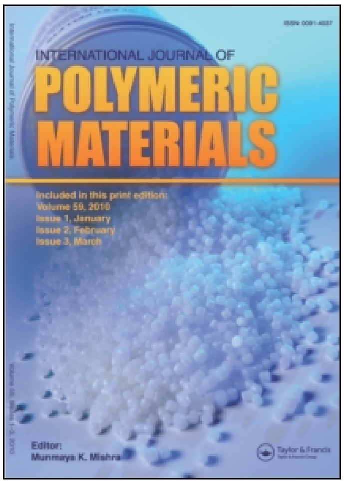

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CHARACTERIZATION OF MICROCELLULAR FOAMED POLYOLEFIN BLEND COMPOSITES WITH WOOD FIBER

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CHARACTERIZATION OF MICROCELLULAR FOAMED POLYOLEFIN BLEND COMPOSITES WITH WOOD FIBER

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The effects of wood fiber content on the void fraction, cell morphology, and notched Izod impact strength of microcellular foamed HDPE/PP blend composites with wood fiber were studied. The influence of wood fiber content on the carbon dioxide adsorption and desorption in the samples was also examined. Adsorption of carbon dioxide decreased with increased wood fiber content. Gas diffusion rates were faster as wood fiber content increased. The void fraction decreased dramatically when wood fiber was introduced in the blend. Environmental scanning electron microscopy (ESEM) was used to investigate the effects of wood fiber content on cell morphology. The 30:70 HDPE/PP polymer blend without wood fiber resulted in a high void fraction, with a uniform and well-developed microcellular structure, but when wood fiber was introduced, a uniform and well-developed microcellular structure could not be produced. The effects of foaming on Izod impact strength were dependent on wood fiber content.

Keywords: polyolefin, composit, wood fiber, microcellular, foam

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INTRODUCTION

Microcellular plastics are foamed polymers characterized by cell densities larger than 10^9 cells/cm^3 per unit volume of the original unfoamed polymer, and cell sizes in the range of 0.1 to 10 μm [1]. They have shown the potential to improve impact strength [2–5]. Research about microcellular polymers has been reviewed in References [6–7]. Most research has centered on amorphous polymers because they are much easier to foam compared to semicrystalline polymers. It is known that microcellular foaming of neat high density polyethylene (HDPE) and neat polypropylene (PP) is very difficult to achieve through a batch foaming process, due to their high crystallinity [2–3, 8–9]. However, a microcellular structure can be developed in a semicrystalline polymer by quenching the polymer during cooling from the melt to achieve relatively low crystallinity [8] or by blending with a suitable ratio of an immiscible polymer [2–3, 9]. Many studies on microcellular foaming of composites with wood fiber in batch processes have been done on PVC, which is an amorphous polymer, by Matuana et al. [4–5, 10–12]. Very little work has been done on microcellular foams containing wood fiber prepared by extrusion [13–16] or injection molding [17]. Only one report of research on foamed wood fiber/polyethylene composites made by a batch process was found in the literature [18]. Microcellular foams of HDPE/PP blend composites with wood fiber made by a batch process have not been extensively studied.

This recent investigation has shown that the void fraction and cell morphology of microcellular foams of HDPE/PP blends and their composites with wood fiber were strongly dependent on processing conditions (foaming time and foaming temperature) and blend composition as well as wood fiber content [9]. The solubility of CO_2 in HDPE/PP blends was related to total crystallinity. Blends decreased in crystallinity of both HDPE and PP [9] and facilitated the formation of a microcellular structure in HDPE/PP blends [2–3, 9]. The cells start to grow at the interface of the polymer blends due to the poorly bonded interphases of immiscible HDPE/PP blends. However, to achieve a uniform and well-developed microcellular structure, foaming time and temperature had to be relatively high (175°C for 30 s) with the appropriate blend ratio (HDPE/PP 50:50 or 30:70 by weight) [2]. Foamed neat HDPE and neat PP with a high void fraction had a large-celled structure on the surface and were unfoamed at the center [2, 9]. Moreover, to improve impact strength, the microcellular structures had to be well developed and uniform with small cell size and high cell-population density [2].

