Microcellular Foam of Polymer Blends of HDPE/PP and Their Composites with Wood Fiber

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ABSTRACT: In this study, the effects of batch processing conditions (foaming time and temperature) and blend composition as well as the effect of incorporating wood fiber into the blends on the crystallinity, sorption behavior of CO_2, void fraction, and cellular morphology of microcellular foamed high-density polyethylene (HDPE)/polypropylene (PP) blends and their composites with wood fiber were studied. Blending decreased the crystallinity of HDPE and PP and facilitated microcellular foam production in blend materials. The void fraction was strongly dependent on the processing conditions and on blend composition. Foamed samples with a high void fraction were not always microcellular. The addition of wood fiber inhibited microcellular foaming. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2842–2850, 2003

Key words: blends; microcellular foams; polyethylene; polypropylene; composites

INTRODUCTION

The U.S. Environmental Protection Agency reported that containers and packaging are the largest category of plastic in municipal solid waste (MSW). Recycling reduces the impact of this waste on limited landfill space. Polyolefins are the largest group of polymers used as packaging materials such as water bottles, milk bottles, juice bottles, rigid bottle packaging for household detergents, and other cleaners. High-density polyethylene (HDPE) is commonly used as the body of the bottle and polypropylene (PP) is commonly used as the cap. These rigid bottles are easy to separate and collect, thus making them one of the top recycled materials. However, separation of plastic waste into individual parts and sorting is costly and time consuming, and separation of HDPE and PP is difficult because of their similar density. Moreover, it is well known that blends of HDPE/PP decrease the material's mechanical properties such as impact strength because HDPE and PP are immiscible and incompatible, despite the similarity of their chemical structures.[1] Substantial research has concentrated on improving the mechanical properties by adding compatibilizer to the polyolefins to improve the interfacial adhesion.[2–4]

Not long ago, microcellular foaming was proposed as an effective technique to toughen plastics.[5] Microcellular foamed polymer is a new class of materials characterized by cell densities larger than 10^9 cells per cubic centimeter of unfoamed materials and cell sizes in the range of 0.1 to 10 μm. Microcellular polymers are produced through the utilization of the thermodynamic instability of gas in a polymer system. Three main steps are involved[6]: (1) polymer/gas solution formation by saturating a polymer with a high pressure gas; (2) microcellular nucleation; and (3) cell growth and density reduction. Microcellular polymers offer a reduction in material usage and are lightweight. They also exhibit enhanced impact strength,[7–10] toughness,[5] fatigue life,[11] and thermal stability.[12] Therefore, this method could be applied to improve the mechanical properties of HDPE/PP blends. However, the research on microcellular foams has been mainly directed at amorphous polymers. Very little work has been done on the foaming of semicrystalline polymers because microcellular foaming of semicrystalline polymers is difficult to achieve because of the high crystallinity and the size of the crystallites.[13] Only one report of research on microcellular foamed HDPE/isotactic PP blends was found.[8]

In this study, microcellular foams of polymer blends of HDPE and PP as well as composites with wood fiber were investigated to determine the effects of processing conditions, blend composition, and wood fiber content on the void fraction and cell morphology of the materials. The effects of blend composition and crystallinity on solubility and diffusion of CO_2 and

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consequently on the void fraction were also investigated.

METHODS

Sample preparation

Injection-molding-grade HDPE [Dow HDPE 00452N, melt index 4 g/10 min (ASTM D1238), density 0.952 g/mL] (Dow Chemical Co., Midland, MI) and extrusion and injection-molding-grade PP [INSPIRE H704-04, melt index 4 g/10 min (ASTM D1238), density 0.90 g/mL] (Dow Chemical Co.) were used as polymeric matrices. Commercial grade carbon dioxide was used as a blowing agent. Aspen hardwood fiber at 30 parts wood fiber per hundred parts resin was used as the reinforcement (Abitibi Corp., Alpena, MI). This ratio was chosen in accord with previous work on microcellular foamed wood/plastic composites.[9] The mesh size of wood fiber was in the range of 30–200.

In this study, the effects of blend composition, foaming time and temperature, and wood fiber content on void fraction and cell morphology of foamed samples were investigated. HDPE/PP blends (100 : 0, 70 : 30, 50 : 50, 30 : 70, and 0 : 100% w/w) and composites with wood fiber were manufactured by using a Baker Perkins model ZSK-30, 30 mm, 26 : 1 corotating twin-screw extruder (Werner and Pfleiderer Corp., Ramsey, NJ) at 100 rpm. Two different temperature profiles were used. For neat HDPE, temperatures were set at 155°C for all six control zones. For PP and HDPE/PP blends, temperatures were set at 180°C in the first two zones and 155°C in the remaining four.

Six-inch lengths of extrudate were compression-molded (Carver Laboratory Press, model M, Menomenee Falls, WI) at 30,000 psi for 5 min, a temperature of 160°C for HDPE and HDPE composites, and 185°C for samples containing PP. The 2-mm-thick panels were cut to 0.5 × 1 in. test specimens.

