EFFECT OF CLAY ON EXTRUSION FOAMING OF WF/PP/CLAY COMPOSITES USING N$_2$

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Abstract

The paper investigated the effect of clay on extrusion foaming of polypropylene (PP)/clay composites and wood fiber (WF)/PP/clay composites that contained a small amount of clay, up to 5 wt%. The composites were prepared by a melt blending masterbatch process. The clay dispersion in the composites was characterized by a X-ray diffractometer while the viscosity of the composites was evaluated by a rotational rheometer. The foaming behaviour of the composites was examined using an extrusion foaming system, in which N$_2$ was used for foams as a physical blowing agent. The results suggested that the organoclay provided higher cell density for PP/clay composites than the natural clay, and the addition of organoclay was more effective in improving the cell morphology (decrease of cell size and more uniform cell size) for the WF/PP/clay composites with lower fiber loading.

Introduction

Wood fiber plastic composites (WPC) have received considerable attention lately within the automotive, construction, and furniture industries due to their low cost and recyclability. However, the density of WPC is higher than those of plastics and wood, which is one of the major obstacles that prevent the expansion of their application.

Foaming technology can decrease the density of WPC, but it is not an easy task to maintain or increase their functional properties when the density is reduced. Since the properties of foams can be improved with decreasing cell size and increasing uniformity [1,2], it is essential to develop WPC foams with reduced cell size and narrower cell-size distribution.

An addition of layered silicate particles (i.e., clay) may be one of the ways to decrease cell size and achieve more uniform cells in WPC. It has been reported that the addition of clay improved cell morphology of various polymers, such as low-density polyethylene (LDPE) [3], high-density polyethylene (HDPE) [4], polystyrene (PS) [5,6], polylactide (PLA) [7], polyamide [8], polypropylene (PP) [9], and maleated PP [10]. However, very few literatures are available on studying the effect of clay on the foaming behavior of WPC. Guo et al. [11] reported that the addition of clay reduces the cell size and increases the cell density of wood fiber/metallocene polyethylene composites in extrusion foaming using a chemical blowing agent.

In this paper, two types of clay (natural clay and organoclay) were blended with PP, and the foaming behaviors of PP/clay composites were examined in extrusion using a physical blowing agent, N$_2$. Since the organoclay was found to be more effective in improving cell morphology of PP (see the

"Results and Discussion" section), it was employed to investigate foaming behavior of WF/PP/clay composites.

Experimental

Materials

PP (PP1024E4, ExxonMobile Chemicals), with a density of 0.91 g/cm^3 and a melt flow index of 12.5 g/10min, was used as a polymer matrix. Wood fiber (2020, American Wood Fibers) of which size is in the range of 250-850 μm was used as a reinforcement. Two types of clay were employed: natural clay (Cloisite Na+, Southern Clay Products) and clay modified with dimethyl dihydrogenated tallow alkyl ammonium (Cloisite 20A, Southern Clay Products). Maleated PP (PP-MA, Polybond 3150, 1.0-1.5 wt% of MAH, MI 60g/10min, Chemtura) was used to improve the adhesion between the hydrophobic PP and the hydrophilic wood fiber or layered silicate. The wood fiber was dried at 70°C for 24 hours in a convection oven prior to mixing in order to remove moisture in the wood fiber.

Preparation of Composites

A masterbatch was prepared by melt-blending PP, PP-MA, and clay (either natural clay or organoclay) with a mixing ratio of 8:1:1 using a high-intensity kinetic mixer (W&P Gelimat). The mixer was run at 3200 rpm with a tip speed of 23 m/s. This mixing encourages a chemical interaction between the hydroxyl groups present on the nanoclay and the PP-MA to disperse the clay particles uniformly throughout the polymer matrix. In addition, the higher melt viscosity of PP offers higher shear stress on the clay. The melt blends were discharged at a preset temperature of 185°C, and then cooled down to room temperature. The solidified blends were granulated using a granulator (S-10-9, C.W. Brabender). The masterbatch granules were dry-blended with PP and wood fiber to yield specific material compositions. Again, the blends were melt-blended and granulated using the same equipment.