In this study, microcellular foaming of HDPE/PP blend composites with wood fiber is investigated. The effects of wood fiber content in HDPE/PP blend composites on the CO_2 adsorption and desorption was investigated first. The effects of wood fiber content on the void fraction of microcellular foams of HDPE/PP blend composites and cell morphology are examined. In addition, the results of Izod impact strength of the foamed samples are compared with those of unfoamed specimens.

MATERIALS

Injection molding grade HDPE [Dow HDPE 00452N, melt index 4 g/10 min (ASTM D1238), density 0.952 g/cc] and extrusion and injection molding grade PP [INSPIRE H704-04, melt index 4 g/10 min (ASTM D1238), density 0.90 g/cc] were used as polymeric matrices. Commercial grade carbon dioxide was used as a blowing agent. Aspen hardwood fiber was used as the reinforcement (Abitibi Corporation, Alpena, MI). The mesh size of wood fiber was in the range of 30–200.

METHODOLOGY

The effects of wood content on carbon dioxide adsorption and desorption, void fraction, and cell morphology, as well as notched Izod impact strength of microcellular foamed HDPE/PP blend composites with wood fiber were investigated. At a foaming condition of 175°C for 30 s, the foamed 30:70 HDPE/PP blend (by weight) evidenced high void fraction [9], and a well-developed uniform microcellular foam structure [2, 9] with a high cell population density and small cell size [2], which significantly increased the impact strength compared to unfoamed samples [2]. Therefore, the 30:70 HDPE/PP blend ratio and the foaming condition of 175°C for 30 s were used in this study.

Sample Preparation

The 30:70 HDPE/PP polymer blend and composites with wood fiber [0, 5, 10, 15 and 30 per hundred parts of blend resins (phr)] were extruded using a Baker Perkins Model ZSK-30, 30 mm, 26:1 co-rotating twin-screw extruder (Werner & Pfleiderer Corporation, Ramsey, New Jersey) as described previously [9]. Six-inch lengths of extrudate were compression-molded into panels (2 mm in thickness) in a hydraulic hot press at 185°C for 5 min using 30,000 psi. From these panels, ½ inch by 1 inch rectangular test specimens were cut for sorption experiments and microcellular foaming experiments and ½ inch by 2.5 inch rectangular specimens were cut for impact test experiments.

Sorption Experiments

The diffusion and concentration of absorbed CO_2 in the samples were measured in the sorption experiments following the approach described in References [4–5, 9, 11–12]. The samples were saturated in a pressure vessel with carbon dioxide at room temperature (23–25°C) and 800 psi for 24 h [4–5, 9, 11]. This length of time was determined to be sufficient for saturation based on the present authors' previous work [9].

The solubility of CO_2 in the HDPE/PP blend composite can be estimated in terms of mass fractions using the following equation [3]:

$$S_c = \{[S_{am,HDPE}(1-\chi_{HDPE}) + S_{cr,HDPE}(\chi_{HDPE})][x_{HDPE}] \\ + [S_{am,PP}(1-\chi_{PP}) + S_{cr,PP}(\chi_{PP})][x_{PP}] + [S_{wood}][x_{Wood}]\} \quad (1)$$

where S_c, $S_{am,HDPE}$, $S_{am,PP}$, $S_{cr,HDPE}$, $S_{cr,PP}$ and S_{wood} are the solubilities of CO_2 in the composite, in the amorphous regions of HDPE and PP, in the crystalline regions of HDPE and PP, and in wood fiber, respectively. χ_{HDPE} and χ_{PP} are the crystalline fractions of HDPE and PP in the HDPE/PP blends, respectively, and x_{HDPE} and x_{PP} are the weight fractions of HDPE and PP, respectively.