Sorption experiments

Saturation of the samples with CO_2 [room temperature (23–25°C), 800 psi for 24 h] was used to determine the diffusion and solubility of CO_2 in the samples. CO_2 uptake (solubility) was measured by weight gain immediately after pressure release. Weight loss as a function of $t^{1/2}/L$ was used to determine the diffusion coefficient.[14–16]

Microcellular foaming experiments

In batch microcellular foaming experiments, the CO_2 saturated samples were immediately immersed in a hot glycerin bath[14–16] at various foaming temperatures (135, 160, and 175°C) for foaming times of 5, 10, 20, or 30 s and then were immediately quenched in cold water.

Characterization of foams

The densities of the samples were measured by a water displacement technique (ASTM D-792). The weights of unfoamed and foamed samples were measured in air (M_a) and distilled water (M_w), and the density was determined by:

$$\text{Density} = 0.9975 \left(\frac{M_a}{M_w} \right) \tag{1}$$

The reported density is the average of five replicates.

The void fraction (VF) was calculated by[14–16]:

$$VF = 1 - \frac{\rho_f}{\rho} \tag{2}$$

where ρ is density of the unfoamed sample and ρ_f is density of the foamed sample. Sample morphology was investigated through an environmental scanning electron microscope (ESEM; ElectroScan 2020 system with a LaB6 filament, Electro Scan Co., Boston, MA) at acceleration voltages of 10 and 20 kV. The samples were immersed in liquid nitrogen and fractured to ensure that the microstructure remained clean and intact.[14]

Differential scanning calorimetry (DSC)

DSC was performed by using 3–5 mg samples (DSC 2010, TA Instruments, New Castle, DE) to investigate the crystallinities of the HDPE, PP, and their blends. Three to five replicates were heated from room tem-

TABLE I
Melting Temperature (T_m) and Percentage Crystallinity (χ) of Blend Samples

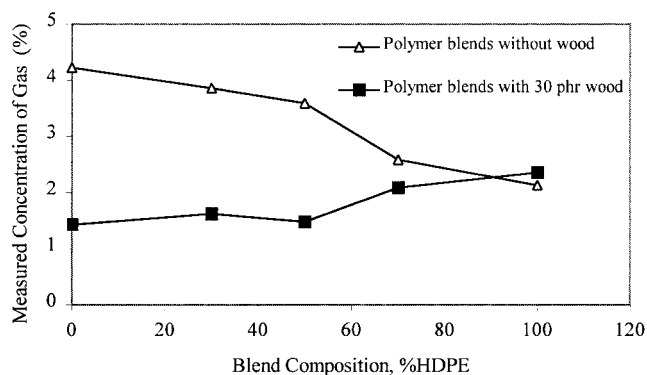| Blends	$T_{m,HDPE}$ (°C)	χ_{HDPE} (%)	$T_{m,PP}$ (°C)	χ_{PP} (%)	Total % χ in blends
HDPE	132.1	73.3	—	—	73.3
70:30	130.0	68.6	163.4	43.4	61.1
50:50	130.0	63.5	162.4	40.1	51.8
30:70	128.8	61.9	163.8	43.8	49.2
PP	—	—	164.3	49.2	49.2

Figure 1 Measured solubility of CO_2 in the polyolefin blends as a function of blend composition.

perature to 200°C at 10°C/min. Nitrogen was used as a purge gas with a flow rate of 50 mL/min. The heats of fusion of HDPE and PP that were used in the

calculation of the crystalline fractions were 293 and 209 J/g, respectively.[17] The calculation of crystallinity (χ) of the HDPE, PP and their blends, and total crystallinity are described in detail elsewhere.[18]

