

Extrusion Foaming of Nano-Clay-Filled Wood Fiber Composites for Automotive Applications

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ABSTRACT

This paper presents the foaming behaviors of high-density polyethylene (HDPE)-based and polypropylene (PP)-based wood fiber composites with a small amount of nanosized clay. Melt compounding was used to prepare various types of clay-filled, wood fiber composites, such as intercalated and exfoliated clay composites. Their morphology was determined by using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The extrusion foaming was conducted using N_2 as the blowing agent. The cell nucleation and growth behaviors of composite foams were studied while varying temperature, pressure, wood fiber content, and clay content. The effects of clay content and exfoliation degree on the final cell morphology of wood fiber/polyolefin/clay nanocomposite foams were identified.

INTRODUCTION

Wood fiber/plastic composites (WPCs) are gaining acceptance due to increasing concern for the environment. The trend toward “recycling and biodegradability” is the driving force behind the increased use of WPCs. However, WPCs have suffered from low impact strength and high density compared to natural wood, which limits their application. In this context, fine-celled foaming of WPCs, by using either chemical blowing agents (CBA) or physical blowing agents (PBA), can dramatically alleviate these drawbacks while significantly reducing material cost, thereby expanding the range of its applications [1-13]. The expanding markets, however, call for high performance WPCs with superior and unique properties (e.g., flame retardance) to meet individual application requirements.

Since the properties of foams are known to improve with decreasing cell size and increasing uniformity [14, 15], it is highly desirable to focus research efforts on developing foams with morphologies that possess a reduced cell size and narrower cell-size distribution. When a CBA is used for

foaming, a higher processing temperature is needed to decompose the blowing agent, which results in the release of a greater amount of volatile gases from wood fibers. Ultimately, it is difficult to obtain a fine-celled structure from the WPC extrusion process using CBAs. In contrast, PBA-based processing has no decomposition temperature requirements; therefore, a lower processing temperature, well below the critical processing temperature, can be applied to suppress the generation of volatile agents, and a better cell morphology is typically achieved [13].

PBA-based plastic foams are produced by introducing a rapid pressure drop within a polymer system, yielding a gaseous thermodynamic instability which can be strategically exploited to beneficial ends [16]. The continuous extrusion foaming of WPCs with a PBA entails several basic steps: (a) the uniform formation of a wood fiber/polymer/gas mixture; (b) cell nucleation; (c) cell growth; and (d) the solidification of the polymer matrix by cooling. Generating a uniform fine-celled or microcellular structure in WPCs has been demonstrated to be extremely important for improving their mechanical properties [11]. Guo *et al.* [17] investigated the foaming behavior of two different polymer-based WPC systems (i.e., mPE and HDPE) with N_2 and CO_2 . They concluded that N_2 is a better blowing agent than CO_2 for the foaming of WPCs; N_2 exhibited greater overall efficiency; and the cellular structure of the final WPC products was superior. The expanding markets, however, are increasingly calling for higher performance WPCs with advanced and unique properties (e.g., flame retardance) in order to meet more tailored application requirements.

The use of layered silicate nano-particles (i.e., clay) to reinforce polymers has drawn a great deal of attention in recent years [18-22]. These nano-particles possess a much larger surface area ($\sim 750 \text{ m}^2/\text{g}$) and a much higher aspect ratio (>200) than conventional macro-sized fillers. In fact, adding a small amount of nanoclay has been shown to substantially improve a number of polymer

properties, such as stiffness and strength, thermal and dimensional stability, flame retardance, and barrier properties [21,22]. Thus, the introduction of nanoclay into WPCs may be advantageous in enhancing their mechanical properties and flame retardance, which are desirable effects, particularly with respect to automotive and construction applications.

