EFFECTS OF WOOD FIBER CONTENT ON THE RHEOLOGICAL PROPERTIES, CRYSTALLIZATION BEHAVIOR, AND CELL MORPHOLOGY OF EXTRUDED WOOD FIBER/HDPE COMPOSITES FOAMS

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When increasing the wood fiber (WF) content in extruded wood fiber/plastic composites (WPC) foams, a good balance between reducing the cost and obtaining good cell morphology should be maintained. This study examines the relationship between WF content and the foam morphology in WPC foams. The role of WF as cell nucleating agent at low concentrations (10 wt.%) was observed, as WPC foam with 10 wt.% WF had lower average cell size and higher cell density than neat HDPE foams. Increasing the WF content further, decreased the average cell size and cell density, and increased the foam density of WPC foams. These results were linked to the rheological properties and crystallization behavior of HDPE and WPC with different WF content.

Keywords: Wood fiber; Rheological properties; Crystallization; Foaming; Cell morphology

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INTRODUCTION

Microcellular foaming technology has been proposed and implemented in response to the industrial need for reducing material costs without major compromise to mechanical properties. The central idea of producing microcellular plastic is to create a large number of bubbles or voids from a single phase polymer-gas mixture by introducing a large thermodynamic instability (Martini et al. 1982). Due to a reduced critical flaw size and a fine cellular microstructure, the impact strength, toughness, and fatigue life of microcellular plastics are generally higher than their unfoamed plastic counterparts (Collias et al. 1995; Doroudiani et al. 1998; Matuana et al. 1998; Seeler et al. 1993).

Over the past decade, microcellular foaming technology has been applied to a large number of plastic materials, including wood fiber/plastic composites (WPC). Developing a fine-celled or microcellular composite structure can effectively eliminate the disadvantages of WPC, such as heavier weight, lower impact strength, and lower ductility. WPC foams can be used in non-structural building products and automotive applications, such as decking, windows, interior panels, etc.

WPC foams can be synthesized by means of a chemical blowing agent (CBA) (Bledzki et al. 2004, 2005, 2006a,b; Li et al. 2003), a physical blowing agent (PBA) (Guo et al. 2005, 2006, 2007, 2008; Matuana et al. 1997; Zhang et al. 2004), and stretching (Kim et al. 2004). Rizvi et al. (2008) extrusion foamed WPC using CBAs with low decomposition temperatures. The moisture contained in the WF has also been found to be an effective blowing agent for foaming high-impact polystyrene (HIPS)/wood fiber

(WF) composites (Rizvi et al. 2000, 2003). Kim et al. (2004) have proposed an innovative stretching technology that induced the generation of voids (cells) at the WF and polymer matrix interface as well as orienting the polymer molecule and WFs in the stretch direction.

Compared to the CBA-based foaming process, the PBA-based foaming process has no minimum decomposition temperature requirement and is more cost- effective, making it a more logical choice for WPC foaming. The effect of die temperature and physical blowing agent content ($CO_{2\,(g)}$) on the cell morphology of HDPE based WPC foams has been investigated before in previous studies (Guo et al. 2005; Zhang et al. 2004). The critical processing temperature was estimated to be 170 °C, below which the volatile emissions from the WF were suppressed signifi- cantly (Guo et al. 2004). The effect of the WF size has also been studied, with the small-sized WF composites demonstrating better cell morphology, with smaller cell size and greater cell uniformity (Guo et al. 2008).

WF content can affect polymer viscosity, crystallization, and gas solubility, all of which are parameters that affect the cell nucleation and cell growth behaviors during the extrusion foaming of WPCs. Zhang et al. (2005) found that increasing WF content over 30wt% led to WPC foams with irregular cell geometry. In order to achieve effective implementation of WPC foams as a structural product, the effects of WF content on the composite properties need to be studied systematically and comprehensively. This paper studied the effects of WF content on the rheological properties, crystallization behavior, and cell morphology of WPC foams produced using HDPE as a model polymer and CO_2 as a physical blowing agent.

EXPERIMENTAL

Materials

High density polyethylene (HDPE) 2710, supplied by Nova Chemicals, was used as the matrix polymer. The WF used for this study was standard softwood (pine) from American Wood Fibers grade 12020. Fifty weight-percent (50 wt.%) of these fibers passed through the sieve of 120 mesh size (125 microns) and were retained on the 140 mesh (106 microns) sieve. The initial specific gravity of WF was 0.4. A coupling agent, maleic anhydride-g-HDPE (Fusabond MB-100D, MFI=2.0 g/10min, DuPont Canada), was used for improving the adhesion between the hydrophobic HDPE and the hydrophilic WF. In order to aid processing of WPC, a lubricant (TPW 113) supplied by Struktol America, was also used. Carbon dioxide (CO_2), with 99.5% purity, supplied by BOC Gas Co. was used as the physical blowing agent. All these materials were used as received.

