE/1.5F/0N/3M	50	50	1.5	0	3
50WF/50HDPE/1.5F/2N/3M	50	50	1.5	2	3
50WF/50HDPE/1.5F/4N/3M	50	50	1.5	4	3
50WF/50HDPE/1.5F/6N/3M	50	50	1.5	6	3

(WF = wood flour, HDPE = high density polyethylene, F = foaming agent, N = nanoclay, M = Coupling agent).
*per hundred resins

Table2. The Compositions of the Studied Formulations

3.2 Measurements

The tensile tests were accomplished according to D638-03, using an Instron machine (Model 1186, England); the tests were performed at crosshead speeds of 2mm/min.

Water uptake tests were carried out according to ASTM D-7031-04 specification. The values of the water absorption in percentage were calculated using the following equation:

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

Where WA (t) is the water absorption at time t, W_0 is the oven dried weight and W (t) is the weight of specimen at a given immersion time t.

The specimens' density was measured by a buoyancy method using a density determination kit supplied by Denver Instrument. The Archimedean principle was applied for determining the specific gravity of the samples. The relative foam density is defined as the ratio of the foamed specimens' density to the unfoamed samples' density, while the volume expansion ratio is the ratio of the unformed sample density to the foam density.

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° /min.

Foam morphology, cell size, and average cell density was characterized using scanning electron microscopy (SEM, Model LEO 440i, Oxford) at 20 kV accelerating voltage. The composite fracture surfaces for examination were obtained after 2min immersion in liquid nitrogen, and the fracture surface was sputter-coated with gold.

The number of cells in a cross field and their size (which was characterized by linear dimension) was determined with the aid of image analysis using software (Image-Pro Plus), based on SEM micrographs. The smallest dimension was measured as cell diameter and the mean values were considered as cell size. The number of cell per unit volume of foam (Nc) is a function of cell size and density of the plastic foam and is given by bellow equation:

$$Nc \approx \frac{10^4 [1 - \frac{\rho f}{\rho p}]}{d^3} \qquad \text{Equation 2}$$

Where N_c is the number of cells per cm^3 of foam, ρ_f is the density of the foam in gr/cm^3, ρ_p is the polymer matrix density in gr/cm^3, and d is the mean cell size in mm.
The statistical analysis was conducted using SPSS programming (Version 16) method in conjunction with the analysis of variance techniques. Duncan multiply range test was used to test the statistical significance at α = 0.05 level.

4. Result and Discussion

The cell size and average cell density (Table 3) increases with increase of chemical foaming agent concentration. The foam type which has been achieved is fine-celled instead of microcellular structure. This probably due to the imperfect dispersion of nanoclay in polymer matrix, so lack of sufficient nucleation centers, and may be because of insufficient bubble growth due to rapid curing in injection molding process [2, 6, 7].

The results showed that by the incorporation of nanoclay into the compound, the cell size decreased. This is due to the extremely fine dimensions and high aspect ratio of nanoclay that help create more foaming nucleation centers in the polymer and at the HDPE/wood flour interface and lead to cell density improvement; consequently, the melt viscosity of the matrix increases with an increase in clay content, generating higher resistance to cell growth in the foaming processes. The bubble growth was partially eliminated when growing bubbles surround by silicate plates, which result in cell size reduction [2].

Formulation (phr)	Cell Size (μm)	Average Cell Density (cells/cm^3)
0 nanoclay/0.5 foaming	63	1.04×10^6
2 nanoclay/0.5 foaming	55	1.54×10^6
4 nanoclay/0.5 foaming	48	1.85×10^6
6 nanoclay/0.5 foaming	42	2.06×10^6
0 nanoclay/1 foaming	81	1.32×10^6
2 nanoclay/1 foaming	74	1.67×10^6
4 nanoclay/1 foaming	63	1.94×10^6
6 nanoclay/1 foaming	57	2.14×10^6
0 nanoclay/1.5 foaming	100	1.63×10^6
2 nanoclay/1.5 foaming	92	1.81×10^6
4 nanoclay/1.5 foaming	84	2.06×10^6
6 nanoclay/1.5 foaming	77	2.26×10^6

Table 3 Cell Size and Cell Density of HDPE/Wood Flour Composite Foams

Figure 1 shows the effect of chemical foaming agent and nanoclay concentration on the density of HDPE/wood flour composites. As can be seen, the chemical foaming agent reduced the density of foamed composites; this factor tends to increase by nanoclay loading, significantly. Density, reach to an optimum at 2 phr nanonoclay and 0.5 phr foaming agent content.