The wood fiber and organoclay contents varied from a range of 0 to 50 wt% and 0 to 5 wt%, respectively, but the PP-MA content was fixed at 5 wt%. The formulation of the composites is summarized in Table 1.

X-ray Diffraction

X-ray Diffraction (XRD) was conducted with a Siemens D5000 diffractometer that uses Cu Kα 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 using a STEP scan method; the step size was 0.02 degrees and the counting time was 2.0 seconds per step.

Viscosity

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 cases, the dynamic stress sweeps were initially performed to define the limits of the linear viscoelastic regime. The dynamic frequency sweep experiments were then conducted to measure the complex viscosity (η*) over a frequency range of 0.1-100 rad/s at 200°C. All measurements were performed under N$_2$ to prevent polymer degradation or moisture absorption.

Extrusion Foaming

The PP/clay or WF/PP/clay pellets were processed in a single-screw, three-zone extruder with a gas injection system. In this study, nitrogen (N$_2$) was used as an environmentally friendly physical

blowing agent. The foamability of the composites was studied in the extrusion using N_2, at 0.3 wt%. The temperature in this extruder maintained at 180°C. A static mixer, a heat exchanger, and a filament die (L/D: 1.5"/0.05") were attached to the downstream of the barrel. Their temperatures were set at 170°C. The die temperature was reduced gradually from 170°C to 135°C in order to prevent gas loss in the extrudate which would consequently reduce the composite density. The foam samples were collected at each stabilized processing condition and characterized for foam density and cell morphology, such as cell size, cell size distribution, and cell density. Each sample was dipped in liquid nitrogen and 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

PP/Clay Composites
<u>Clay Dispersion and Viscosity</u>

Figure 1 (a) shows the X-ray diffraction patterns of PP/clay composites with natural clay. The interlayer spacing of the pure natural clay before compounding is 1.1 nm. After compounding, the X-ray diffraction peaks of the composites with 3 and 5 wt% clay as well as the master batch shifted to higher angles. The results suggest that the interlayer spacing slightly decreased to around 1.0 nm for all the composites. Figure 1 (b) shows the X-ray diffraction patterns of PP/clay composites with organoclay. The interlayer spacing of pure organoclay before compounding is 2.6 nm. After compounding, the X-ray diffraction peaks of all the composites were broadened, which suggests that the interlayer thickness was disordered.

Figure 2 shows the complex viscosity of PP/clay composites at different frequencies. This figure indicates that the addition of natural clay created few changes to the viscosity of PP. However, the addition of organoclay increased viscosity of PP at a low frequency level, which suggests that there is an interaction between the organoclay and PP.

<u>Foaming Behavior</u>

Figure 3 shows the foam density of PP/clay composites at different die temperatures. The density of PP/clay composites was decreased to around 0.6 g/cm^3 by foaming. Also, it was observed that the foam density of the composites was insensitive to the die temperature, while the clay type and content little affected the foam density. However, as shown in Figure 4, the cell density increased with the increase of clay content for both natural clay and organoclay composites. Furthermore, the organoclay composites showed higher cell density than natural clay composites.

It is speculated that the addition of clay particles increased the nucleation rate of bubbles in keeping with the principles of heterogeneous nucleation [12]. In heterogeneous nucleation, the activation energy barrier to nucleation is reduced in the presence of filler particles. As a result, the addition of clay particles increases cell nucleation. The higher cell density in the organoclay composites than natural clay composites can be explained by the larger interfacial area between clay and PP matrix. The organoclay composites had clay with intercalated structure and larger number of particles, which provided more sites for cell nucleation. In addition to the enhanced cell nucleation, it is surmised that the larger interfacial area suppressed the cell growth. A higher fraction of polymer chains is confined by clay, and thus their mobility is restricted, which increased melt viscosity of the composites (see Figure 2).

WF/PP/Clay Composites
The results from PP/clay composites indicated that organoclay improve cell morphology of PP more than natural clay. Therefore, organoclay was selected as the clay for WF/PP/clay composites.