RESULTS AND DISCUSSION

Effect of blending on crystallinity

The results of the effect of blending on crystallinity are summarized in Table I. Blending decreased the crystallinity of both HDPE and PP. The crystallinity of HDPE decreased gradually with an increase in the PP component. Melting temperature of HDPE decreased somewhat gradually with an increase in the PP content. For PP, there was no statistically significant difference between the crystallinities in the three blends; all were less than pure PP. In a similar pattern the melting temperatures of all blends were slightly lower
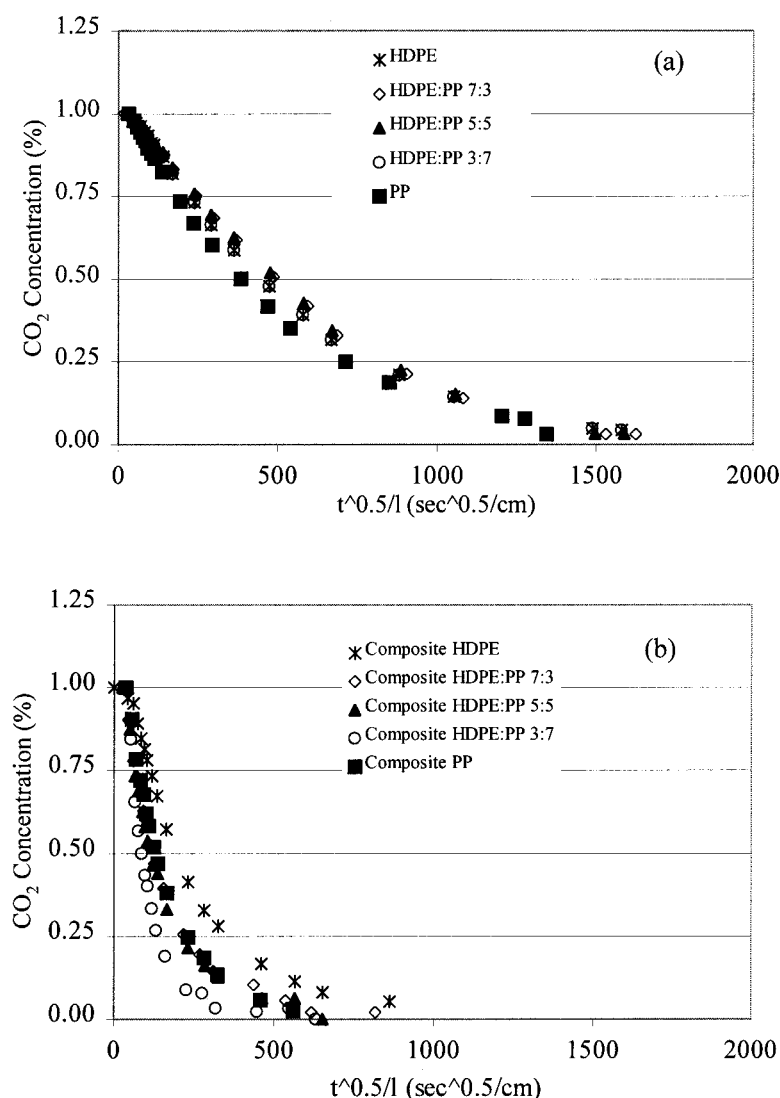

Figure 2 Desorption curves of polymer blends and composites with wood fiber (a) polymer blends, (b) composites with wood fiber.
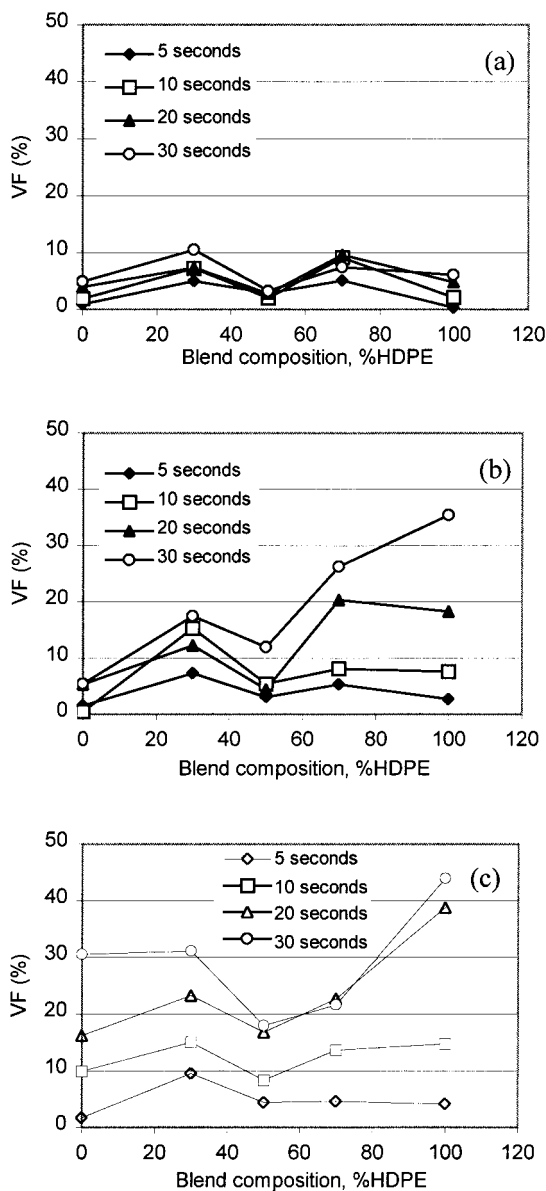
Figure 3 Effects of foaming time and blend composition on the void fraction of unfilled HDPE/PP blends foamed at (a) 135°C, (b) 160°C, (c) 175°C.

than that of pure PP, but had no consistent pattern. The total amount of crystallinity of the blends decreased as PP content increased (Table I).