Furthermore, in comparison to the conventional micron-sized filler particles generally used in foaming processes, the incorporation of nano-sized clay particles may offer additional benefits. The large surface area of the exfoliated clay nano-particles with their extremely fine dimensions (i.e., high aspect ratios over 100), as well as the intimate contact that occurs between the particles and the polymer matrix, may greatly alter both cell nucleation and growth behaviors. Lee *et al.* [23] demonstrated that achieving a higher degree of exfoliation for nanoclays was the key for enhancing the cell density of low-density polyethylene (LDPE)/clay nanocomposite foams even when small amounts of clay (less than 1.0 wt%) were used in the fabrication of the nanocomposite foams. They also proved that, in comparison with pure HDPE, HDPE/clay nanocomposites produced much finer and more uniform cell structures [24]. Han *et al.* [25,26] showed that the addition of a small amount of clay (5 wt%) could reduce cell size and increase cell density in polystyrene (PS)/clay nanocomposite foams when CO₂ was used in both extrusion foaming processes and batch processes. Wingert *et al.* [27] investigated the combined effects of nanoclay and CO₂ on polymer melt rheology in extrusion. Without the presence of CO₂ the viscosity of the nanocomposite increased with nanoclay loading; however, when the nanocomposite melt was swollen by CO₂ the nanoclay acted to reduce viscosity compared to that in pure PS/CO₂ systems. Zheng *et al.* [28] demonstrated that supercritical CO₂ is helpful for further expanding the layer spacing between clay particles and promoting the clay dispersion in PP/clay nanocomposites during the foaming process. Nam *et al.* [29] studied the influence of clay particles (2-7.5 wt%) on cell density, cell size, cell wall thickness, and bulk density of foamed maleated polypropylene (PP)/clay nanocomposites. TEM observation showed that the biaxial flow during cell growth induced the alignment of clay particles along the cell boundary. Fujimoto *et al.* [30] foamed polylactide (PLA)/clay (3.5 wt%) nanocomposites using a batch process in an autoclave using supercritical CO₂ as a foaming agent. The morphological correlation between the dispersed clay particles with nanometer dimensions in bulk and the closed-cell structure of the foam was examined. Yuan *et al.* [31] explored the processing benefits and property improvements of combined nanocomposites with microcellular injection molding. Compared to the corresponding base polyamide microcellular parts, the microcellular nanocomposites exhibited better cell structures and cell distributions, as well as enhanced mechanical properties.

Both WPCs and polymer/clay nanocomposites have been explored extensively, but have always been done separately. Very few researchers have tried to combine wood fiber, nanoclay, and polymer to produce WPCs with

improved performance capacities. Guo *et al.* [3] showed that the addition of clay reduces the cell size and increases the cell density of metallocene polyethylene/wood fiber composites in extrusion foaming using a CBA.

In this respect, the introduction of a small amount of well-dispersed nanoclay into WPCs with a PBA may yield better cellular structures in foaming and thereby produce high-performance WPC foams with superior properties. The objective of this paper is to explore the effects of nanoclay particles on the cell morphology and foam density of wood fiber/polyolefins (HDPE and PP)/nanoclay composites foamed with a PBA, using a single-screw extrusion system.

EXPERIMENTAL

Materials

The polymer matrices used in this study were HDPE (SCLAR 2710, Nova Chemicals) with a density of 0.95 g/cm³ (ASTM D792) and a melt index of 17g/10min (ASTM D1238), and PP (PP1024E4, ExxonMobile Chemical) with a density of 0.91 g/cm³ and a melt index of 12.5g/10min. Two different grades of softwood fibers, supplied by American Wood Fibers, were used: 12020 (average particle size 75-125 μm) and 2020 (average particle size 250-850 μm). Clay modified with dimethyl dihydrogenated tallow alkyl ammonium (Cloisite 20A, Southern Clay Products) was employed as a layered silicate. The maleic anhydride-g-HDPE (PE-g-MAn, Fusabond MB-100D, 0.9-1.1 wt% of MAH, MI 2.0g/10min, DuPont Canada) and maleic anhydride-g-PP (PP-g-MAn, Polybond 3150, 1.0-1.5 wt% of MAH, MI 60g/10min, Chemtura) were used for improving the adhesion between the hydrophobic HDPE and the hydrophilic wood fiber or layered silicate. Nitrogen (N₂), an environmentally friendly physical blowing agent (PBA), was used in this study to investigate the cell morphology of the WPCs.

Preparation of Composites

In order to investigate the effects of clay dispersion, two different mixing procedures were used: masterbatch and direct melt blending. For wood fiber/HDPE/clay composites in the masterbatch mixing process, a masterbatch was first prepared by melt-blending organoclay and PE-g-MAn (10:90) using a high-shear kinetic mixer (W&P Gelimat) at 3200 rpm. This mixing encouraged a chemical interaction between the hydroxyl groups present on the nanoclay and the maleated PE to disperse the nanoclay particles uniformly throughout the wood fiber composites. The melt-blended bundles were discharged at a preset temperature of 170°C and were subsequently cut into small granules by a granulator (C.W. Brabender). Next, the masterbatch granules were dry-blended with enough HDPE and wood fiber to yield specific material compositions. The wood fiber and organoclay contents varied across a range of 0 to 30 wt% and 1 to 5 wt%, respectively. For all the composites, the weight ratio of PE-g-MAn to organoclay was fixed at 9.0. The wood fiber was dried at 70°C in order to remove any

inherent moisture and thereby prevent the deteriorating effects of moisture on the cell structure. The dried wood fiber was dry-blended with HDPE pellets and the masterbatch granules. Using the same high shear kinetic mixer, the blended mixture was melt-blended at 170°C and then granulated. The granules were compounded using a counter-rotating, intermeshing, twin-screw extruder (C. W. Brabender: Model D6/2, L/D=7:1) at a screw speed of 50 rpm. The extruder possessed a barrel temperature profile that ranged from 140 to 170°C, which spanned the feeding zone to the die zone. The extrudate was cooled by blowing air over it and was subsequently pelletized. In the direct mixing process, wood fiber, HDPE, PE-g-MAN, and organoclay were added to the kinetic batch mixer at the same time, where they were compounded and subsequently melt-blended in a counter-rotating, intermeshing, twin-screw extruder. The compounded composites were dried at 70°C for 24 hours.

