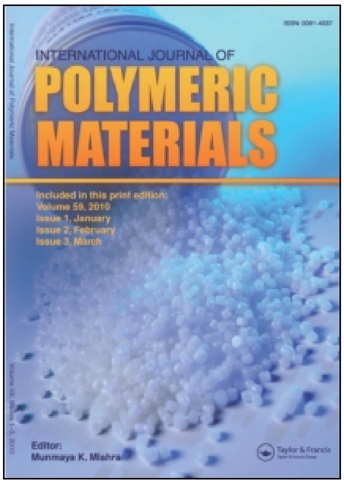

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Batch Foam Processing of Polypropylene/Polydimethylsiloxane Blends

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Batch foaming processes were employed to prepare plastic foams from polypropylene (PP)/polydimethylsiloxane (PDMS) blends. Various amounts of PDMS were added to a PP matrix, and the resulting blends were batch foamed at different saturation pressures using carbon dioxide (CO_2) as the blowing agent. Ultimately, the blend foams exhibited better cell morphologies and higher cell densities in comparison with those prepared from PP alone. The increased solubility of CO_2 in PDMS made it as a CO_2 reservoir to induce more nucleation. When the PDMS content exceeded a certain level, however, it exerted a negative influence on cell density. Moreover, as the saturation pressure was raised, the cell density of the blend foams increased significantly. It was also noted that the addition of PDMS to the PP matrix generated some very small cells in the larger cell walls.

Keywords cell density, expansion ratio, polydimethylsiloxane, polypropylene

INTRODUCTION

In thermoplastic foam processing, it is desirable to produce a fine-cell structure since polymeric foams with a small cell size and a more uniform cell

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distribution are known to exhibit better mechanical properties [1–3]. Polypropylene (PP) is commonly employed as a base material in foam processing; however, because of its weak melt strength, it is difficult to achieve good foams using PP [4,5]. In order to obtain foams with fine-cell structures, researchers have explored compensatory measures, such as physical blending [6], grafting [7], and the use of branched PP [8,9].

Consequently, PP is often blended with other materials so as to yield foams with enhanced morphologies under batch or continuous processing conditions. Research conducted by Doroudiani et al. [10] and Rachtanapun et al. [11] showed that microcellular foams were improved significantly when PP was blended with high-density polyethylene (HDPE) and supercritical CO_2 was used as a blowing agent. Zhang and her colleagues [12] also blended PP with HDPE as well as low-density polyethylene (LDPE); they obtained good blend foams across a very narrow temperature range. Nanoparticles, such as clay [5,13], calcium carbonate [14], and talc [15] have been proven to be effective nucleation agents in PP foaming; when added to PP, they increase the foam's cell density significantly. Reichelt [16] et al. investigated the blend ratio of high melt strength PP and linear PP on the extensional rheology, foamability, and mechanical properties of final foam products. They were ultimately concerned with the effects of introducing heterogeneous nucleation and enhancing the extensibility of the polymer blend. Park and his colleagues have conducted extensive research on the volume expansion ratio of PP blends [17–19].

PDMS exhibits high CO_2 solubility and low surface tension [20,21], which are both advantageous qualities for achieving successful foaming. Researchers have explored the use of block or graft copolymers containing PDMS as the core block or grafted segment in foam processing; these kinds of copolymers have been found to behave not only as potential heterogeneous nucleation sites, but also as CO_2-philic reservoirs that trap CO_2. For example, CO_2-philic graft copolymers, such as PMMA-g-PDMS, were found to increase cell density across all pressures and temperatures above the critical micelles' concentration in poly (methyl methacrylate) (PMMA) [22]. Pieter Spitael et al. have investigated the blending of PS-b-PDMS diblocks with a polystyrene (PS) matrix; the foaming results showed a bimodal cell size distribution, as well as a modest increase in cell concentration [21].

In this study, four types of foams comprised of PP/PDMS blends were prepared using a batch foaming system, respectively. Maleic anhydride grafted PP (PP-g-MAH) was used as a compatibilizer to promote the dispersion of PDMS in PP, and a comparison between the cell morphologies yielded with the PP/PDMS blend and the PP/PDMS/PP-g-MAH blend was made. The effects of PDMS on the cell morphology and the expansion ratio were investigated under circumstances where CO_2 was used as a blowing agent.