Effects of polymer blend composition and wood fiber content on solubility and diffusivity of carbon dioxide

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 amount of the gas dissolved in the polymer and the rate of gas diffusion.[5,9,11–13] Figure 1 shows that the amount of CO_2 gas dissolved decreased as the ratio of HDPE increased in the blends

without wood fibers. The measured solubility of gas was strongly dependent on the total crystallinity of the polymer (Table I). When the HDPE component increased, the total crystallinity increased and the solubility of gas decreased. The measured solubility of gas decreased with the addition of wood fiber into the polymer matrix, perhaps because of the high crystallinity of the fiber, as suggested by Matuana et al.[10,14] However, the measured solubility of gas in composites tended to increase with the increased HDPE component. The reason for this behavior is not fully understood.
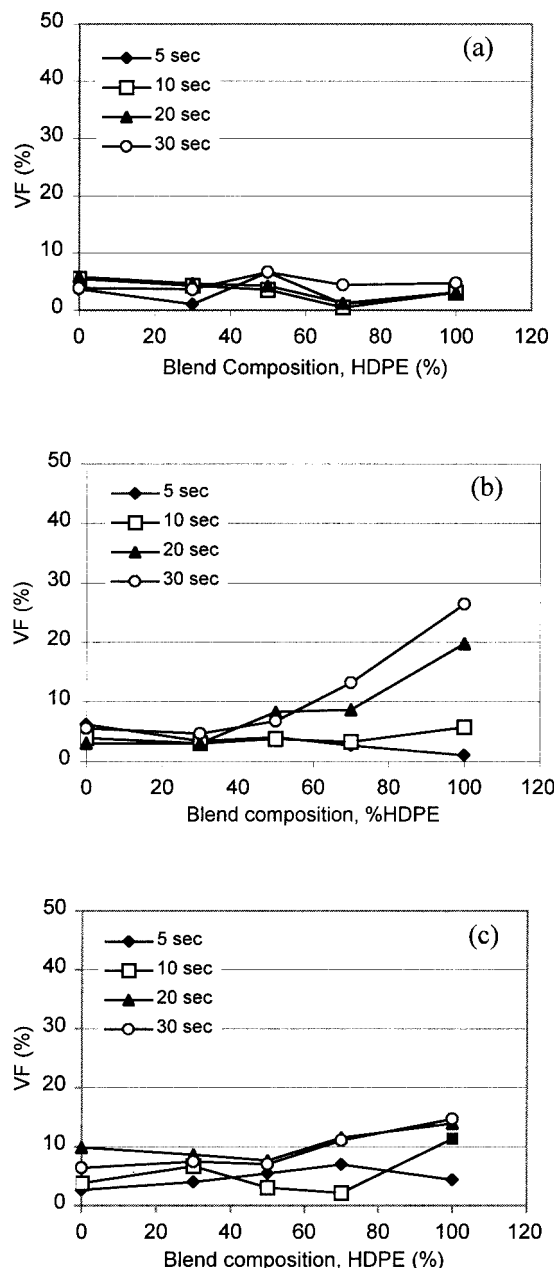

Figure 4 Effects of foaming time and blend composition on the void fraction of HDPE/PP blend filled with 30 phr wood fibers foamed at (a) 135°C, (b) 160°C, (c) 175°C.
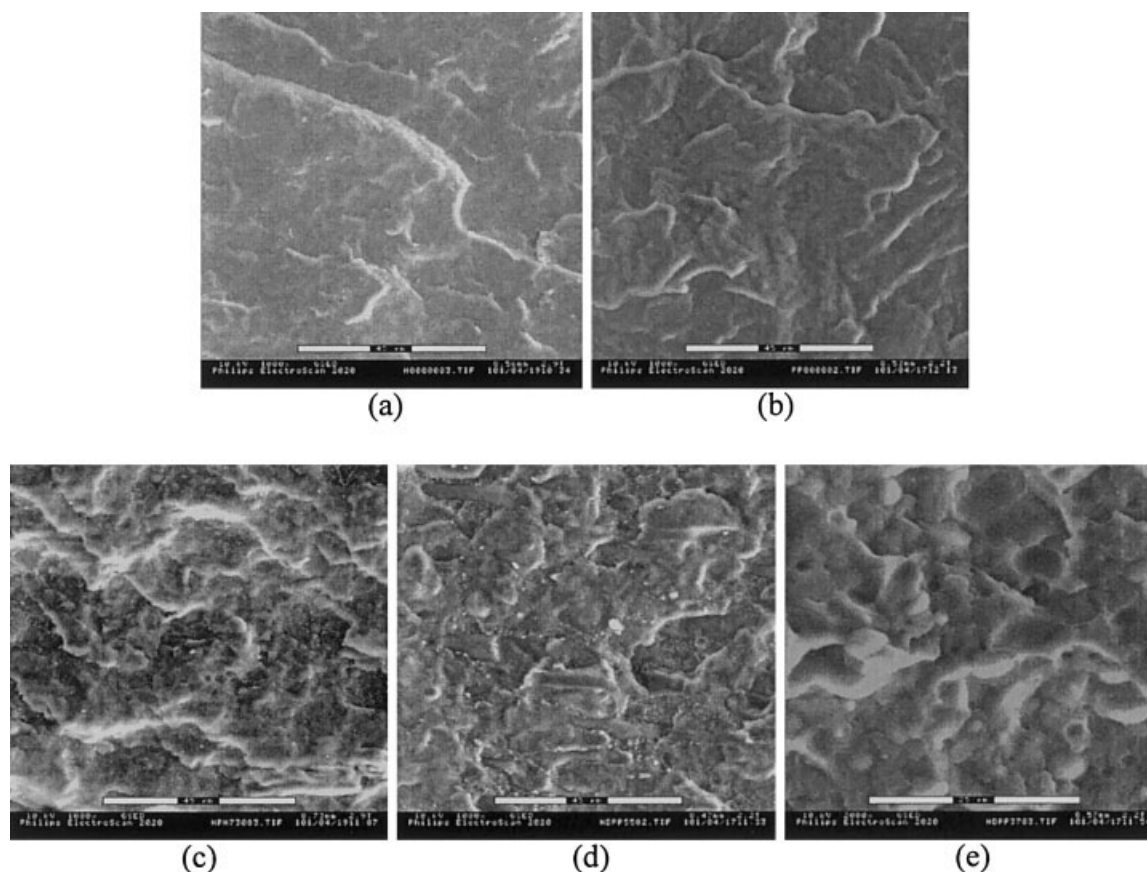
Figure 5 ESEM micrographs of unfoamed polymers and their blends: (a) HDPE, (b) PP, (c) HDPE/PP 70 : 30, (d) HDPE/PP 50 : 50, and (e) HDPE/PP 30 : 70 (all scale bars 45 μm except (e) 25 μm).

