Aspects of Foaming a Glass-Reinforced Polypropylene with Chemical Blowing Agents

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ABSTRACT: This work explores the influence of a chemical blowing agent on different aspects of producing a short glass-fiber-reinforced polypropylene foam, examining the rheology of the system, the developed morphology of the part, and the resulting mechanical properties. Two different forms of an endothermic blowing agent, namely powder versus masterbatch, were compared to determine their effects on the process history and properties of an injection molded part. Samples were produced on an injection molding machine between 230 and 270°C using the low-pressure foaming technique. Rheology of the resulting plasticized melt by the two different blowing agents was measured on an in-line rheometer, showing a greater reduction in shear viscosity for the masterbatch additive, which correspondingly reduced the extent of fiber breakage observed. The final molded samples were analyzed for their foam structure (i.e., cell size, cell density, and skin thickness) as well as the properties of the glass fibers incorporated (namely, fiber length distribution). Tensile properties were found to diminish with increasing blowing agent content, though differences were observed based on the type of CBA used despite the similarities in foam structure produced. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4696–4706, 2006

Key words: chemical blowing agent; foaming; glass fibers; tensile properties

INTRODUCTION

Reinforced thermoplastic foams have been present in the market for approximately three decades, used in applications such as furniture, appliances, and transportation.[1] These materials comprised of multiple phases offer lighter weight, and higher specific stiffness and strength when compared with their nonfoamed counterparts. The addition of reinforcing agents to the foamed matrix can increase the electrical, thermal, and physical properties, depending on the filler used, making these composites more suited to engineering applications. The improved properties are related to the individual attributes of the foamed matrix and the fibers, as well as being strongly influenced by the developed microstructure that results from the chosen processing method. The complex microstructure formed involving the glass fibers, gas phase, and polymer matrix in the final part is difficult to understand without comprehending the impact these constituents first had on processing. For example, several researchers[1–5] have outlined the influence that the gas has on reorientation of glass fibers in the matrix as foam growth occurs. Zhang and Thompson[6] have shown that a chemical blowing agent used in the generation of foam can have a significant influence on the fiber breakage mechanism during processing prior to the mold cavity and the occurrence of foaming. In that work, longer fibers were observed in the molded part as the concentration of blowing agent used in the process was increased. Both of these changes to the fibers present in the matrix (i.e., being longer and reoriented) may significantly impact the final properties of the molded part.[7–13] The findings of these different researchers[1–6] revealed interactions that took place during processing which indicated that the constituents were performing beyond their intended function; for example, the blowing agent was not simply involved in creating a foam structure. This article further explores aspects regarding the interactions of chemical blowing agents with the processability and final properties of a thermoplastic foam composite.

Foaming occurs in the presence of a blowing agent which may be either a physical type (PBA) where the species undergoes only a change of physical state during processing as foam growth occurs in the polymer melt, or a chemical type (CBA) that normally decomposes thermally within the temperature range of the process, though there are examples of CBA that require chemical activation instead.[14] For thermoplastic polyolefins and their composites, CBAs have historically been more popular because of their

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ease of use when high density (i.e., 450–950 kg/m^3) and, to some extent, medium density (i.e., 100–450 kg/m^3) foams are required.[7] However, the reaction of a CBA leading to gas generation leaves behind residues that are not always desired by processors. Typically, CBAs are classified based on whether the decomposition reaction is exothermic or endothermic.[7,14,15] The focus of this article will be on endothermic blowing agents because of their popularity in research and industry; their popularity is due to low toxicity and the fact that their residual byproducts do not discolor the plastic or experience die plate-out in the same manner as azodicarbonamides (an example of an exothermic CBA). Endothermic CBAs are often referred to as inorganic CBAs since a carbonate species, sometimes sodium bicarbonate, is used in the generation of gases (mostly CO_2 with a minor content of H_2O).[15] An endothermic CBA usually includes several polycarboxylic acid/salt species to control the activation temperature and gas evolution rate. Excellent reviews of CBAs are available in the literature.[14,15] The active ingredients of an endothermic CBA can be introduced during polymer processing as either a powder or within a polymer pellet comprised of a low melting temperature carrier resin. Unfortunately, there is no known study in the literature comparing these two different methods of addition, i.e., masterbatch versus powder, so that processors may appreciate the differences in processability and final part properties that arise.

Those components of an endothermic blowing agent that are most likely to significantly influence processability and the mechanical properties of a material include the inorganic carbonate species (powder nominally 1–10 μm in size) and the carrier resin (if present). The aim of this article was to investigate the major differences in performance between two endothermic blowing agents possessing one or both of these components on the low pressure injection molding process for a high-density reinforced polypropylene foam.