EXPERIMENTAL

Materials

The Hunan Petrochemical Co. provided the PP (Daploy WB260HMS); it is a PP/PE random copolymer with a melt flow index (MFI) of 2.5 dg/min (ISO 1133. 230°C/2.16 kg). We also used a high-viscosity PDMS polymer (Dow Corning 200 Fluid) that exhibits an average kinematic viscosity of 60000 cs and a melt point of -23°C. Orevac CA 100 is a PP-g-MAH random copolymer available from Gudi; it has a high MAH content and a high MFI of 150–200 dg/min (ISO 1133. 230°C/2.16 kg). The blowing agent used in this study was CO_2, with a purity of 99.97%, supplied by Baiyun Chemistry Company (Guangdong, CHN).

Sample Preparation

One PP/PDMS/PP-g-MAH blend and four PP/PDMS blends containing different PDMS contents (shown in Table 1) were compounded at 180°C in a counter-rotating twin-screw mixer (model D6/2 from C.W. Brabender) at a rotor speed of 45 rpm for 10 min. After their removal from the mixer chamber, the blends were pressed at 180°C in a hot press to obtain a thin disk-shaped film for batch foaming. A differential scanning calorimeter (model DSC 2910) was used to analyze the thermal behavior of the polymer blends. The batch foaming experiments were performed using a batch-foaming simulation system whose components and methodology have been described previously [23–25]. The sample in the chamber was heated up to 140°C before the CO_2 was injected. The saturation pressure was maintained at the targeted pressure for 30 min before the gas was released; the pressure-drop rate was constant at -30 MPa/s for all experiments. The foamed samples were collected and the cell morphologies were analyzed using a scanning electron microscope (SEM) (Hitachi 510).

Table 1: Composition of PP/PDMS blends and DSC results.

Sample	PDMS (phr)	PP-g-MAH (phr)	T_m (°C)	T_c (°C)	T_{co} (°C)
PP	–	–	145.7	113.3	118.0
PP/PDMS/ PP-g-MAH	5.5	5.5	146.1	120.4	124.7
PP/PDMS1	2.3	0	145.4	115.7	119.3
PP/PDMS2	5.5	0	145.2	115.8	119.1
PP/PDMS3	11	0	143.0	114.2	118.1

T_m is the temperature at the melting peak; T_c is the crystallization temperature; T_{co} is the onset crystallization temperature.

The solidified foam samples were randomly collected at each processing condition and were characterized using the SEM. The volume expansion ratio and the cell population density were measured. The volume expansion ratio of each sample was calculated as the ratio of the bulk density of pure PP (ρ_P) to the bulk density of the foam sample (ρ_f). The bulk density of the foam sample was determined via water displacement:

$$\Psi = \rho_P / \rho_f \tag{1}$$

The cell density, defined as the number of cells per unit volume with respect to the unfoamed polymer, was determined from SEM micrographs using the following equation [26]:

$$N = \left(\frac{nM^2}{A}\right)^{\frac{3}{2}} \times \Psi \tag{2}$$

where, N is the cell density (cells/cm^3); n is the number of cells on the micrograph; M is the magnification factor of the micrograph; and A is the area of the micrograph (cm^2). It should be noted that the influence of the expansion ratio (Ψ) was not considered when calculating the cell density of the batch-foamed sample. Since the batch-foamed samples were very small, the application of the expansion ratio variable would have resulted in aberrant bulk density measurements.

RESULTS AND DISCUSSION

Three PP/PDMS blends (i.e., PP/PDMS1, PP/PDMS2, and PP/PDMS3) and one PP/PDMS/PP-g-MAH blend were prepared and explored in this work. Table 1 displays certain thermal behavior parameters that were crucial to obtaining accurate data in this study. According to Kaewmesri et al. [26], the melting point can be lowered by more than 14°C under the operating CO_2 pressures employed in this study. All of the blends reach their melting points at approximately 145°C, as shown in Table 1, which means that with the help of supercritical CO_2, they can be almost completely melted at 140°C. So, in the batch foaming experiments we conducted, the effects of crystals on foaming can be ignored when the foaming temperature was set to 140°C. We observed an important trend that is displayed in Table 1: the addition of PP-g-MAH to PP/PDMS enhanced the melting point and the crystallization point of the blend significantly. It is believed that the presence of PP-g-MAH decreased the mobility of the PP molecules, which led to early crystallization and hence a high crystallization temperature.