Desorption isotherm curves for the polymer blends and composites with wood fiber are illustrated in Figure 2. As expected, gas diffusion rates were higher in the composites than in the polymers. In general, the addition of fiber to the polymer without pretreating the wood surface leads to poor adhesion between the wood fiber and the polymer matrix. The poor surface adhesion of the polar wood to the nonpolar polymer provides a channel through which gas can quickly escape from the composite.[10,14]

Effects of foaming conditions, blend composition, and wood fiber content on void fraction of foamed samples

The effects of foaming time, foaming temperature, and blend compositions on the void fractions of both unfilled HDPE/PP blends and HDPE/PP blends filled with 30 phr wood fiber are shown in Figures 3 and 4, respectively.

Figure 3 shows that at the lowest foaming temperature (135°C) regardless of foaming time and at short foaming times (5 and 10 s) regardless of foaming temperature, a high void fraction (above 20%) was not achieved. However, when the foaming temperature was well above the melting temperature of the sample

and foaming time was long enough (20 and 30 s), the void fraction increased dramatically as foaming time and temperature increased. Thus, when the foaming temperature of HDPE at 30 s increased from 135 to 160 and 175°C, the void fraction increased from 5.8 to 35.4 and 43.9%, respectively.

The ability to use high temperature to achieve high void fraction is limited by the rapid decrease of strength of the polymer at temperatures above the melting point. This results in substantial deformation of the polymer matrix, even though the softened polymer matrix is favorable to bubble growth.[14,15] For example, foaming HDPE samples at 175°C for 30 s provided a high void fraction, but the high temperature and long foaming time resulted in deformation of the samples.