EXPERIMENTAL

Materials

A 20 wt % short glass-fiber-reinforced polypropylene composite (G20P100-01UV) was supplied by Rhetech for this study. The material was determined to have a density of 1.055 g/mL and a melt flow index of 5 g/10 min (ASTM D 1238, 230°C/2.16 kg). The glass fiber diameter was 14 μm with an average fiber length of 640 μm. The foaming agents used for these trials were both endothermic chemical blowing agents (CBAs) with their principal ingredients responsible for generation of the gas being an alkali carbonate and citrate species. The masterbatch

CBA chosen was Hydrocerol$^®$ HK-40E (donated by Clariant), which blends the active ingredients into a polyethylene matrix. The powder form of CBA was Tracel$^®$ HTF 215 (donated from Dempsey Corp.). Based on ash testing of the two CBAs in a vacuum oven at 600°C for 1 h, it was determined that ∼ 25% of the active ingredients were composed of inorganic carbonate species, and combined with information provided by the suppliers, we know that the carrier resin used for the masterbatch accounts for ∼ 60% of the total additive mass. Particle size measurement by optical microscopy of the inorganic constituents that remained after ashing the two CBA species revealed an average dimension of 4.17 μm for the powder and 16.0 μm in the masterbatch. The melt flow index of the carrier resin was subsequently quantified, being 35 g/10 min (ASTM D 1238) after the active ingredients had been allowed to decompose in a vacuum oven at 250°C under a nitrogen atmosphere for 1 h.

The powder CBA is solely composed of the active ingredients that evolve gases as they undergo decomposition. The masterbatch CBA is formulated from a powder CBA mixed into a polyethylene carrier for easier dry blending with the feedstock of a polymer process. From infrared and gravimetric analyses of the powder and masterbatch types used in this work as well as consultation with the suppliers, it was determined that 1 g of masterbatch CBA was equivalent to 0.36 g of powder CBA on the basis of generating similar content of gas. For clarity of comparison in this article, all references to the concentration of blowing agent made in the discussion will refer to the actual concentration of active CBA ingredients present. This means that in the case of the masterbatch CBA, we are not referring to the actual masterbatch weight added since that includes the mass of the carrier resin as well. For this work, the CBA content, both powder and masterbatch, was varied between 0 and 2 wt % (based on active ingredients) for the experimental trials in the injection molding machine.

Injection molding process

The experiments were conducted on a 55-ton Arburg injection molding machine at two processing temperatures: 230 and 270°C. DSC characterization of the two blowing agents confirmed that under both processing temperatures, full decomposition of the active ingredients would occur under the chosen injection molding conditions. Two sets of experiments were conducted in this work. In the first set of experiments, the machine was used in its original setup to produce molded test bars for mechanical analysis. The injection flow rate was set to 100 cm^3/s, which represents the highest shear rate possible for

the machine, higher shear rates being more indicative of industrial operating conditions. Injection of the gas–polymer solution followed after the accumulated melt had been allowed to reside in the nozzle for 20 s to ensure complete decomposition of the CBA as well as to improve melt temperature uniformity. A fixed short shot size was used (85% of the full pack volume) to provide room for the material to expand once in the mold. A mold temperature of 23°C was used during the trials. In the second set of experiments, a modified nozzle was used on the injection molding machine to provide in-line rheological monitoring of the process. Details of the in-line rheometer are given in Ref. [16]. For each level of CBA content in the polymer matrix, six different injection flow rates (5–100 cm^3/s) were examined to vary the shear rate from 10^4 – 10^6 s^{-1}. Each run within the second set of trails was performed as an ''air-shot'' (i.e., the nozzle was moved back from the mold and the extrudate exited into the air.). Once again, a 20-s dwell time was used prior to passing the melt through the instrumented capillary die. The rheological data presented in this article was based on averaged pressure measurements taken from at least five replicate runs.