If the solubility of CO_2 in the crystalline regions of the polymer matrix [3, 8] and in the wood fiber [11] are neglected, the theoretical solubility of CO_2 in the HDPE/PP blend composites (S_c), may be rewritten as [3]:

$$S_c = S_{am,HDPE}(1-\chi_{HDPE})(x_{HDPE}) + S_{am,\,PP}(1-\chi_{PP})(x_{PP}) \quad (2)$$

The solubilities of CO_2 in the amorphous regions can also be calculated from the measured solubilities of CO_2 in pure HDPE ($S_{measured\ HDPE}$) and PP ($S_{measured\ PP}$) from the sorption experiments [9], and the crystallinities of pure HDPE and PP from DSC experiments [9] using the following equations [3]:

$$S_{measured\ HDPE} = S_{am,HDPE}(1-\chi_{HDPE}) \quad (3)$$

$$S_{measured\ PP} = S_{am,PP}(1-\chi_{PP}) \quad (4)$$

From the authors' previous study, the crystallinities of the HDPE and PP were found to be 73.2% and 49.2%, respectively [9]. The measured solubilities of CO_2 in the pure HDPE and PP were 2.1 and 4.2 wt%, respectively [9]. The calculated $S_{am,HDPE}$ and $S_{am,PP}$ are 8.0 and 8.3 wt%, respectively, and these values were substituted in Eq. 2. Therefore, the solubility of CO_2 in the HDPE/PP blend composites can be calculated by:

$$S_c = 7.99(1 - \chi_{HDPE})(x_{HDPE}) + 8.30(1 - \chi_{PP})(x_{PP}) \qquad (5)$$

The measured crystalline fractions of HDPE (61.9%) and PP (43.8%) in the 30:70 HDPE/PP blend [9] were substituted in Eq. 5. The predicted solubility of CO_2 in the HDPE/PP blend composites can be estimated by the following equation:

$$S_c = 3.04(x_{HDPE}) + 4.67(x_{PP}) \qquad (6)$$

Weight loss as a function of $t^{1/2}/l$ was used to determine the diffusion coefficient [9–12]. The diffusivity of gas (D) was determined following the approach described elsewhere [11].

Microcellular Foaming Experiments and Foam Characterization

In batch microcellular foaming experiments, the samples were saturated with CO_2 at a high pressure (800 psi) and room temperature for 1 day. Next the CO_2 saturated samples were immediately immersed in a hot glycerin bath [2, 9–12] for foaming and then were immediately quenched in cold water [19] to freeze the foam structures and minimize cell coalescence [19]. The void fractions (VF) may be calculated by ($VF = 1 - \rho_f/\rho$), where ρ_f and ρ are the density of the foamed and unfoamed samples [9–12]. The average cell diameter and the cell-population density of foamed samples were determined following the approach described in References [10–12].

The notched Izod impact strengths of unfoamed and foamed samples were determined using a Tinius Olsen model 92 Impact Tester following ASTM D 256-97 [20]. At least 8 foamed samples and 14 unfoamed samples were tested. All foamed samples were allowed to desorb gas for at least two weeks before property testing to eliminate the effects of the remaining gas in the samples [21–22].

Statistical Analysis

Data were analyzed by ANOVA and Tukey's Studentized Range (HSD) test using the SAS software program ($\alpha = 0.05$).

RESULTS AND DISCUSSION

Effect of Wood Fiber Content on Sorption Behaviors of CO_2

It is known that the foamability of polymers is affected by the sorption of gas in the polymer, and that the mechanisms of cell nucleation and cell growth are influenced by the solubility of gas in the polymer and the rate of gas loss [8, 10–12]. It has been well demonstrated that solubility of gas is reduced and the diffusivity of CO_2 increased by the addition of wood fiber into the PVC matrix [11, 12], but no work has been found on HDPE/PP blend composites. Therefore, the effect of wood fiber content on the sorption behaviors of CO_2 in HDPE/PP blend composite with wood fiber was investigated first. The results are summarized in Table 1, and Figure 1 shows the desorption curves for CO_2 used to calculated the diffusivity of CO_2 in the samples. The data clearly show trends similar to those reported in previous research [11, 12].