The void fraction of the foamed polymer blends was strongly dependent on the blend compositions. Polymer blends of 70 : 30 and 30 : 70 HDPE/PP resulted in a higher void fraction, but 50 : 50 HDPE/PP behaved strangely. Its void fraction was lower than that of the other blends at all foaming times and temperatures and generally was even lower than pure HDPE and PP. By the rule of mixing, the void fraction of 50 : 50 HDPE/PP would be expected to be between the void fractions of HDPE and PP. For instance, the void frac-
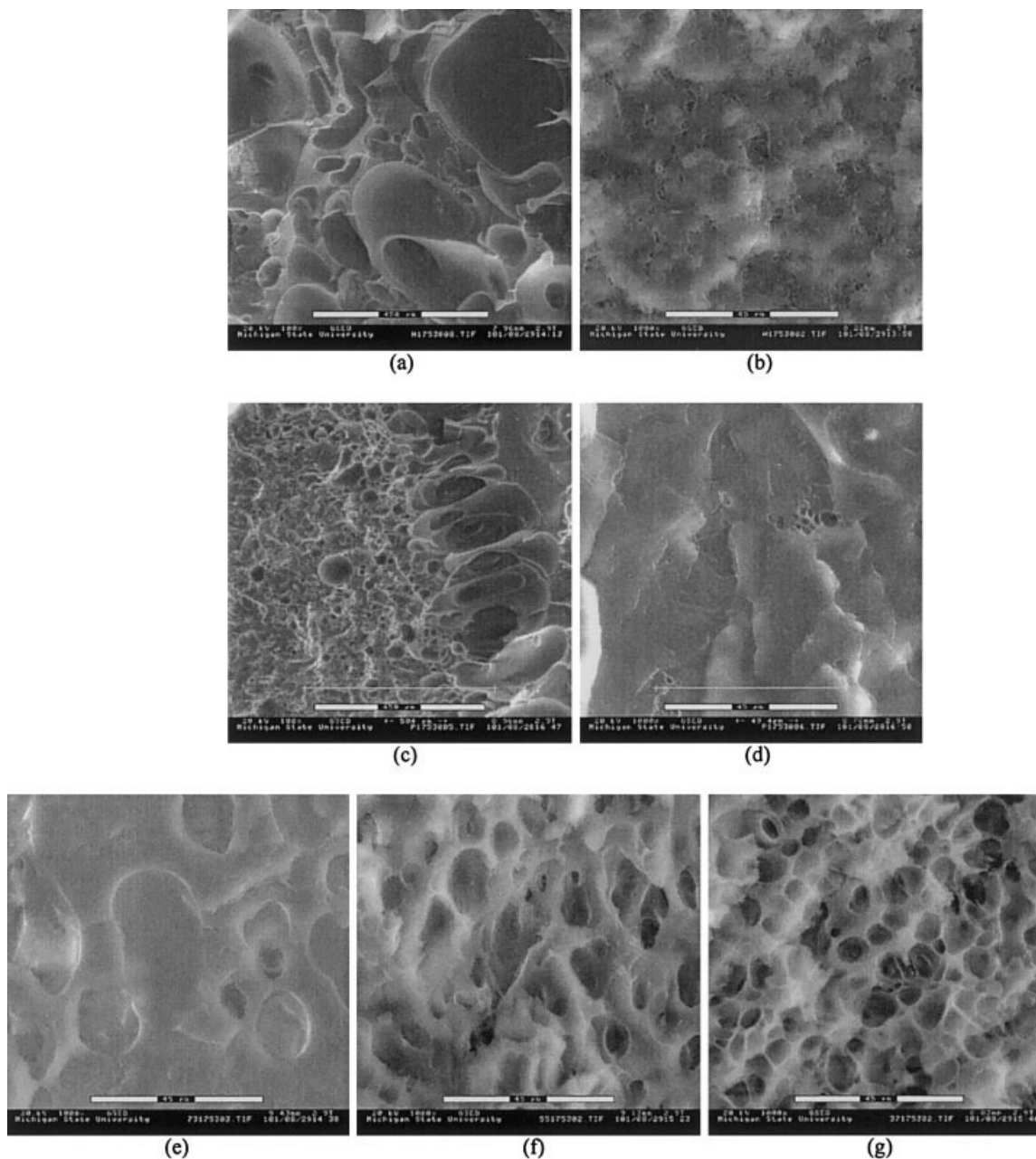
Figure 6 ESEM micrographs of foamed polymer blends at 175°C for 30 s (a) HDPE (surface), (b) HDPE (center), (c) PP (surface), (d) PP (center); (e) HDPE/PP 70 : 30, (f) HDPE/PP 50 : 50, and (g) HDPE/PP 30 : 70 ((a) and (c) scale bars 450 μm; all other scale bars 45 μm).

tion of 50 : 50 HDPE/PP blend was less than 20% for a foaming time of 30 s at 175°C, whereas the void fraction of HDPE was above 40% and PP was around 30%. This was especially surprising in view of the results of Doroudiani et al.,[8] who achieved the highest void fraction at this composition. This behavior should be investigated further.

As shown in Figure 4, the addition of wood fiber decreased the void fraction because of lower CO_2 uptake (Fig. 1); microcellular foams with a high void fraction were not achieved. HDPE composites had a reasonably high void fraction at high foaming temper-

atures and times, but were not microcellular, as will be discussed in the next section. The mechanism of cell growth is governed by the stiffness of the gas/polymer matrix, the rate of gas diffusion, and the amount of gas loss.[14,15] The void fraction decreased dramatically with the addition of wood fiber as it increased both matrix stiffness and the rate of gas loss (Fig. 2).

Cell morphology of foamed HDPE/PP blends

ESEM micrographs of unfoamed polymer blends are shown in Figure 5. Both HDPE and PP exhibited a
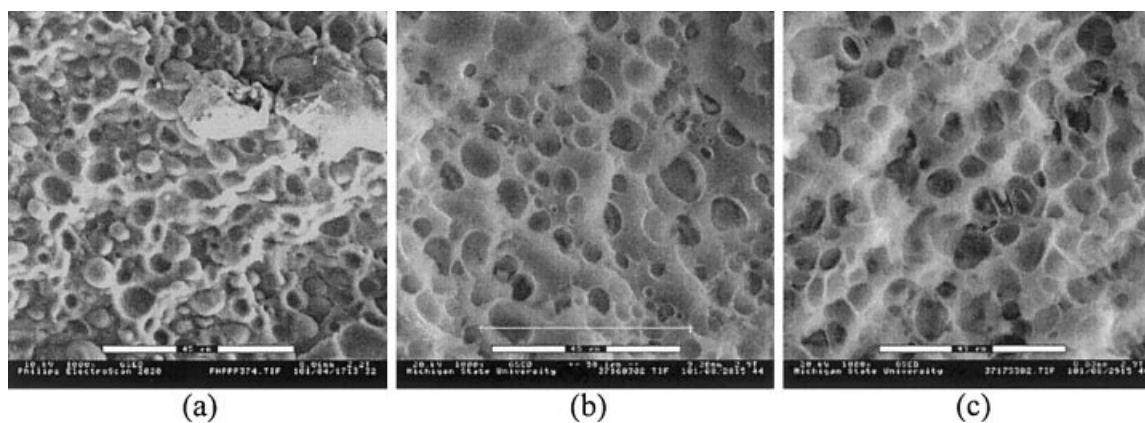
Figure 7 ESEM micrographs of foamed HDPE/PP 30 : 70 samples at (a) 135°C for 10 s, (b) 160°C for 30 s, (c) 175°C for 30 s (all scale bars 45 μm).