Characterization

The tensile modulus of molded test bars was measured according to ASTM D 638 on an Instron 3366 operated with a strain gauge extensometer. ASTM Type I test bars were tested at a cross-head speed of 5 mm/min. The Young's modulus (tension) was chosen for the measured mechanical property in this work because of the broad range of mechanical models available in the literature to characterize influential factors from the morphology of the molded foam samples. The cell size, cell density, and skin thickness, along with observations of sample morphology, were investigated by scanning electron microscopy (SEM). The specimens were prepared by cryogenic fracture producing viewable cross sections parallel and perpendicular to the flow direction from the center of the test bar. Cell density (N_f) was calculated according to

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

where ''n'' is the number of cells viewed at magnification M within the area A of the micrograph. The density of each foamed sample was determined according to ASTM D 1622. Sample ashing was carried out at 600°C in a muffle furnace for 1 h to determine the fiber length distribution. A dilute suspension in ethanol was made from the collected glass fibers, which was cast onto a glass plate so that the fibers could be digitally photographed under magnification by an optical microscope. Classification of the fiber length was manually determined from more than 450 fibers for each sample.

The determined shear viscosity values from the second set of trials were calculated by pressure measurements across the in-line rheometer. The Bagley procedure was followed to correct the shear stresses for exit effects and entrance losses, and the shear rate was adjusted using the Rabinowitsch correction. The validity of the isothermal assumption attributed to the calculation of shear viscosity was confirmed in this work by thermocouples before and after the capillary die. The temperature difference between the two thermocouples showed only a variation between 1 and 2°C. To validate the shear viscosity measurements made on the in-line rheometer, viscosity data for the neat (nonfoamed) reinforced polypropylene were compared with results from a ROSAND twin-bore capillary rheometer at temperatures of 230 and 270°C. The viscosity measurements for our reinforced polypropylene resin were found to be in good agreement between the two different rheometers.

RESULTS AND DISCUSSION

Rheology

Rheological characterization of a polymer melt with CBA by an in-line rheometer provides test conditions that maintain the evolved gases in solution and ensures relevancy of the results to industrial processing equipment. The only notable drawback to the instrument was that measurements at low shear rates (in our case, below 5000 s^{-1}) were difficult to make because of process instability. Figure 1 shows the relative flow curves determined by the in-line rheometer for gas–polymer solutions processed with either the powder or masterbatch CBA at 230°C. The relative viscosity values for samples processed with either blowing agent lie below unity, indicating a reduction in the resistance to flow when compared with the nonfoamed material (i.e., 0 wt % CBA), with those samples prepared including the masterbatch CBA exhibiting the lowest viscosities. As expected, the dissolved gas had a plasticizing effect on the material. The curves also indicate that the slope of the viscosity curve, i.e., the pseudoplasticity of the material, was changed by the presence of gas in the polymer. At a shear rate of 6000 s^{-1} in the plot, the reduction in viscosity for the masterbatch-processed samples, in comparison with the nonfoamed sample, was 10 and 12% at 1 and 5 wt % CBA respectively, while between the powder-processed samples and the nonfoamed samples the reduction in viscosity was less, being 3 and 6% at 1 and 5 wt %
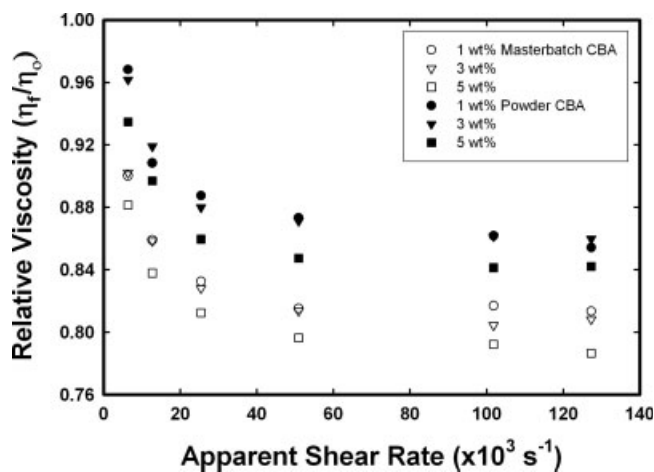
Figure 1 Relative shear viscosity at high shear rates determined from the in-line rheometer at 230°C for different concentrations of the powder and masterbatch endothermic chemical blowing agent. η_f refers to the viscosity of the foamed samples and η_0 refers to the viscosity of the material without CBA present.

CBA respectively. In light of the fact that the maximum standard error in our calculated viscosities for both temperatures was 4.4% for powder CBA and 5.2% for the masterbatch CBA, the rheological changes made by the powder were relatively minor. The flow curves for our gas–polymer solutions at 270°C were not presented, since even less distinction was observed based on CBA concentration and type, though the masterbatch CBA still produced the largest reduction in viscosities.