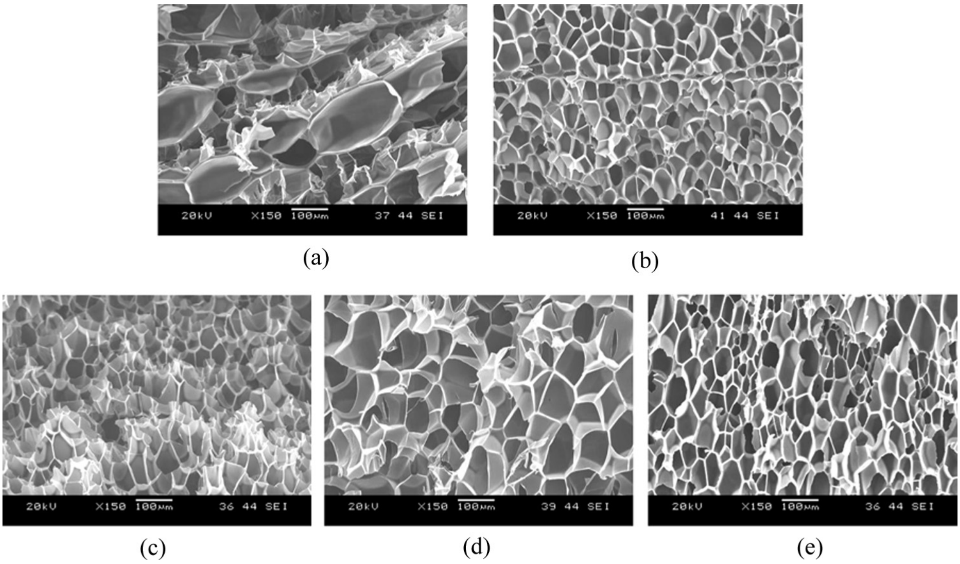
BATCH FOAMING FOR PP/PDMS BLENDS

Effects of PDMS Content on Cell Morphology

Figure 1 shows the cell morphology of neat PP, PP/PDMS blends, and PP/PDMS/PP-g-MAH blends obtained at 14 MPa and 140°C. Based on the data, it is evident that the morphologies generated in the blends differed dramatically from that achieved in the neat PP foam. Neat PP does not yield foam with good cell structure since it is vulnerable to cellular collapse and coalescence (see Figure 1 (a)). During the foaming of pure PP, abundant gas was available for cell growth; however, excessive growth incited cell rupture and gas loss. As a result, the neat PP foams were characterized by heavy cellular collapse.

By contrast, the cell morphologies of the blends were far superior to the morphology characteristic of the pure PP foams. The blend foams demonstrated a more uniform cell distribution and smaller cell sizes; the cell densities were therefore much higher. There are three reasons why the presence of PDMS improved the cell densities of the blend foams. First, PDMS is a CO_2-philic polymer; the presence of PDMS in the PP matrix thus enhanced CO_2 solubility, which was beneficial to nucleation. Second, it is likely that the introduction of other phases into the PP matrix resulted in heterogeneous nucleation at the interface between the compounds. Third, PDMS has a very low surface energy, which helped to stimulate greater cell nucleation.

Figures 1 (b), (c), and (d) show the cell structures of the three PP/PDMS blend foams. The cell densities were 1.23×10^7cells/cm^3, 1.43×10^7cells/cm^3,