single phase, whereas the blends showed phase separation. In the 70 : 30 HDPE/PP blend, HDPE was the continuous phase and PP was the dispersed phase. The size of the PP regions increased with increasing PP content. Interpenetrating inversion structures were observed in 50 : 50 HDPE/PP. Phase inversion was observed in 30 : 70 HDPE/PP; PP became the continuous phase and HDPE became the dispersed phase.[19]

The effect of blend composition on cell morphology at fixed foaming time and foaming temperature (30 s, 175°C) is shown in Figure 6. In both HDPE and PP, a high void fraction could be achieved but cell morphology was not favorable; HDPE had a large-celled structure on the surface [Fig. 6(a)] and a microcellular structure toward the middle of the samples [Fig. 6(b)]. For foamed PP, a high void fraction was also achieved. However, cellular structures developed only locally near the surface of the samples [Fig. 6(c)], and the center of the sample could not be foamed [Fig. 6(d)]. When HDPE and PP were blended, the microcellular structures were significantly improved and more uniformly distributed [Fig. 6(f, g)]. However, the void fraction of 70 : 30 HDPE/PP blend did not increase at this condition [Fig. 3(c)] because of cell coalescence [Fig. 6(e)]. Foaming 50 : 50 HDPE/PP gave uniform structures but a high void fraction was not achieved for reasons not understood.

The effect of foaming temperature on cell morphology is shown in Figure 7. It is known that the poorly bonded interfacial regions of immiscible polymer blends have a lower activation energy for bubble nucleation.[20] Therefore, the interface of the immiscible HDPE/PP blends could be favorable for nucleating sites for bubble growth. Therefore, the blend of 30 : 70 HDPE/PP was investigated at a low foaming temperature (135°C) and short time (10 s). Bubbles nucleated between the HDPE globules and PP matrix [Fig. 7(a)]; however, a high void fraction was not achieved. It is difficult to distinguish marks from the pull-out of HDPE globules from true microcellular bubbles.

When the foaming time and temperature increased the void fraction increased (Fig. 3), resulting in a uniformly distributed microcellular foamed structure [Fig. 7(b, c)].

The effect of foaming time on the cell morphology was studied by maintaining the blend composition at 30 : 70 HDPE/PP and the foaming temperature at 175°C and varying the foaming times (5, 10, 20, and 30 s). The void fraction increased when the foaming time increased [Fig. 3(c)] and ESEM micrographs showed the development of cell growth (Fig. 8). When the foaming time increased, the average cell size increased. Cell growth with increased foaming time is shown in Figure 8.

The effect of wood fiber on the cell morphology was studied by maintaining the foaming conditions at 175°C for 30 s. The void fraction decreased when wood fiber was added to the polymer matrix. Some cellular structures could be found in HDPE composites, but these features were not evident in the PP or the blends (Fig. 9). Addition of wood fiber to the polymers decreased the solubility and increased the rate of CO_2 gas diffusion in the samples, accelerating the gas loss during foaming. Only a small portion of gas remained for nucleation and cell growth. Therefore, development of microcellular structures and a high void fraction were inhibited by adding the wood fiber.