Experimental Setup and Procedure

The WF was oven-dried (Gravity Convection Oven, DX400, Yamato Co.) at 100 °C for 12h to 3% moisture content. The HDPE, WF, coupling agent (3 wt.% of the total weight of WF and HDPE), and lubricant (3 wt.% of the total weight of WF and HDPE) were dry blended and then compounded in a co-rotating twin screw extruder (Leistritz Co.) with a screw diameter of 27 mm, and a length-to-diameter ratio of 40. The mixing ratios based on oven dried weight of WF and HDPE were 10:90, 30:70, and 50:50, respectively. The screw configuration, as shown in Fig. 1, was designed to provide dispersive and distributive mixing for uniformly dispersing WF in HDPE (Zhang et al. 2009). The compounding temperature was 150 °C, and the screw speed was 100 rpm. The extrudate was cooled in water and was fed into a pelletizer to obtain WPC pellets. These

pellets were then dried at 100 °C for 12 h prior to being used for foaming.

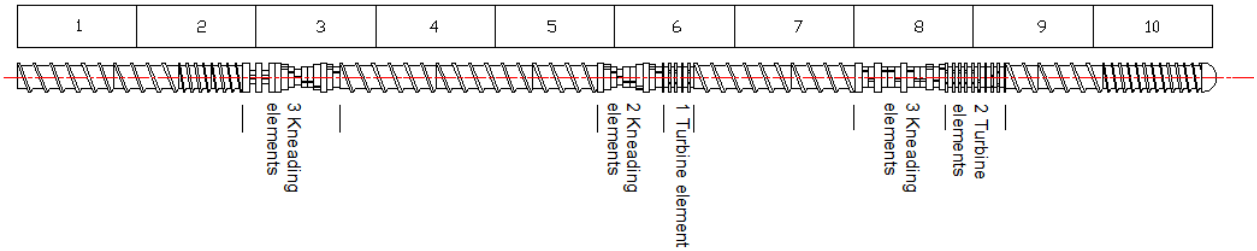

Fig. 1. Schematic of the screw configuration of twin-screw extruder

The foaming of WPC was performed in a single-screw extrusion system, as shown in Fig. 2. A dissolution-enhancing device and a heat exchanger were attached to the extruder exit for promoting homogeneous dissolution of gas into the plastic melt and providing uniform cooling for the melt, respectively (Behravesh et al. 1998). A filament die (L/D=0.02/0.001 m) was used to nucleate the bubble by providing a large thermodynamic instability. The temperatures in the single-screw extruder were maintained at 80 °C, 150 °C, and 150 °C in Zones 1, 2, and 3, respectively. The temperature of the dissolution enhancing device, heat exchanger, and filament die were all set at 150 °C at first. Then CO_2 was injected into the WPC melt, and the die temperature was reduced at an interval of 5°C from 150°C to 135°C. The foam samples were randomly collected at each 5 °C intervals after obtaining stable processing conditions.