Clay Dispersion and Viscosity
        Figure 5 shows the X-ray diffraction patterns of WF/PP/clay composites as well as pure organoclay. After compounding, X-ray diffraction peaks of all the composites shifted to lower angles (3.6 nm or so). The result indicates that the interlayer spacing was increased by the intercalation of polymer, but the organoclay still retains an ordered structure. It is expected that the compounding of viscous wood fibre composites facilitated the intercalation of the organoclay.
        Figure 6 shows the complex viscosity of WF/PP/clay composites at different frequencies. For both composites with 25 wt% and 50 wt% wood fiber composites, the viscosity of the composites increased with the increase of clay content. It is also noted that the viscosity of the composites increased with the wood fiber content (see Figure 2 for 0 wt% wood fiber composites).

Foaming Behavior
        Figure 7 shows the foam density of WF/PP/clay composites with 25 wt% wood fiber at different die temperatures. Similar to PP/clay composites, foam density of the composites was insensitive to the die temperature and clay content little affected the foam density.
        Figure 8(a) shows the cell size and cell size distribution of WF/PP/clay composites with 25 wt% wood fiber at a die temperature of 140°C. With the increase of clay content, the average cell size of the composite decreased, and the cell size became more uniform, which is indicated by the steeper curves on the graph. Analogous to the PP/organoclay composites, the improvement in cell morphology of WF/PP/clay composite foams with the increase of organoclay can be explained by two effects: (i) clay particles act as nucleating agents, thus promoting heterogeneous nucleation, and (ii) the melt viscosity of the matrix increases with an increase in clay content (see Figure 6), generating higher resistance to cell growth in the foaming processes.
        However, for WF/PP/clay composite with 50 wt% wood fiber (Figure 8(b)), there was no significant improvement in cell size and cell size uniformity with the addition of organoclay (up to 5 wt%). This can be attributed to the higher interfacial area between wood fiber and PP matrix for cell nucleation as the wood fiber content is increased (from 25 wt% to 50 wt%), which decreased the effectiveness of the organoclay particles as nucleating agents.

Conclusions

        The foaming behavior of PP/clay composites and WF/PP/clay composites were examined in extrusion. The results from the PP/clay composites suggest that the cell density increased with the increase of clay content for both natural clay and organoclay composites. However, composites with organoclay showed higher cell density than those with natural clay. The results from WF/PP/clay composites suggest that, in the composites with 25 wt% wood fiber, the average cell size decreased and the cell size became more uniform with the increase of organoclay content while cell size and cell size uniformity of the composites with 50 wt% wood fiber increased slightly with the addition of organoclay.

Acknowledgement

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11.   G. Guo, K.H. Wang, C.B. Park, Y.S. Kim, and G. Li, *J. Appl. Polym. Sci.,* **104**, 1058 (2007).
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Table 1. Material Information of the Composite Materials Prepared in This Study.

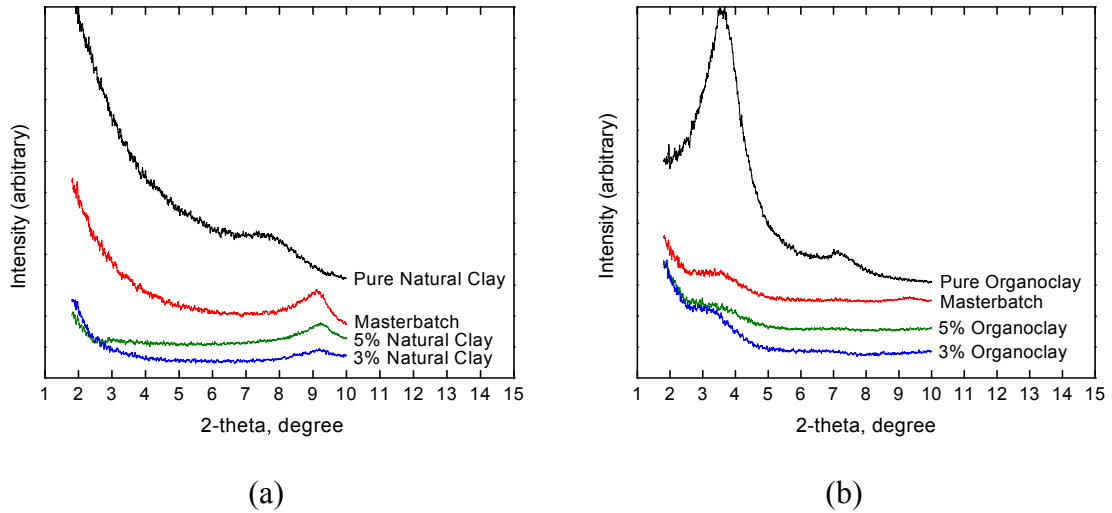| No	Wood Fibre (wt%)	PP (wt%)	PP-MA (wt%)	Clay (wt%)	
				Organoclay	Natural clay
1	0	95	5	0	0
2	0	92	5	3	0
3	0	90	5	5	0
4	0	92	5	0	3
5	0	90	5	0	5
6	25	70	5	0	0
7	25	67	5	3	0
8	25	65	5	5	0
9	50	45	5	0	0
10	50	42	5	3	0
11	50	40	5	5	0