CONCLUSION

In this article, the microcellular foams of polymer blends of HDPE and PP as well as composites with wood fiber were studied to produce foamed samples with high void fraction. To achieve this study, the effects of batch processing conditions (foaming time and temperature) and blend composition as well as the effect of incorporating wood fiber into the blends on the crystallinity, sorption behavior of CO_2, void fraction, and cellular morphology of microcellular
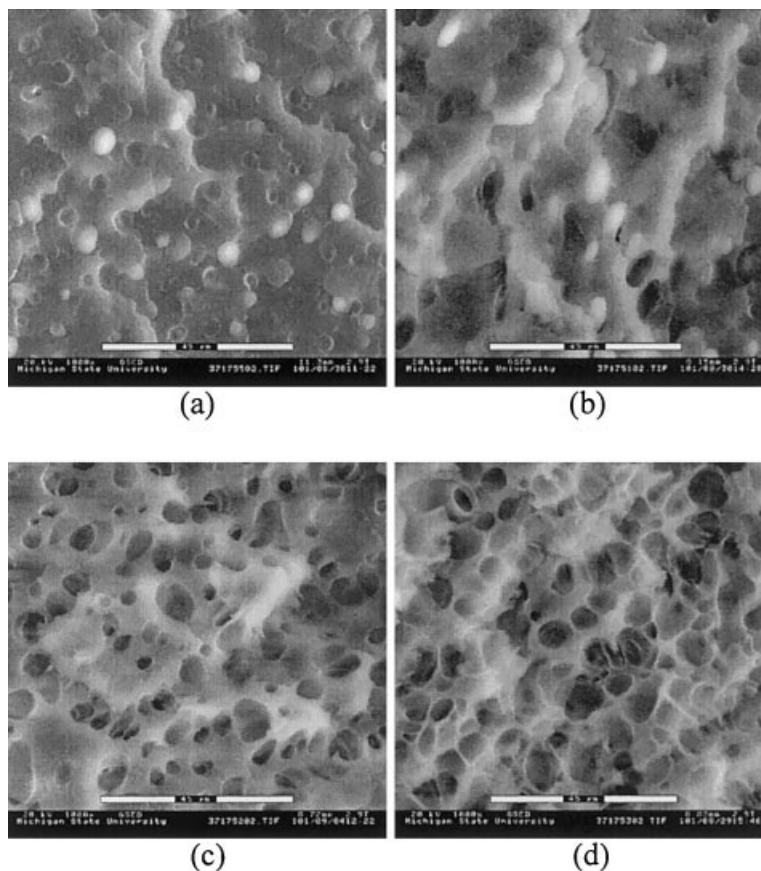
Figure 8 ESEM micrographs of foamed HDPE/PP 30 : 70 samples at 175°C for (a) 5 s, (b) 10 s, (c) 20 s, (d) 30 s (all scale bars 45 μm).

foamed HDPE/PP blends and their composites with wood fiber were investigated.

The effects of solubility and diffusivity of CO_2 in polymer blends and their composites as well as crystallinities in polymer blends were studied first. As expected, solubility of CO_2 in polymer blends decreased with increased HDPE content, related to total crystallinity. Measured solubility of CO_2 in the composites was lower than polymer blends because of crystallinity of wood fiber. A trend of increasing the solubility of CO_2 in composites with an increase in HDPE content was observed for reasons not well understood. Blends decreased in the crystallinity of both HDPE and PP.

Second, the effects of the solubility, diffusivity, crystallinity, processing conditions, blend composition, as
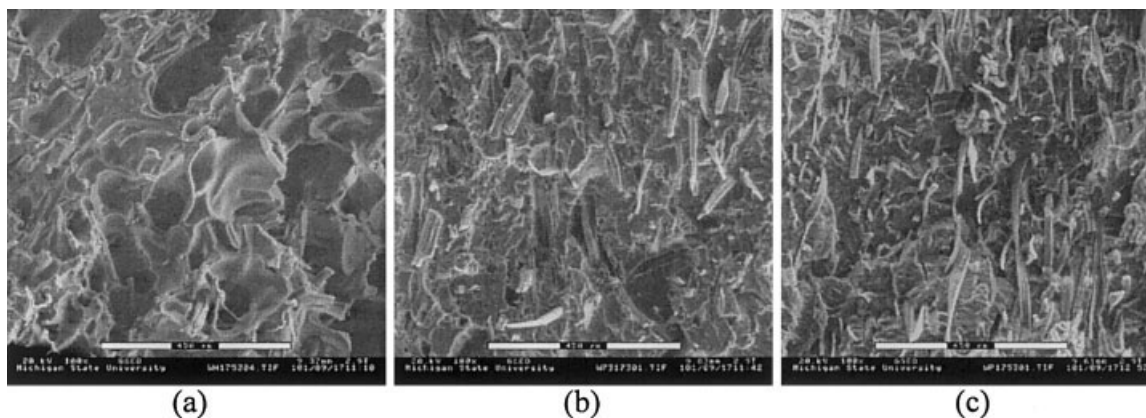

Figure 9 ESEM micrographs of foamed composite with wood fiber at 175°C for 30 s (a) HDPE, (b) HDPE/PP 70 : 30, (c) PP (all scale bars 450 μm).

well as the effect of incorporation of wood fiber into the blend on the void fraction and cell morphology were investigated. A high void fraction was dependent more on the rate of gas loss (diffusivity) than on the solubility of gas in the polymers or composites. The amount of crystallinity affected the cell structure. It can be concluded that blending facilitated the formation of microcellular foam structures in polyolefins. All polymer blends foamed with a uniform fine cellular structure, whereas large-celled structures were observed near the surface in pure HDPE and PP. Blend composition, foaming time, and temperature strongly affected the void fraction and cell morphology. Use of blends increased the ability to produce microcellular foams. To achieve high void fraction, the foaming temperature had to be well above the melting temperature of the polymer and foaming time must be long enough. Addition of wood fiber in the polymers inhibited the foaming ability, related to less gas and fast loss.

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