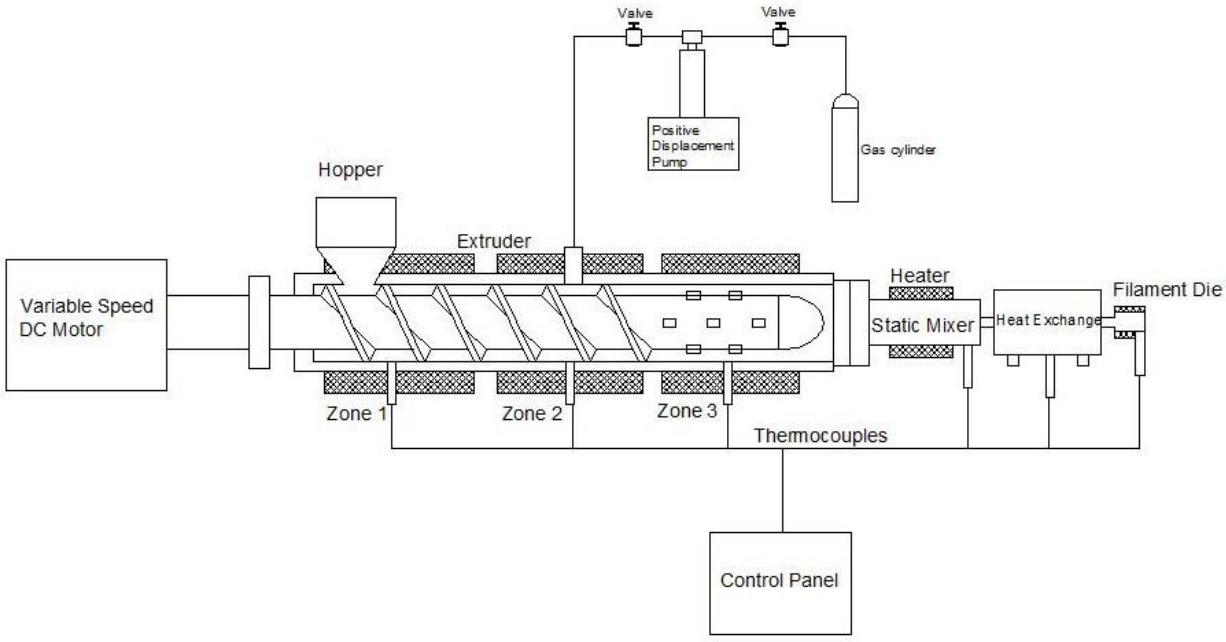

Fig. 2. Schematic of the single-screw extrusion foaming system.

Sample Characterization

The morphological properties, such as average cell size and cell density, were examined using a scanning electron microscope (SEM, Hitachi 510). Prior to examination the foamed samples were dipped in liquid nitrogen, fractured, and the fractured surface was gold-coated, using a sputter coater (E 50000C PS3). A micrograph showing 20 to 50 bubbles was chosen, and the number of bubbles, n, in the micrograph was determined by the software, Scion Image. If the area of the micrograph was A cm^2 and the magnification factor was M, the cell density can be estimated by

$$N_f = \left(\frac{nM^2}{A} \right)^{3/2} \quad (1)$$

The average cell size was the average circle equivalent diameter for all the bubbles in the micrograph.

The foam density of the WPC foams was measured by a water displacement technique (ASTM standard D792). It can be determined as,

$$\rho_f = 0.9975(\frac{M_a}{M_w}) \quad (2)$$

where M_a is the weight measured in air, and M_w is the weight measured in distilled water.

Rheological Measurement

The unfoamed WPC pellets were compression molded into a disc (25 mm diameter, 1.4 mm thick) at 170 °C and 10 MPa for 20 min. The disc was then subjected to oscillatory shear in a Dynamic Stress Rheometer (Rheometric Scientific SR-200) with a parallel plate configuration (25 mm diameter). A dynamic frequency sweep test was performed over a frequency range of 0.1-100 rad/s at 170 °C.

Thermal Analysis

The melting and crystallization behavior of WPC with different WF contents were investigated with a differential scanning calorimeter (DSC, Q2000, TA Instruments). The measurement procedure consisted of heating the WPC sample up to 170 °C using a heating rate of 10 °C/min followed by annealing the sample at this temperature for 20 minutes to erase any thermal history. The sample was then cooled to 25 °C using a controlled cooling rate of 10 °C/min. The average values of three repeated tests were taken for each sample.

RESULTS AND DISCUSSION

Effects of WF Content on Rheological Properties

The complex viscosity and loss tangent are two important parameters affecting the bubble growth process during foaming. The complex viscosity indicates the force that the bubbles would have to overcome to grow successfully. The loss tangent, which is defined as the ratio between the loss modulus and the storage modulus, is responsible for sustaining cell growth and stabilizing the final foam morphology. The effects of WF content on the dynamic rheological properties of WPC at a melt temperature of 170 °C are illustrated in Fig. 3, which shows that WPCs with a higher WF content exhibited

higher complex viscosity. The complex viscosity increased with increasing WF content. This indicates that the force against bubble growth increased with increasing WF content. The loss tangent decreased with the increase of WF content, indicating the cell morphology, becomes unstable when increasing the WF content. It can be noted that the values of the loss tangent were all above one except for WPC with 50 wt.% WF. Therefore, for neat HDPE and WPC with 10 wt.% and 30 wt.% WF, the loss modulus was larger than the storage modulus, which means that the material exhibited more viscous rather than the elastic behavior. However, for WPC with 50 wt.% WF content, the storage modulus was higher than the loss modulus (loss tangent < 1) indicating a solid-like material behavior.