Figure 1. XRD Patterns of PP/Clay Composites: (a) Natural clay and (b) Organoclay
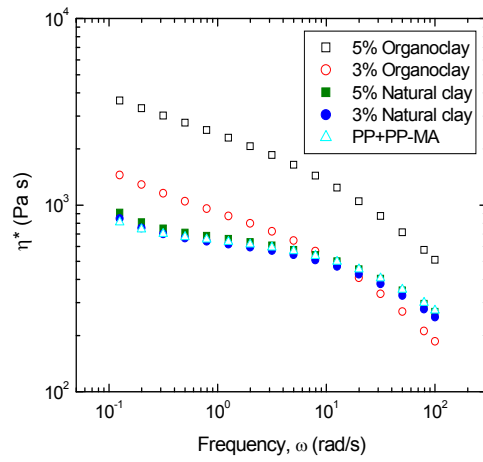

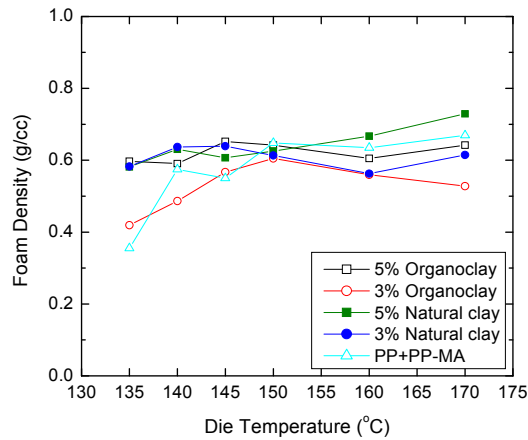**Figure 2.** Complex Viscosity (η*) of PP/Clay Composites as a Function of Frequency

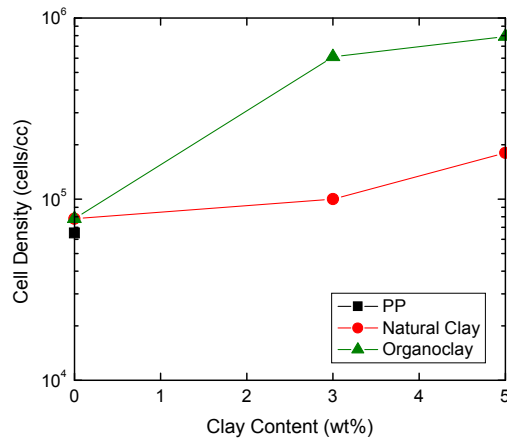**Figure 3.** Foam Density of PP/Clay Composites as a Function of Die Temperature