On the other hand, in the case of PP composites, some neat PP, with its higher melt viscosity due to the low one of PP-g-MAN, was mixed with PP-g-MAN and nanoclay in a masterbatch stage in order to offer the higher shear stresses generated by PP (PP/PP-g-MAN/clay=8/1/1). The wood fiber and nanoclay contents varied across a range of 0 to 50 wt% and 3 to 5 wt%, respectively.

Characterization of Nanocomposites

The nanocomposite structure, in clay masterbatches and WPCs, was characterized by XRD and TEM. These technologies enabled us to capture the interlayer spacing of the layered nano-particles, as well as their spatial distribution. XRD was conducted with a Siemens D5000 diffractometer that uses Cu K α radiation (1.548Å) and a Kevex solid-state detector. Measurements were performed at 50 kV and 35 mA. The data was recorded in the reflection mode (i.e., range of $2\theta = 1.5\text{--}10^\circ$) using a STEP scan method; the step size was 0.02 degrees and the counting time was 2.0 seconds per step. Materials with a periodic structure similar to the layered silicate clays typically show characteristic (001) diffraction peaks. These peaks are related to the spacing distance of the layers which is determined using Bragg's law, $\lambda = 2 d_{001} \sin\theta$, where λ is the wavelength of the radiation, d_{001} is the interlayer spacing, and 2θ is the diffraction angle. For the TEM analysis, the specimen was cut to an ultrathin section (i.e., 100 nm thickness) using a microtome with a diamond knife. The structure was observed with a Hitachi HD-2000 microscope at 200 kV.

Rheological Characterization

The samples were subjected to oscillatory shear in a dynamic stress rheometer (Rheometric Scientific SR-200) with parallel plates (25 mm in diameter) and at a gap of 1.0 mm. In all the cases, dynamic stress sweeps were initially performed to define the limits of the linear viscoelastic regime. Dynamic frequency sweep experiments were then conducted to measure the complex viscosity (η^*) over a frequency range of 0.1–100

rad/s at 180°C and 200°C for HDPE and PP, respectively. All measurements were performed under N₂ to prevent polymer degradation or moisture absorption.

Extrusion Foaming and Characterization of WPCs

The WPC pellets were processed in a single-screw, three-zone extruder with a gas injection system. The cellular foamability of these samples was studied in extrusion using N₂, at 0 wt% and 0.3 wt%. The foam samples were randomly collected at each stabilized processing condition and characterized for foam density and cell morphology, such as cell size and cell size distribution. Each sample was dipped first in liquid nitrogen and then fractured. The fractured surface was then gold-coated using a sputter coater (E 50000C PS3). The cellular morphology was examined using scanning electron microscopy (SEM, JEOL JSM-6060).

RESULTS AND DISCUSSION

HDPE/WOOD FIBER/CLAY NANOCOMPOSITES Clay Dispersion

The level of clay dispersion in nanocomposites was determined by the measurement of the clay interlayer spacing (d_{001}) from the 2θ position of the clay (001) diffraction peak using Bragg's law. Figure 1 compares the X-ray diffraction patterns for the PE-g-MAN-based clay masterbatch, the wood fiber/HDPE/nanoclay composites made from the masterbatch, and the composites made by the direct mixing method with different clay contents. For all composites made by direct mixing processes, X-ray diffraction peak shifts of smaller angles (compared to that of pure organoclay) were apparent regardless of the PE-g-MAN content, indicating the presence of an intercalated structure. Meanwhile, X-ray diffraction characteristic peaks disappeared for the clay masterbatch, as well as the 1%, 3%, and 5% clay composites made from it; this suggested that an exfoliated structure was formed.

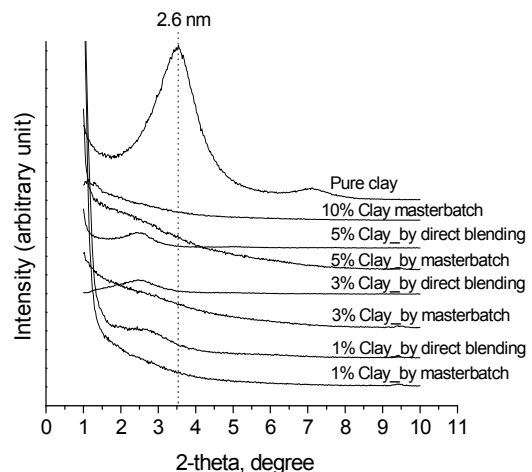


Figure 1. XRD patterns for 30% wood fiber/HDPE/nanoclay composites with respect to preparation method of the composites and clay contents (weight ratio of PE-g-MAN to clay = 9.0).