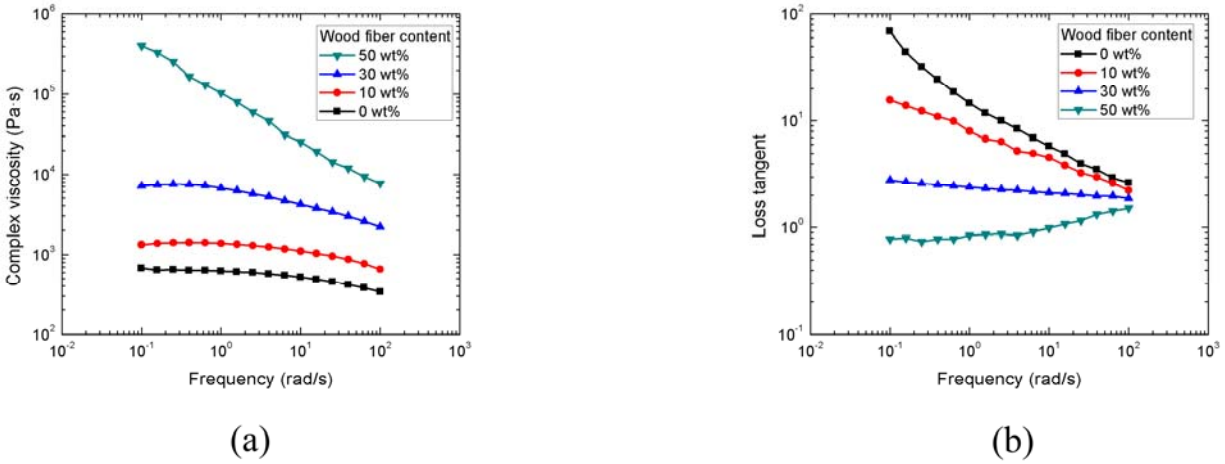

Fig. 3. (a) Complex viscosity and (b) loss tangent of neat HDPE and the WPC with different WF contents

From the rheological properties it can be seen that WPCs with higher WF content exhibited higher viscosity and lower loss tangent values, which may suppress bubble growth process. The WPCs with lower WF content exhibited lower viscosity and larger loss tangent values, which may cause unstable bubble growth and coalescence (Gendron et al. 2003). Thus, an optimal balance between WPC visco- elastic properties would be preferred in order to facilitate proper bubble growth without bubble coalescence.

Effects of WF Content on Crystallization Behavior

The melting and crystallization behaviors of neat HDPE and WPC, based on DSC measurements, are shown in Fig. 4, and the corresponding parameters are summarized in Table 1. It can be seen that with increasing the WF content, the melting temperature (T_m) decreased, the crystallization temperature (T_c) increased, and the exothermic peaks narrowed. The increasing of T_c is because the WF can act as sites for heterogeneous crystal nucleation in the WPC. The results indicate that WPC with higher WF content will be melted earlier when being heated up, and it will form a crystalline structure earlier when being cooled down. Therefore, the bubble growth time for WPC with a higher WF content was shorter than that for WPC with lower WF contents.

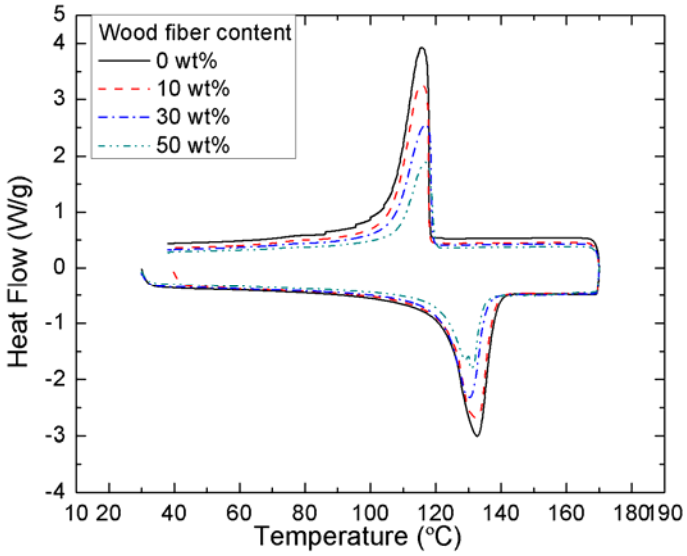

Fig. 4. Melting and crystallization curves of neat HDPE and the WPC with different WF content

Table 1. Melting and Crystallization Parameters of HDPE and WPCs with Different Wood Fiber Content

	Melting point (°C)	Crystallization temperature (°C)	Crystallinity fraction of HDPE component in WPC
HDPE	132.7±0.1	115.7±0.1	0.66±0.01
WPC with 10 wt.% WF	132.5±0.1	115.7±0.1	0.62±0.01
WPC with 30 wt.% WF	130.4±0.1	116.7±0.1	0.57±0.01
WPC with 50 wt.% WF	129.2±0.2	117.0±0.2	0.52±0.02

The crystallinity values (X) of the HDPE component in WPC were calculated using Eq. (2),

$$X = \left(\frac{\Delta H_m}{\Delta H_m^*}\right) \cdot \left(\frac{100}{w}\right) \quad (2)$$

where ΔH_m^*=287.3 J/g for the melting enthalpy of 100% crystalline HDPE (Mirabella et al. 2002) was taken, and *w* is the mass fraction of HDPE in the WPC.