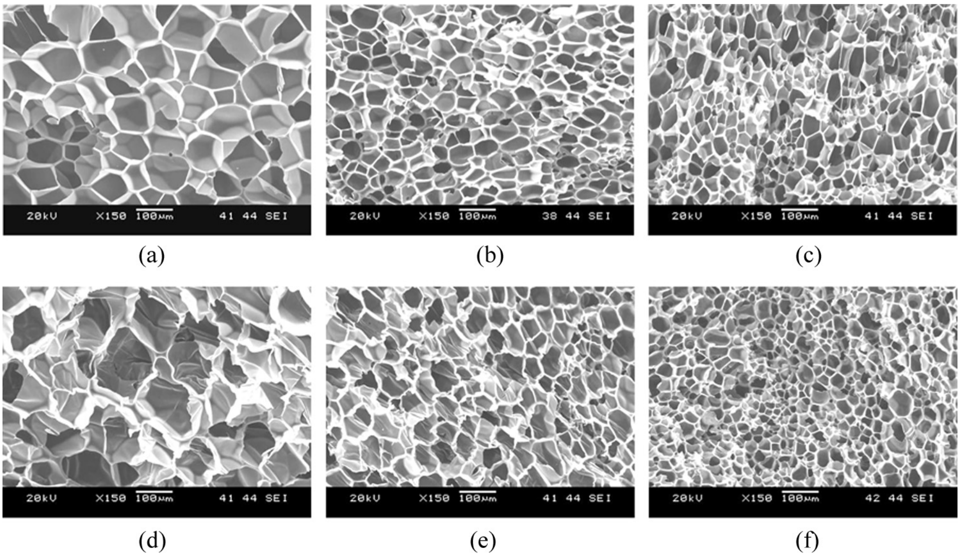
(a) (b)

(c) (d) (e)

Figure 1: Cell morphology of samples foamed at 14 MPa and 140°C: (a) PP, (b) PP/PDMS1, (c) PP/PDMS2, (d) PP/PDMS3, (e) PP/PDMS/PP-g-MAH.

and 4.1×10^6cells/cm^3, respectively. It appears that the cell size was the largest and cell density was the lowest when the PDMS content was at its highest (Figure 2 (d)). The cell density of the PP/PDMS2 foam (Figure 1 (c)) was almost the same as that of the PP/PDMS1 foam (Figure 1 (b)). Furthermore, it is evident that the cell wall of the PP/PDMS2 blend foam was much thinner than that of the PP/PDMS1 blend foam (See Figures 2 (c) and (b)). These results indicated that an increase in the PDMS content served mainly to support enough gas for cell growth as opposed to induce additional nucleation. As the PDMS content was increased further, the cell density decreased substantially. This was likely due to two factors. First, a high PDMS content offered abundant gas for cell growth; the fully grown cells therefore exhibited large sizes and low cell densities. Second, an excessive PDMS content led to a severe aggregation of PDMS in the PP matrix [27], which effectively reduced nucleation.

Typically, the addition of PP-g-MAH as a compatibilizer in foam blends improves the dispersion of PDMS in PP [27]. We expected that the improved dispersion of PDMS would change the cell morphology; however, as shown in Figures 1 (c) and (e), the presence of the compatibilizer did not improve the cell morphology considerably under the given operating conditions. Thus, the cell densities of these two blend foams did not demonstrate any obvious changes (i.e., 1.43×10^7cells/cm^3 and 1.22×10^7cells/cm^3, respectively). In the following discussion, the cell morphology of these two blends obtained at different CO_2 pressures will be analyzed in detail.



(a) (b) (c)

(d) (e) (f)

Figure 2: SEM images acquired from foamed PP/PDMS1 blend and PP/PDMS3 blend at 140°C and different pressures: PP/PDMS1: (a) 12 MPa, (b) 16 MPa, (c) 18 MPa. PP/PDMS3: (d) 12 MPa, (e) 16 MPa, (f) 18 MPa.