As expected, the solubility of CO_2 in HDPE/PP blend composites was affected by the addition of wood fiber in the blend. The measured solubility of gas decreased as the ratio of wood fibers increased [12]. Because the solubility of gas in the crystalline regions of the polymer blend and wood fibers is negligible, increasing wood fiber content in the blend reduces the volume of the amorphous portion of the polymer in the HDPE/PP blends available for gas solution [12, 19]. Consequently, the gas uptake by the HDPE/PP blend composite with wood fibers is much lower than that absorbed by the unfilled HDPE/PP blend. It should also be mentioned that the predicted solubility of gas was higher than the measured values, regardless of wood fiber content. The lower measured solubility values might be due to a significant gas loss that occurred during CO_2 uptake measurement [12, 19].

TABLE 1 The Solubility and Diffusivity of CO_2 in HDPE/PP 30:70 Blends and Their Composites with Wood, and Percent Void Fraction in Foamed Samples as a Function of Wood Content

Wood content (phr)	Solubility of CO_2 (wt%)		Diffusivity of CO_2 (cm^2/s)	VF (%)
	Measured	Predicted (Eq. 6)		
0	3.9	4.2	1.1E-04	31.1
5	3.8	4.0	1.4E-04	17.1
10	3.1	3.8	2.1E-04	10.4
15	2.8	3.6	2.6E-04	9.1
30	1.6	3.2	5.6E-04	7.7

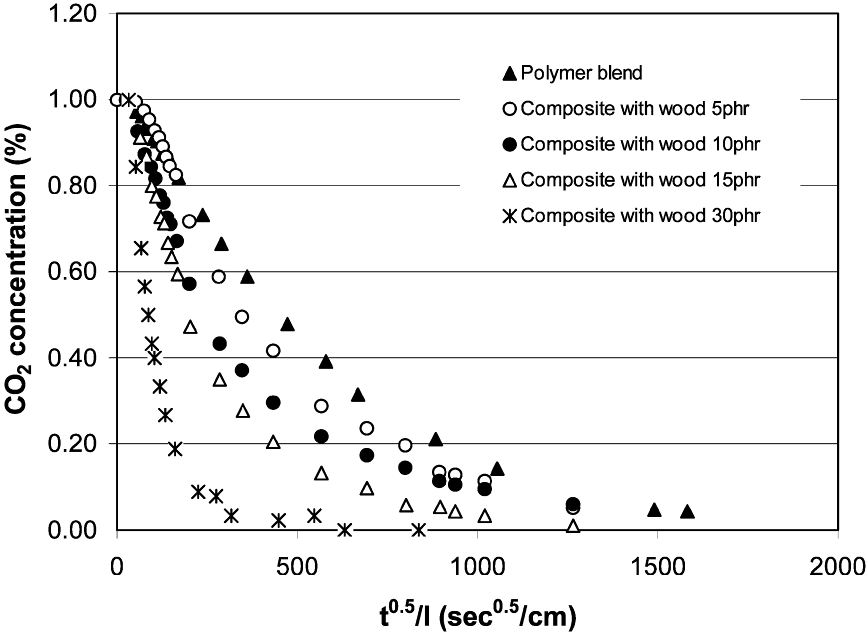

FIGURE 1 Effect of wood fiber content on desorption curves of 30:70 HDPE/PP blend with wood fiber.

The diffusivity (*D*) of CO_2 in HDPE/PP blend was also affected by the incorporation of wood fiber in the blend. As expected, the diffusivity of CO_2 increased with increasing wood fiber content, due to the poor interfacial adhesion between the fiber and the blend matrix [12]. Matuana et al. [12] have reported that poor surface adhesion between components allows gas to diffuse quickly through channels in the composites, thus increasing gas diffusivity.