The crystallinity of the HDPE component in WPC, as shown in Table 1, slightly decreased with the increase of WF content. The decreased crystallinity will increase the solubility and diffusivity of CO_2 in the material (Doroudiani et al. 1996). Thus, the solubility and diffusivity of CO_2 in the HDPE phase in WPC with a higher WF content should be slightly higher than that in WPC with a lower WF content.

Effects of WF Content on Cell Morphology and Foam Density

Figure 5 shows typical SEM pictures for neat HDPE and WPC foams with different WF contents when processed at a die temperature of 140 °C and a CO_2 content of 1 wt.%. It can be seen that significant amounts of bubble growth and coalescence occurred in HDPE and WPC foams with 10 wt.% WF. This is attributed to the low

viscosity and the high loss tangent of neat HDPE and WPC with 10 wt% WF. When the WF content increased, the bubble coalescence phenomena decreased due to increased viscosity and decreased loss tangent of WPC.

The average cell size, cell density and foam density of HDPE and WPC foams at different die temperatures and a CO_2 content of 1% are shown in Fig. 6. It can be seen that all of the WPC foams had a lower average cell size and a higher cell density than HDPE foams. This indicates that the WF can act as sites for heterogeneous gas bubble nucleation during the foaming of WPCs. The WPC foam with 30 wt.% WF content showed the smallest average cell size (26.4 μm at 135 °C), while WPC foam with 10 wt.% WF content showed the highest cell density (3.4×10^6 cells/cm^3). Since WPCs with a higher WF content (greater than 10 wt.%) exhibit a higher viscosity and a lower loss tangent, bubble nucleation and growth during foaming is suppressed; therefore, the average cell size and cell density decreases. The reason for the slightly larger average cell size of WPC foams with 50 wt.% WF content may be due to the greater amounts of volatile gases, of appropriate solubility and diffusivity, generated from WF. Such gases may have facilitated the bubble growth process.

The foam density of HDPE foam was lower than that of WPC foams, and moreover, the foam density of WPC foams increased with the increase of WF content. The reason for this is related to the rheological character of the WPC and gas loss. The increased WF contents increases the viscosity and decreases loss tangent of WPC, which suppresses the bubble growth and foam expansion. Also the increased area of the interface between WF and polymer may provide channels for gas loss (Matuana et al. 1997). For HDPE and all the WPC foams, the smallest foam density was observed at a die temperature of 135 °C (approaching the melting temperature). Lower temperature can decrease gas loss due to the decreased diffusivity and increased stiffness of the material, leading to more gas retention, therefore, decreasing the foam density.

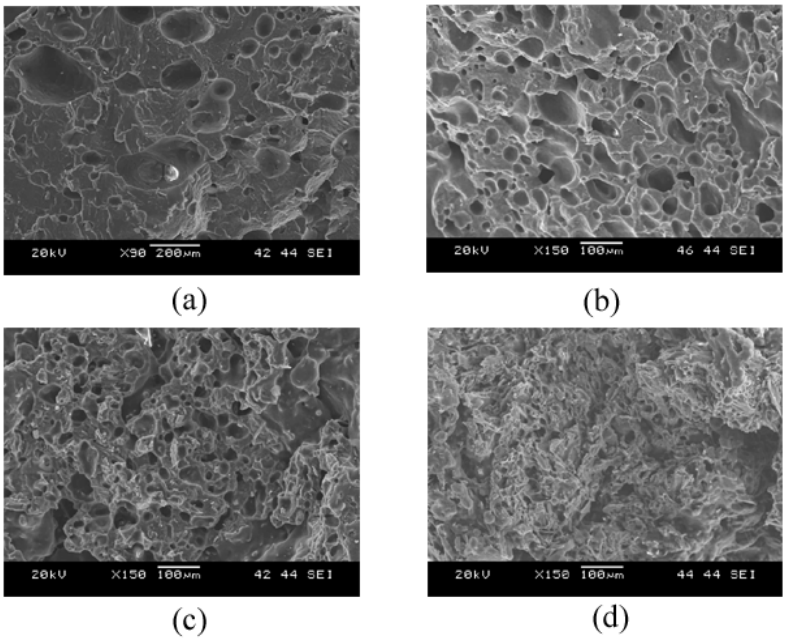

Fig. 5. The SEM pictures for (a) neat HDPE foams and WPC foams with different WF content at the die temperature of 140 °C and a CO_2 content of 1 wt.%; (b) 10 wt.% WF; (c) 30 wt.% WF; and (d) 50 wt.% WF