The larger reduction in viscosity (found from the rheological results) attributed to the masterbatch CBA, when compared with the powder, did not appear related to the gas evolved. Findings presented in a later section show that the quantity of gas produced by either CBA type was nearly equivalent based on the analysis of the foam structure and apparent density. Beyond the immediate plasticizing effect of the gas, the rheology of the gas–polymer solutions was potentially affected by the newly introduced constituents of the CBA type chosen and the glass fibers compounded into the polypropylene. The inorganic constituents found in both CBAs were micrometer-scale particulate which never exceeded a concentration of 0.5 wt % in the system. These particle additives acted as reinforcement agents with regard to mechanical properties (as shown in the analysis of tensile measurement) and yet had no discernable impact on the flow properties of the polymer melt. The carrier resin of the masterbatch CBA acted as a diluent and likely as a lubricant in the molten polymer. The low viscosity of the carrier when compared with the glass-fiber-reinforced polypropylene, at a maximum concentration of 3 wt % in the tests, would have been sufficient to lower the

viscosity of the solution. In addition, as the carrier concentration was increased in the polymer because of the CBA, it would have lowered the volume fraction of the glass fiber reinforcement in the matrix by dilution. The absence of the carrier resin within the powder CBA is a plausible reason for the difference in viscosity noted in Figure 1.

It has been shown in earlier studies[16–18] that the plasticizing effect of a blowing agent on a polymer reduces the viscosity without affecting other material behavior such as its shear-thinning nature. However, for the present gas–polymer solutions which included glass fibers, the above-mentioned description does not appear to properly fit the observed rheology. For the glass-fiber-filled polypropylene samples, the pressure drop across the rheometer decreased with increasing CBA content for the same shear rate condition, which is normal for a gas-plasticized polymer melt. However, the pressure drop gradient with respect to shear rate for polymer melts containing a blowing agent are normally similar to that of the corresponding pure polymer, only the magnitude of the pressure drop is lower for gas-laden systems, and yet for the reinforced polypropylene with CBA the gradient is observed to reduce with increasing shear rate. The implication of the pressure drop dependency on shear rate is that the shear-thinning behavior of the polymer was changed with CBA content. Figure 2 plots the pressure drop across the rheometer versus injection rate for both the masterbatch and powder CBA trials at 230°C. The higher processing temperature yielded the same phenomenon, though the differences in pressure drop were smaller as the CBA concentration was varied. Looking at the highest flow rate where the differences are most clearly seen in the figure, the powder CBA demonstrated only a weak concentration effect while the masterbatch CBA yielded a stronger influence on the pressure drop as its concentration was increased. The difference in the pressure drop gradient shown by the glass-fiber-filled polypropylene when compared with the pure polymer could not be attributed directly to the foaming additive, since the phenomenon was not previously observed with either a homogeneous LDPE[16] or a heterophasic TPO[18] using the same masterbatch CBA. Rather, we suggest that the variation observed for the rheological behavior of the composite is attributed to the impact that the CBA had on the mechanism of glass fiber breakage, an influence which was different based on the type of CBA used.

Effect of CBA on fiber breakage

The fiber length of added glass in the melt has been shown to have a significant impact on the pseudoplasticity of the reinforced material; a polymer with
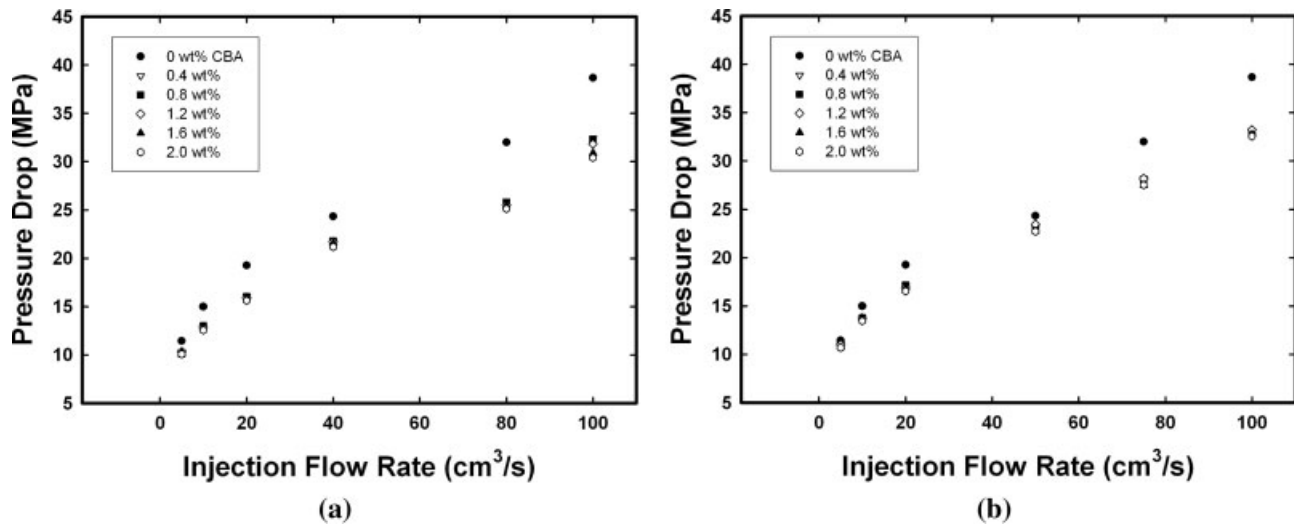
Figure 2 Pressure drop versus flow rate for the glass-filled polypropylene at 230°C with varying CBA content: (a) masterbatch type and (b) powder type.