From the current authors' experimental data, it can be concluded that both the solubility and diffusivity of CO_2 in HDPE/PP blends are strongly dependent on the wood fiber content.

Effects of Wood Fiber Content on the Void Fraction and Cell Morphology of Foamed HDPE/PP Blend Composites

The variation of void fraction of microcellular foamed HDPE/PP blends as a function of wood fiber content is listed in Table 1. The void fraction of foamed HDPE/PP blends dramatically decreased with increasing wood fiber content. The nucleation of bubbles and their growth, which govern the void fraction during the foaming process, are strong functions of gas uptake in the material (solubility) and the rate of gas loss (diffusivity). The void fraction dramatically decreased with the addition of 5 phr wood fiber, despite the slight change in amount of CO_2 absorbed by the sample. This indicates that sorption parameters are not the only variable affecting the void fraction of filled polymer blends. Void fraction is also affected by the viscoelastic properties of the matrix. Several investigators [10] have shown that high melt viscosity and high stiffness provide high resistance for cell growth. Because wood fiber increases the stiffness of the matrix [4, 13], it is believed that increasing wood fiber content into the HDPE/PP blend coupled with lower gas solubility and high diffusivity have prevented bubble growth. Thus blend composites with high void fractions could not be produced.

Figures 2–4 illustrate the cell morphology of microcellular foamed neat HDPE/PP blends and blend composites with wood fiber. The microcellular structure of the neat 30:70 HDPE/PP blend foamed at 175°C for 30 s was uniform and well developed (Figure 2) with a high void fraction (above 20%) (Table 1). The average cell size and cell-population density are 4 μm and 1.37E+9 cell/cm^3, respectively. Even though the HDPE/PP blend facilitated microcellular foaming (Figure 2), addition of wood fiber into HDPE/PP blend composites had a deleterious effect on the foamability of HDPE/PP blends. A microcellular structure could be generated in HDPE/PP blend composites at low wood fiber content (5 phr), but the microcellular structure was not well developed and was non-uniform. The addition of 5 phr wood fibers in the HDPE/PP blend composites resulted in reduction of average cell size (3.5 μm) and cell-population density (8.83E+8 cell/cm^2), compared to the pure HDPE/PP blend.

With 10 phr wood fiber, the average cell size (2 μm) and cell population density decreased further (Figure 4). The reduced cell size may be attributed to the fast diffusion of gas (gas loss) to the environment during the foaming process. Moreover, the ESEM micrographs (Figures 3 and 4) show clean surfaces of pockets due to the pull out of fibers, indicating poor interfacial adhesion between the polymer matrix and wood fibers. These pockets are channels for the gas to easily and quickly escape to the environment [9].

Effect of Wood Content on Impact Strength of Samples

The effects of foaming and wood fiber content on notched Izod impact strength of HDPE/PP blends are shown in Figure 5. The notched Izod impact strength of unfoamed samples tended to slightly decrease with increasing wood fiber content up to 10 phr. However,