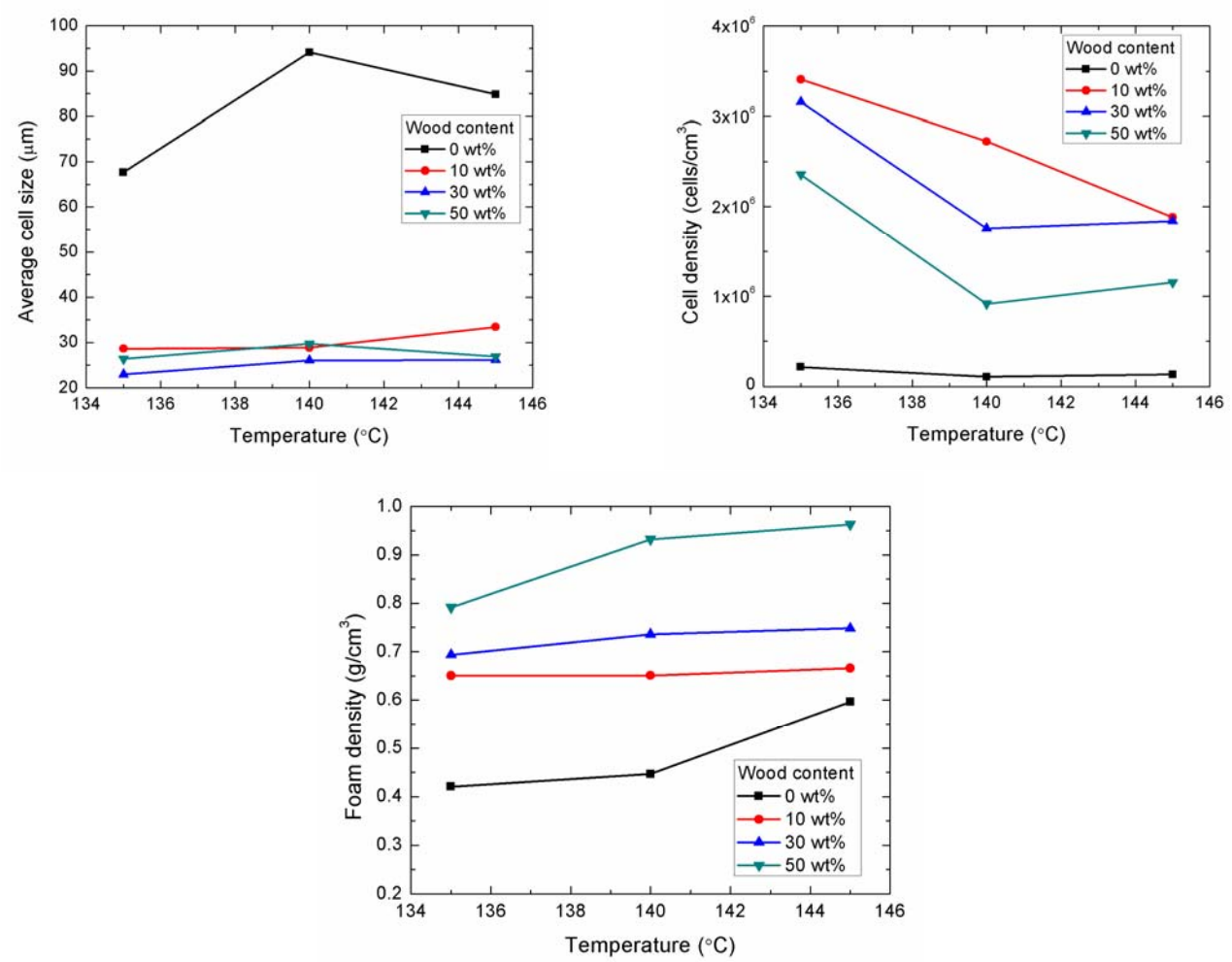

Fig. 6. (a) average cell size, (b) cell density and (c) foam density of foamed HDPE and WPC with different WF content at different die temperatures and a CO_2 content of 1%

The objective of this work was to investigate the connections between WF content and cell morphology. Therefore, an attempt was made to characterize the average cell size and cell density measured at a die temperature of 135 °C and a CO_2 content of 1 wt.%, as illustrated in Fig. 7. To hypothesize, if we take an acceptable cell morphology to be one, where the average cell size is below 50 μm and the cell density is above 3×10^6 cells/cm^3, then the range of WF content with the acceptable cell morphology is the shaded area (between 10 and 30 wt.%) in Fig. 6. This indicates that adding a small amount of WF can be beneficial for improving cell morphology. However, too much WF deteriorates it. A medium amount of WF content should be chosen in order to obtain the right balance of WPC melt visco-elasticity required for enabling bubble nucleation and growth without bubble coalescence.