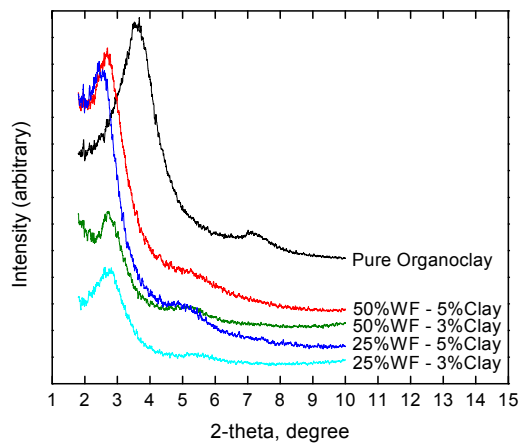**Figure 4.** Cell Density of PP/Clay Composites as a Function of Clay Content

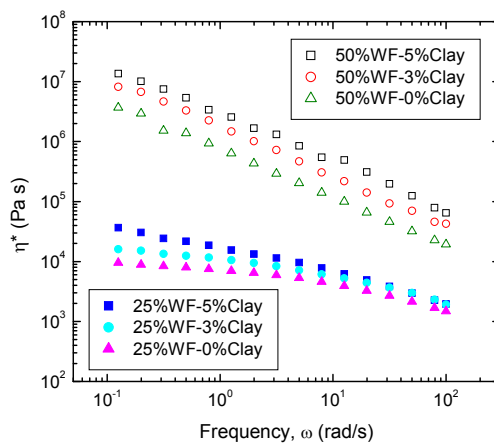**Figure 5.** XRD Patterns of WF/PP/Clay Composites

Figure 6. Complex Viscosity (η^*) of WF/PP/Clay Composites as a Function of Frequency
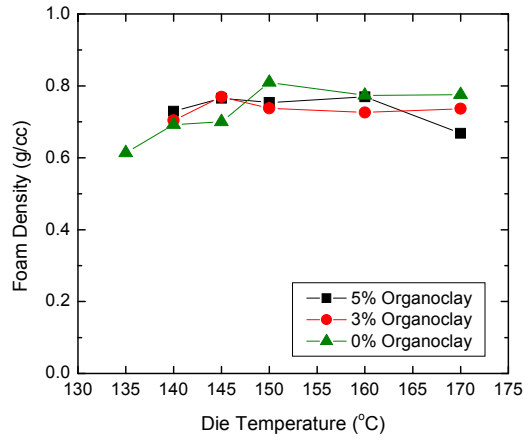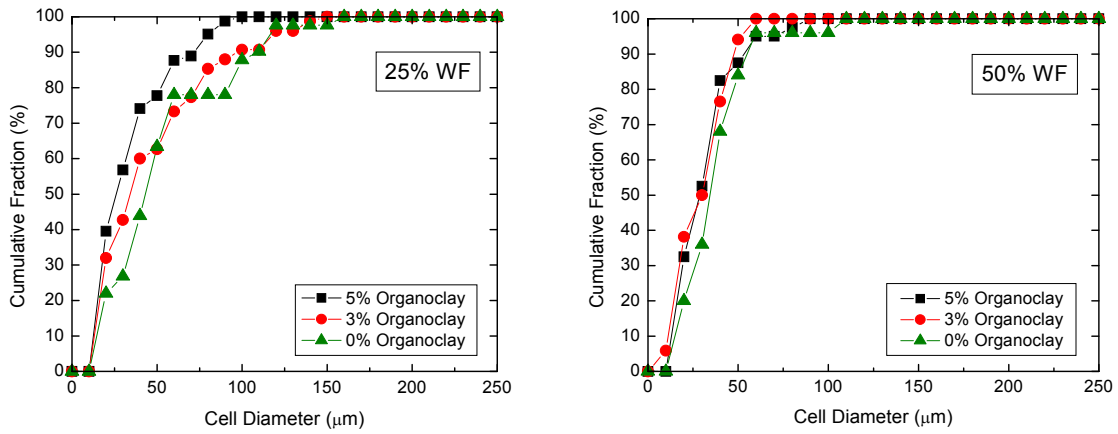
Figure 7. Foam Density of WF/PP/Clay Composites with 25 wt% Wood Fiber
as a Function of Die Temperature

| (a) | (b) |

Figure 8. Cumulative Cell Size Distribution of WF/PP/Clay Composite Foams
at a Die Temperature of 140°C: (a) 25 wt% Wood Fiber and (b) 50 wt% Wood Fiber