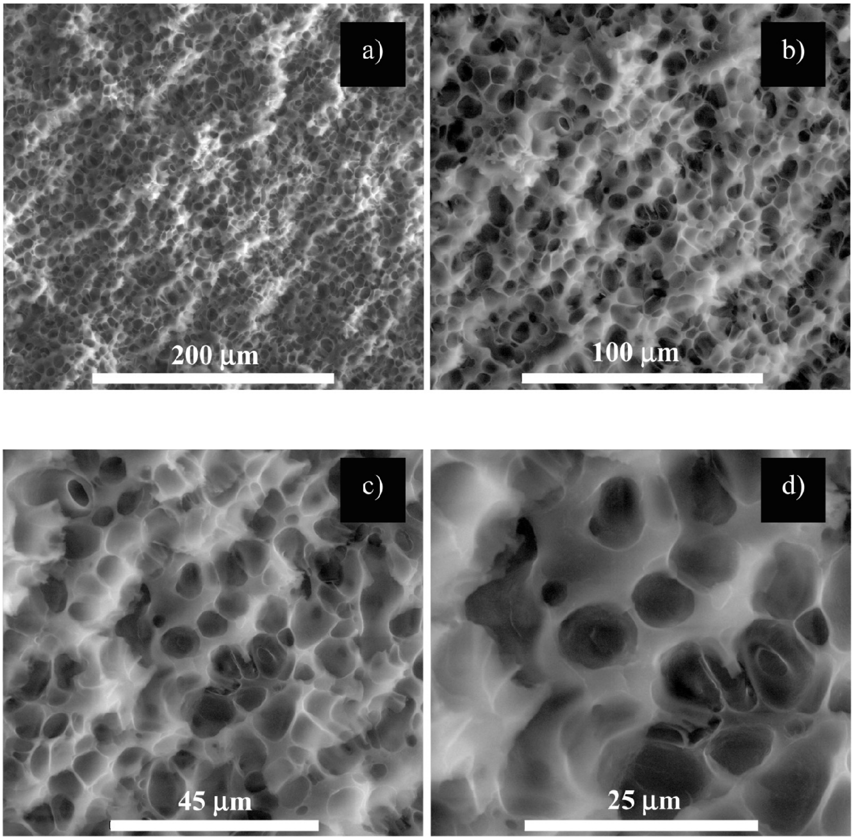

FIGURE 2 ESEM micrograph of foamed neat 30:70 HDPE/PP blend observed at different magnifications: (a) 250 ×, (b) 500 ×, (c) 1000 ×, and (d) 2000 ×.

there are no statistically significant differences between the average impact strengths of unfoamed HDPE/PP blend composites between 0 phr and 15 phr. The impact strength of unfoamed HDPE/PP blend composites with 30 phr wood fiber (~23% wood fiber content) was significantly higher than the impact strengths of other unfoamed samples. A similar observation was made by Raj et al. [23] in an early study on composites of LLDPE with aspen fiber. They found that the unnotched Izod impact strength of LLDPE composites with aspen increased with increasing wood content until around 20% wood fiber content. The impact strength dramatically decreased with a further increase in wood fiber content [23]. They concluded that