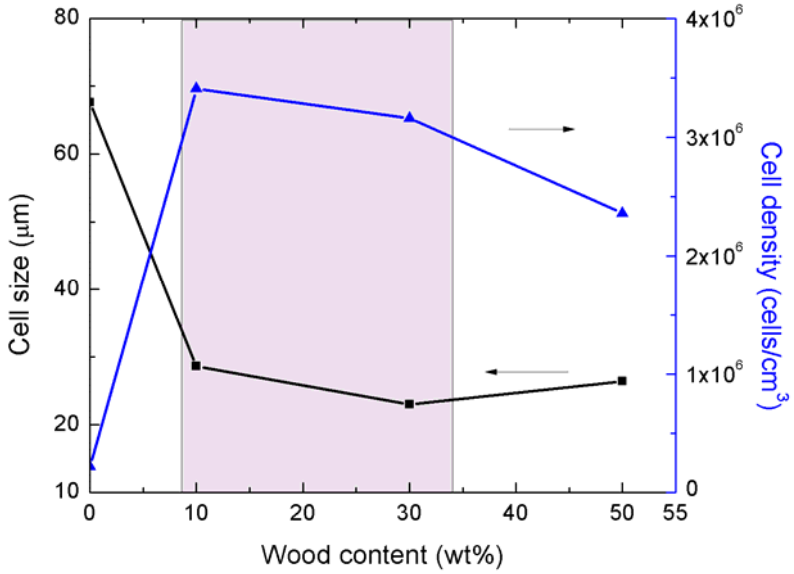

Fig. 7. Average cell size and cell density, measured at the die temperature of 135 °C and the CO_2 content of 1 wt%, expressed as a function of WF content

CONCLUSIONS

The effects of wood fiber (WF) content on rheological properties, crystallization behavior, and cell morphology of HDPE and WPC foams were investigated. Adding WF into HDPE decreased the average cell size and increased the cell density due to heterogeneous gas bubble nucleation at the HDPE-WF interface. However, the addition of too much WF resulted in lower average cell size, lower cell density, and higher foam density, due to the rheological character of WPC melt and gas loss. WF contents that maintain a balance between viscosity and loss tangent of WPC should be selected to enable bubble nucleation and growth without bubble coalescence. Increasing the WF content slightly increased the crystallization temperature and decreased the crystallinity of the HDPE phase in the WPC.

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REFERENCES CITED

Behravesh, A. H., Park, C. B., and Venter, R. D. (1998)."Approach to the production of low-density, microcellular foams in extrusion," Annual Technical Conference - ANTEC, Conference Proceedings, Atlanta, 2, 1958-1967.

Bledzki, A. K., and Faruk, O. (2004)." Extrusion and injection moulded microcellular wood fibre reinforced polypropylene composites," *Cell. Polym.* 23, 211-227.

Bledzki, A. K., and Faruk, O. (2005)." Effects of the chemical foaming agents, injection

parameters, and melt-flow index on the microstructure and mechanical properties of microcellular injection-molded wood-fiber/polypropylene composites" *J. Appl. Polym. Sci.* 97, 1090-1096.

Bledzki, A. K., and Faruk, O. (2006a)." Influence of different endothermic foaming agents on microcellular injection moulded wood fibre reinforced PP composites," *Cell. Polym.* 25, 143-158.

Bledzki, A. K., and Faruk, O. (2006b). "Microcellular injection molded wood fiber-PP composites: Part I - Effect of chemical foaming agent content on cell morphology and physico-mechanical properties," *J. Cell. Plast.* 42, 63-76.

Collias, D. I., and Baird, D. G. (1995). "Impact behavior of microcellular foams of polystyrene and styrene-acrylonitrile copolymer, and single-edge-notched tensile toughness of microcellular foams of polystyrene, styrene-acrylonitrile copolymer, and polycarbonate," *Polym. Eng. Sci.* 35, 1178-1183.

Doroudiani, S., Park, C. B., and Kortschot, M. T. (1996). "Effect of the crystallinity and morphology on the microcellular foam structure of semicrystalline polymers," *Polym. Eng. Sci.* 36, 2645-2662.

Doroudiani, S., Park, C. B., and Kortschot, M. T. (1998). "Processing and characterization of microcellular foamed high-density polyethylene/isotactic polypropylene blends," *Polym. Eng. Sci.* 38, 1205-1215.