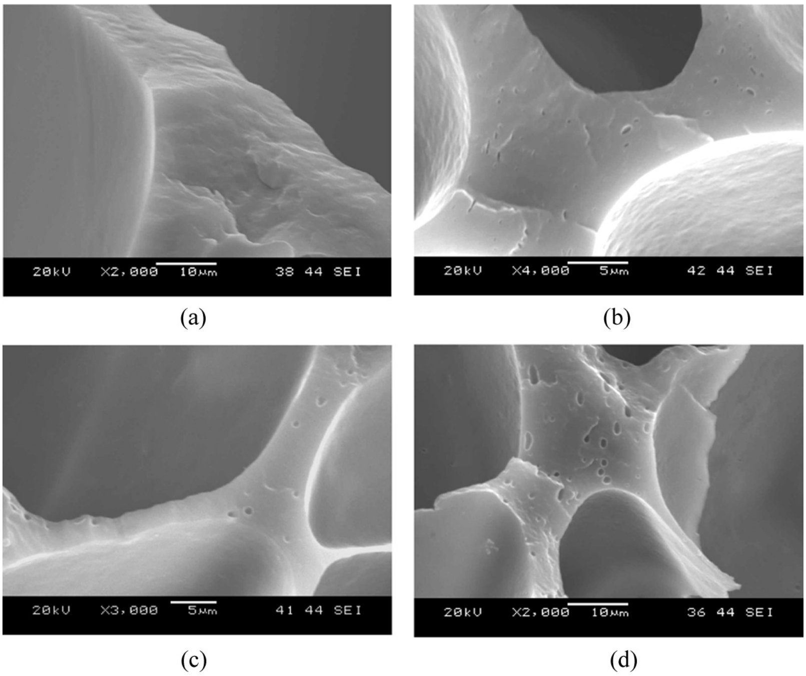
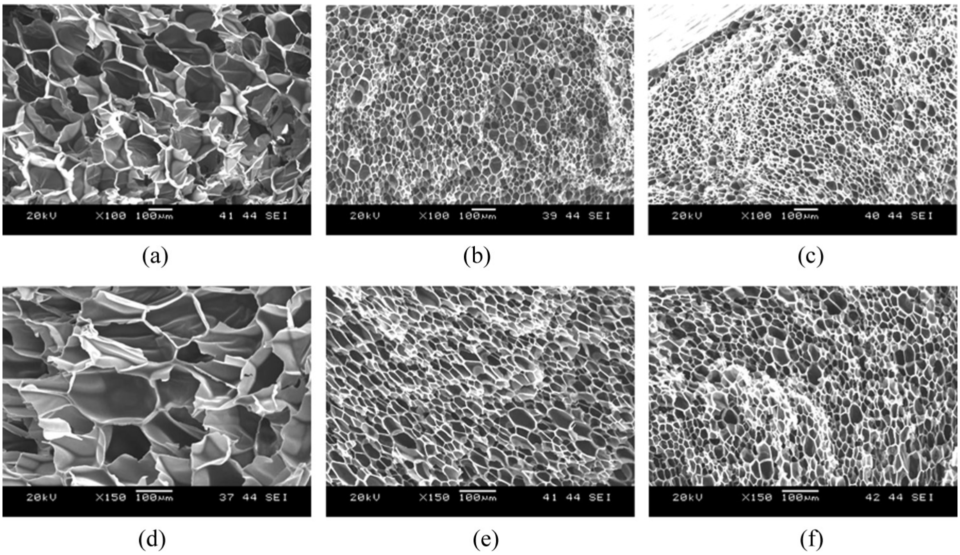


Figure 3: Closer look of the cell morphology at a foaming temperature of 140°C and a saturation pressure of 14 MPa: (a) PP; (b) PP/PDMS1; (c) PP/PDMS2; (d) PP/PDMS/PP-g-MAH.

Effects of CO_2 Pressure on the Cell Morphology of Blends

In order to discern the effects of CO_2 pressure on cell size and density, PP/PDMS blend foams were prepared at different saturation pressures but at the same temperature (140°C) and pressure drop rate (-30 MPa/s). The SEM images of the foams reveal the influence of CO_2 pressure on cell morphology (see Figures 2 and 4): as the saturation pressure rose, the cell size decreased dramatically and the cell density increased steeply. At high pressures, the availability of CO_2 for bubble nucleation increased, which in turn resulted in an elevated cell density. Figure 5 shows the cell densities of blend foams as a function of saturation pressures. It can be seen that the cell densities of all four blends followed the same trend: they increased as the saturation pressure was raised. Furthermore, the cell densities of the PP/PDMS2 and PP/PDMS/PP-g-MAH foams were virtually almost equivalent at all the saturation pressures. It is known that these two blends contain the same amount of PDMS content from Table 1, so this new discovery indicates that adding a compatibilizer to the blend did not have any tangible effect on its cell density. In fact, it may be that, in contrast to our expectations, adding PP-g-MAH did not remarkably improve the dispersion of PDMS.