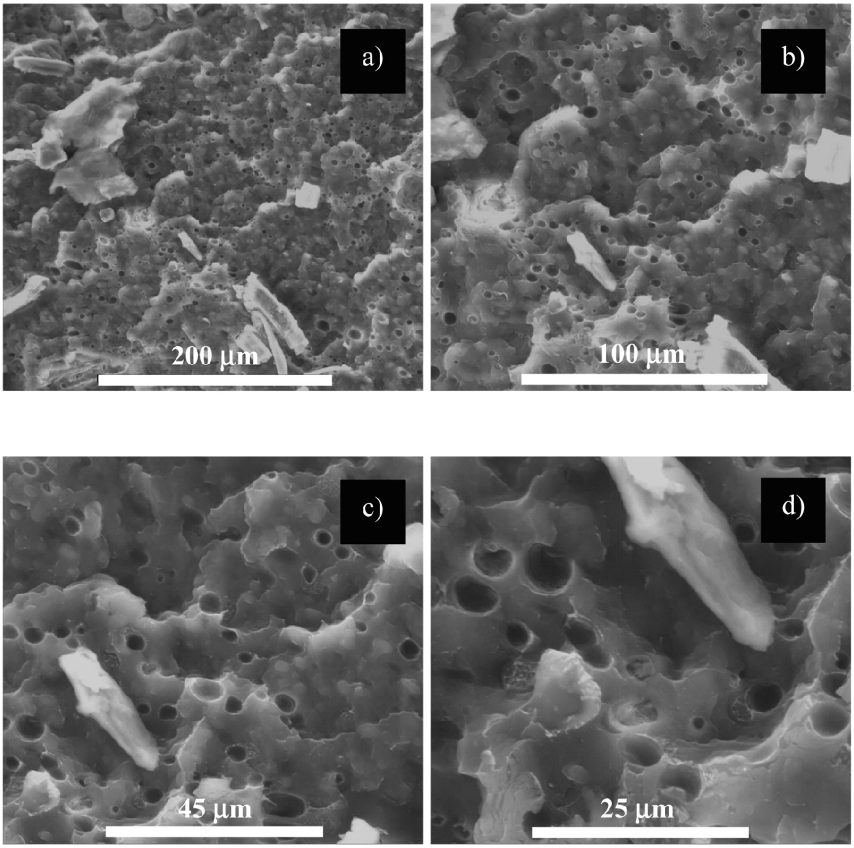

FIGURE 3 ESEM micrographs of foamed HDPE/PP 30:70 blend composite samples with 5 phr wood fiber observed at different magnifications: (a) 250 × , (b) 500 × , (c) 1000 × , and (d) 2000 × .

the impact strength decreased at higher filler content in the composites [23].

The impact strength of foamed neat HDPE/PP blend samples without wood fiber (0 phr) significantly improved, nearly doubling compared to unfoamed counterpart samples (Figure 5), because the microcellular structure was uniform and well developed (Figure 2) with a high void fraction (Table 1). The authors' previous study showed that the cell morphology has a strong relationship with the impact strength [2]. To improve the impact strength, the cell morphology has to be uniform with fully-grown cells (well-developed) [2]. For HDPE/PP blend composites with wood fiber (5, 10, and 15 phr),

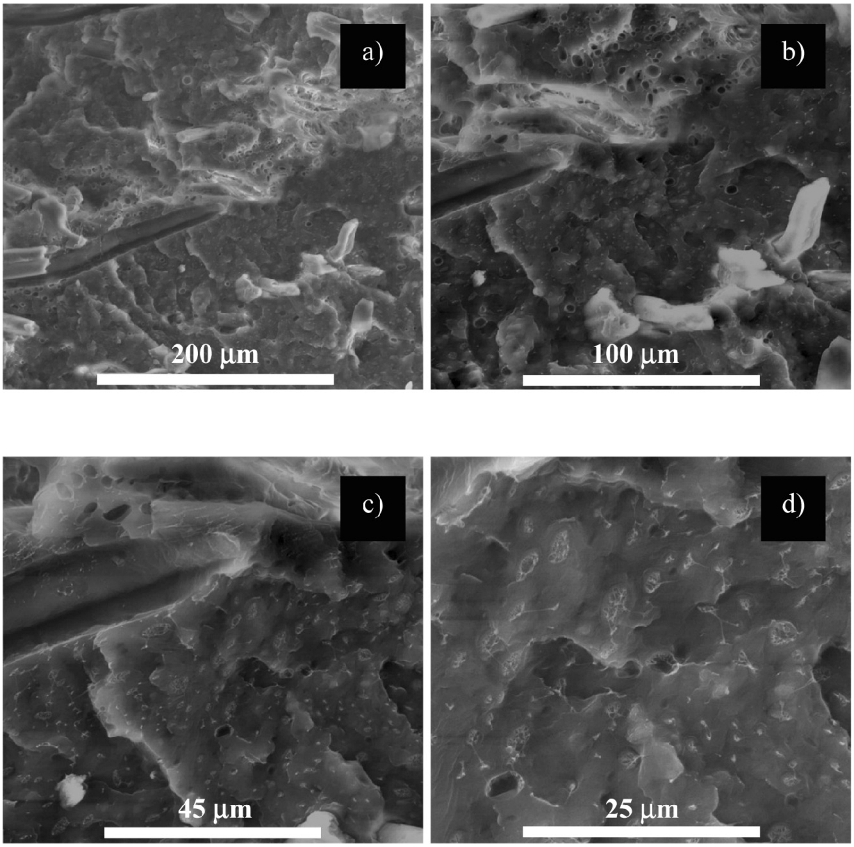

FIGURE 4 ESEM micrographs of foamed HDPE/PP 30:70 blend composite samples with 10 phr wood fiber observed at different magnifications: (a) 250 ×, (b) 500 ×, (c) 1000 ×, and (d) 2000 ×.