Gendron, R., and Vachon, C. (2003). "Effect of viscosity on low density foaming of poly(ethylene-co-octene) resins," *J. Cell. Plast.* 39, 71-85.

Guo, G., Lee, Y. H., Rizvi, G. M., and Park, C. B. (2005). "PBA-based extrusion foaming of HDPE/wood-fiber composites," Annual Technical Conference - ANTEC, Conference Proceedings, Boston, MA, United States, 92-96.

Guo, G., Lee, Y. H., Rizvi, G. M., and Park, C. B. (2008). "Influence of wood fiber size on extrusion foaming of wood fiber/HDPE composites," *J. Appl. Polym. Sci.* 107, 3505-3511.

Guo, G., Rizvi, G. M., Lee, Y. H., and Park, C. B. (2006). " Morphology in WPC during extrusion foaming with N2" Annual Technical Conference - ANTEC, Conference Proceedings, Charlotte, NC, United States, 947-951.

Guo, G., Rizvi, G. M., and Park, C. B. (2007). "Comparison of N_2 and CO_2 in extrusion foaming of wood-fiber composites," Annual Technical Conference - ANTEC, Conference Proceedings, Cincinnati, OH, United States, 2206-2210.

Guo, G., Rizvi, G. M., Park, C. B., and Lin, W. S. (2004). "Critical processing temperature in the manufacture of fine-celled plastic/wood-fiber composite foams," *J. Appl. Polym. Sci.* 91, 621-629.

Kim, Y. S., Guo, G., Wang, K. H., Park, C. B., and Maine, F. W. (2004). "Processing/structure/property relationships for artificial wood made from stretched PP/wood-fiber composites," Annual Technical Conference - ANTEC, Conference Proceedings, Chicago, IL., United States, 1608-1613.

Li, Q., and Matuana, L. M. (2003). "Foam extrusion of high density polyethylene /wood-flour composites using chemical foaming agents," *J. Appl. Polym. Sci.* 88, 3139-3150.

Martini, J., Waldman, F., and Suh, N. P. (1982). "Production and analysis of microcellular thermoplastic foams," Annual Technical Conference - Society of Plastics Engineers, San Francisco, CA, USA, 674-676.

Matuana, L. M., Park, C. B., and Balatinecz, J. J. (1997). "Processing and cell morphology relationships for microcellular foamed PVC/wood-fiber composites," *Polym. Eng. Sci.* 37, 1137-1147.

Matuana, L. M., Park, C. B., and Balatinecz, J. J. (1998). "Cell morphology and property

relationships of microcellular foamed PVC/wood-fiber composites," *Polym. Eng. Sci.* 38, 1862-1872.

Mirabella, F. M., and Bafna, A. (2002). "Determination of the crystallinity of polyethylene/α-olefin copolymers by thermal analysis: Relationship of the heat of fusion of 100% polyethylene crystal and the density," *J. Polym. Sci. Polym. Phys.* 40, 1637-1643.

Rizvi, G. M., Park, C. B., and Guo, G. (2008). "Strategies for processing wood plastic composites with chemical blowing agents," *J. Cell. Plast.* 44, 125-137.

Rizvi, G. M., Matuana, L. M., and Park, C. B. (2000). "Foaming of PS/wood fiber composites using moisture as a blowing agent," *Polym. Eng. Sci.* 40, 2124-2132.

Rizvi, G. M., Park, C. B., Lin, W. S., Guo, G., and Pop-lliev, R. (2003). "Expansion mechanisms of plastic/wood-flour composite foams with moisture, dissolved gaseous volatiles, and undissolved gas bubbles," *Polym. Eng. Sci.* 43, 1347-1360.

Seeler, K. A., and Kumar, V. (1993). "Tension-tension fatigue of microcellular polycarbonate: Initial results," *J. Reinf. Plast. Comp.* 12, 359-376.

Zhang, J., Park, C. B., Rizvi, G. M., Huang, H., and Guo, Q. (2009)." Investigation on the uniformity of HDPE/wood fiber composites in a twin-screw extruder," *J. Appl. Polym. Sci.* 113, 2081-2089.

Zhang, H., Rizvi, G. M., and Park, C. B. (2004). "Development of an extrusion system for producing fine-celled HDPE/wood-fiber composite foams using CO_2 as a blowing agent," *Adv. Polym. Technol.* 23, 263-276.

Zhang, S., Rodrigue, D., and Riedl, B. (2005). "Preparation and morphology of polypropylene/wood flour composite foams via extrusion," *Polym. Comp.* 26, 731-738.

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