As it is shown in Figure 2, water absorption was affected by cell density and cell size. In fact, the void content was increased by rise in foaming agent amounts; consequently water absorption was increased [7]. By addition of nanoclay to HDPE/wood flour composites, water absorption was decreased. It seems that the barrier properties of nanoclay fillers inhibit the water permeation in the polymer matrix.
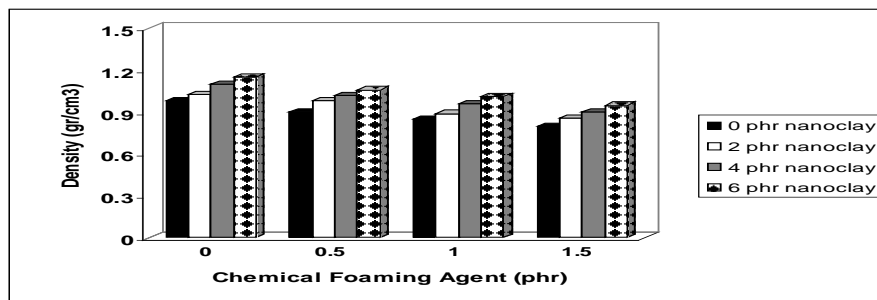

Figure 1 Influence of chemical foaming agent and nanoclay concentration on density of HDPE/wood flour composites
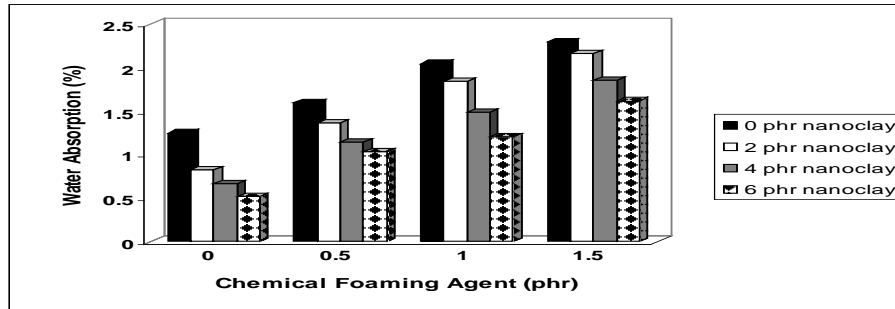
Figure 2 Influence of chemical foaming agent and nanoclay concentration on water absorption of HDPE/wood flour composites

According to figure 3, the tensile modulus decreased as the foaming agent increased. These trends may be due to the increased bubble density and probably due to partially cell coalescence, which was brought by increasing the foaming agent concentration [2, 7]. Counter wise, the tensile modulus increased with increase of nanoclay up to 4 phr at the same concentration of chemical foaming agent and then decreased. The reinforcing efficiency of the nanofiller is balanced by two opposite phenomena; a negative effect is attributed to migration of nanoparticles into the wood-plastic interface, at higher dosage of clay, causing decreased performance. At 6 phr of nanoclay, agglomeration of nanoparticles could decrease the reinforcement of clay.
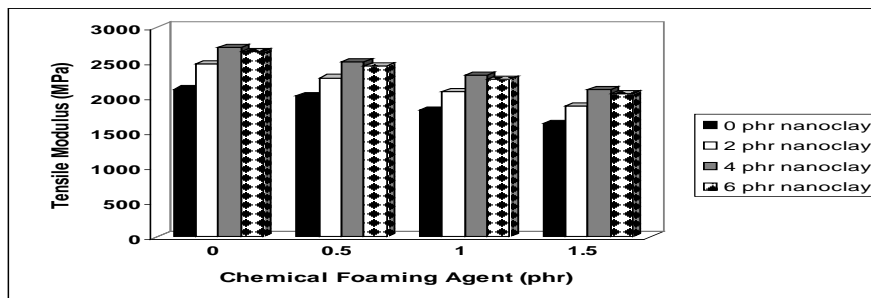

Figure 3 Influence of chemical foaming agent and nanoclay concentration on tensile modulus of HDPE/wood flour composites

The increment of the modulus depends on the morphology of nanocomposites [9]. 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 4 phr and then decreased. The peaks appearing at 2.8^0 correspond to powdered nanoclay with $d_{001} = 31.5$ nm. In the sample with the addition of 2 phr nanoclay, the peak was shifted to a lower angle ($2\theta = 2.39^0$, $d_{001} = 36.8$ nm), which implies formation of the intercalation morphology. The increase of the interlayer distance and relative intercalation might result from the stronger shear during processing when the wood flour introduced. These data show that the order of intercalation was higher for 4 phr of nanocaly ($2\theta = 2.24^0$, $d_{001} = 39.3$ nm).

Also, the clay was not exfoliated, since the peak still obviously existed. In other words, formation of the intercalation morphology and better dispersion was shown in 4 phr of nanoclay, because the peak of that was shifted to a lower angle.

Nanoclay Content (phr)	2θ (°)	d-spacing (nm)	Relative Intercalation (%)
Pure nanoclay	2.8	31.5	-
2	2.39	36.8	16.83
4	2.24	39.3	24.76
6	2.32	38.4	21.90

Table 4 Summary of XRD Data of Nanoclay Content in HDPE/Wood Flour Composites

According to above mentioned, also an increase in foaming agent and nanoclay concentration caused a counter effect in many cases, the optimal condition in our experimental samples was attained by incorporating 0.5 phr blowing agent and 4 phr nanoclay in composite formulation.

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