foaming tended to improve the impact strength. However, the differences were small and not statistically significant. ESEM micrographs (Figures 3 and 4) showed foamed HDPE/PP blend composites with low wood fiber content (5 and 10 phr) had a microcellular structure, but it was non-uniform and not well developed with a low void fraction (Table 1). Therefore, the impact strength of these HDPE/PP blend composites did not significantly improve. These results agree well with the previous study [2]. The foamed HDPE/PP blend composites with 30 phr wood fiber did not improve in impact strength at all because they did not foam well; the impact strength remained unchanged compared to the foamed counterpart samples.

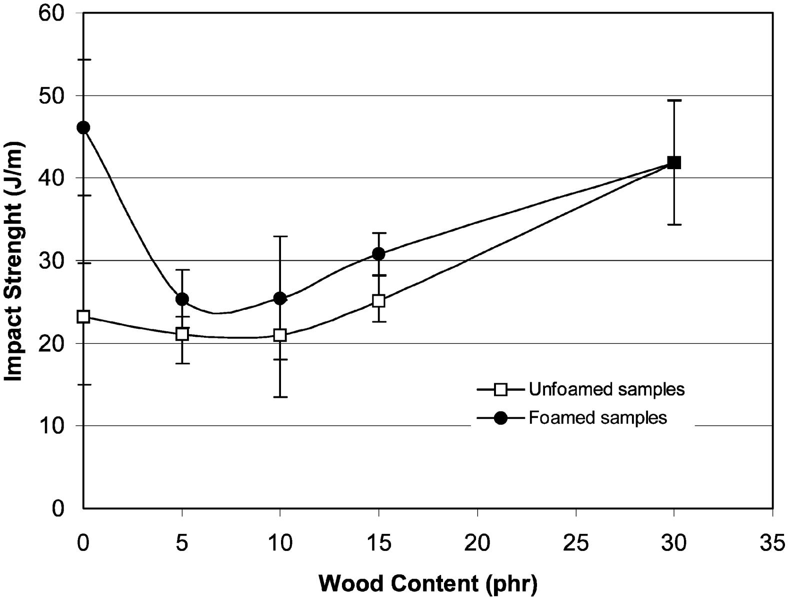

FIGURE 5 Effect of wood content on impact strength of microcellular foamed HDPE/PP 30:70 blend composites with wood fiber.

CONCLUSIONS

The effects of wood fiber content on the sorption behaviors of gas, cell morphology, and impact strength of microcellular foamed HDPE/PP blend were investigated.

The solubility of CO_2 in HDPE/PP blend decreased with increased wood fiber content due to the smaller volume of amorphous polymer in the composites, which meant less gas can be absorbed. The diffusion of CO_2 in HDPE/PP blends increased with increased wood fiber content, likely due to the poor interfacial adhesion between the polar wood fiber and non-polar polymer matrix providing channels through which gas can rapidly diffuse from the composites.

The addition of wood fiber to HDPE/PP blends affected the void fraction and cell morphology of microcellular foamed HDPE/PP blends. The void fraction of foamed HDPE/PP blends dramatically decreased with the addition of wood fiber content, due to the decreased solubility of CO_2 gas, increased rate of CO_2 gas diffusion, increased matrix stiffness, and acceleration of gas loss during foaming. Foaming of a 30:70 blend of HDPE/PP resulted in a uniform and well-developed microcellular morphology. Addition of wood fiber tended to reduce the average cell size and cell-population density.

The impact strength of HDPE/PP blends and their composites was related to wood fiber content and cell morphology. The impact strength of foamed HDPE/PP blends with a uniform and well-developed cell morphology significantly improved. The impact strengths of the foamed HDPE/PP blend composites with wood fiber were dependent on the cell morphology. There was little improvement if the microcellular structure was not well developed and uniform.

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