(a) (b) (c)

(d) (e) (f)

Figure 4: Cell morphology of PP/PDMS2 and PP/PDMS/PP-g-MAH blends taken at different saturation pressures. PP/PDMS2 blend: (a) 12 MPa, (b) 16 MPa, (c) 18 MPa. PP/PDMS/PP-g-MAH blend: (d) 12 MPa, (e) 16 MPa, (f) 18 MPa.

Another interesting trend evident in Figure 5 is the isobaric variation of cell density with increasing PDMS concentration. At the lowest pressure (12 MPa), the cell densities of all the blend foams did not have a clear distinction. Above this pressure, however, a clear difference between the cell densities of the four blends foams was visible. The PP/PDMS3 blend, which

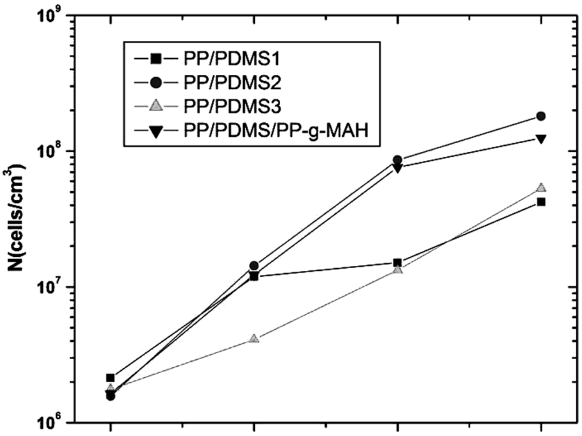


Figure 5: Foam cell density as a function of saturation pressure.

contained the highest amount of PDMS, had a much lower cell density in comparison to the other three foams. In addition, at higher pressures (16 and 18 MPa), PP/PDMS2 and PP/PDMS/PP-g-MAH foams had much higher cell densities than did PP/PDMS1 and PP/PDMS3 foams. These results suggest that an optimal PDMS content can remarkably improve cell morphology; however, if the PDMS content is too high or too low, it cannot enhance nucleation in any productive way.

A closer look at blend foams' structures shows that a few small cells of the order of 0.2–1 microns were interspersed between the large cells (as shown in Figure 3), while no small cells appeared in the cell walls of the neat PP foams. This suggests that the presence of PDMS resulted in these small cells.

It is widely known that PDMS has a much higher CO_2 solubility in comparison to PP, which means a large CO_2 concentration gradient exists between these two phases in blends. When the pressure is released, the PP/PDMS system shifts away from the equilibrium state and the CO_2 concentration gradient across the PP/PDMS interface causes the diffusion of CO_2 from the PDMS phase to the PP phase during depressurization. In this study, we surmised that there are two stages that characterize the nucleation and growth processes. We discovered that in the first stage, the PDMS phase acted as a CO_2 reservoir to support interfacial nucleation and nucleation in PP phase, whereas during the second stage, it operated as the site of homogeneous nucleation. During the first stage, the CO_2 content in the PP phase could be higher than the CO_2 saturation concentration in the PP in a long period because of diffusion, which would have led to more cell production. The gas content in the PDMS phase, however, might have been less than the CO_2 saturation concentration in the PDMS as a result of diffusion. Thus, the cell nucleation in the PDMS was hindered. After the first stage, it was impossible for nucleation to occur in the PP phase or at the interface, yet it could nonetheless take place in the PDMS phase because of its very low surface tension. The nuclei that formed during the first stage (i.e., when PDMS was behaving as a CO_2 reservoir) benefited from having had sufficient gas and a longer time to grow; they eventually yielded large cells. By contrast, the nucleation that transpired in the PDMS phase resulted in very small cells.

CONCLUSIONS

In these studies, in the case of batch foaming, introducing PDMS into the PP matrix had a pronounced influence on the cell morphology. The structures of blend foams can be tailored by altering the saturation pressure and the PDMS content. A higher saturation pressure resulted in a significantly improved cell structure. An excessively high PDMS concentration, however, had a negative effect on cell density. Furthermore, adding PDMS into the PP matrix resulted in the development of some very small cells in the wall of the large cells.

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