longer fibers (i.e., filler of higher aspect ratio) has been found to become more shear thinning than the same polymer with shorter fiber lengths.[19] The shear rate dependent pressure drop observed for our foamed composite by the in-line rheometer and the implication of increased shear thinning, therefore, could be reasonably explained provided that a dependency of the fiber length can be found with the CBA type and content used. Figure 3 shows the fiber length distribution determined for the samples processed at 230 and 270°C with the two different CBAs. Significant differences were observed in the lengths of fibers found in samples processed at 230°C based on the CBA concentration. The mean fiber length

was found to be 350 μm in the processed sample without CBA, similar to the value found for the sample processed with 2 wt % powder CBA, though the length increased to 500 μm with 2 wt % masterbatch CBA. We note the similarity in the extent of change in the fiber length distribution attributed to CBA concentration to that of the measured pressure drop in Figure 2. For the samples processed with the powder CBA we observed that the extent of fiber breakage did not significantly change as the concentration of the blowing agent increased. The aspect ratio of the fibers found in the samples processed at both the lowest and highest concentration of powder CBA remained similar to those found in the nonfoamed
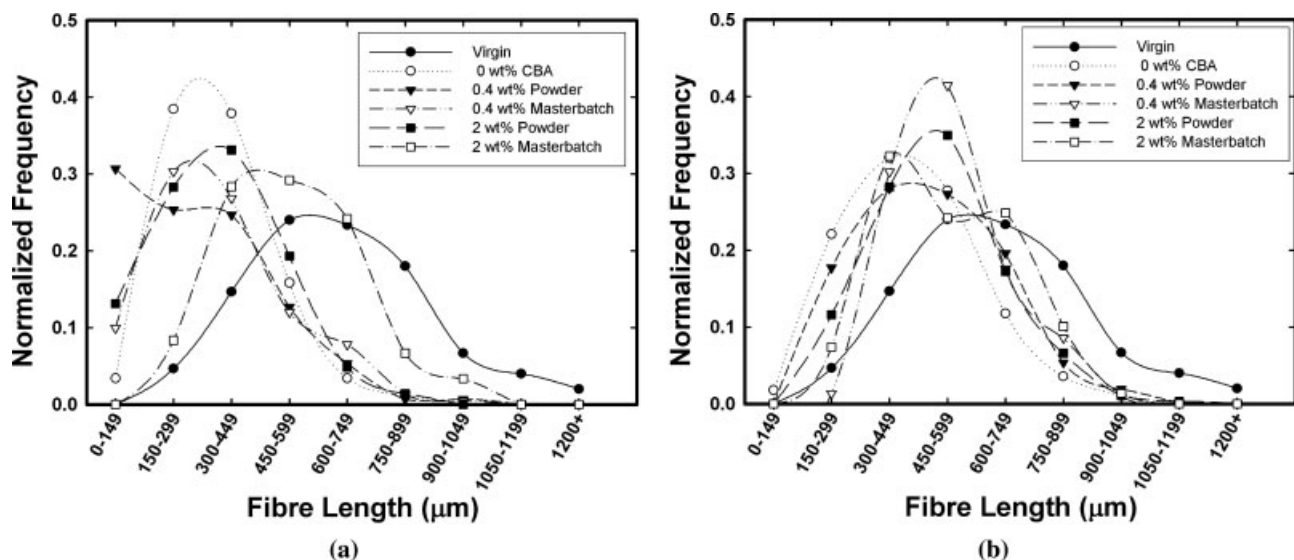
Figure 3 Fiber length distribution of the molded reinforced foams processed at (a) 230°C and (b) 270°C based on the concentration and type of chemical blowing agent (curve for the virgin sample represents the as-received material; lines are included for clarity only).
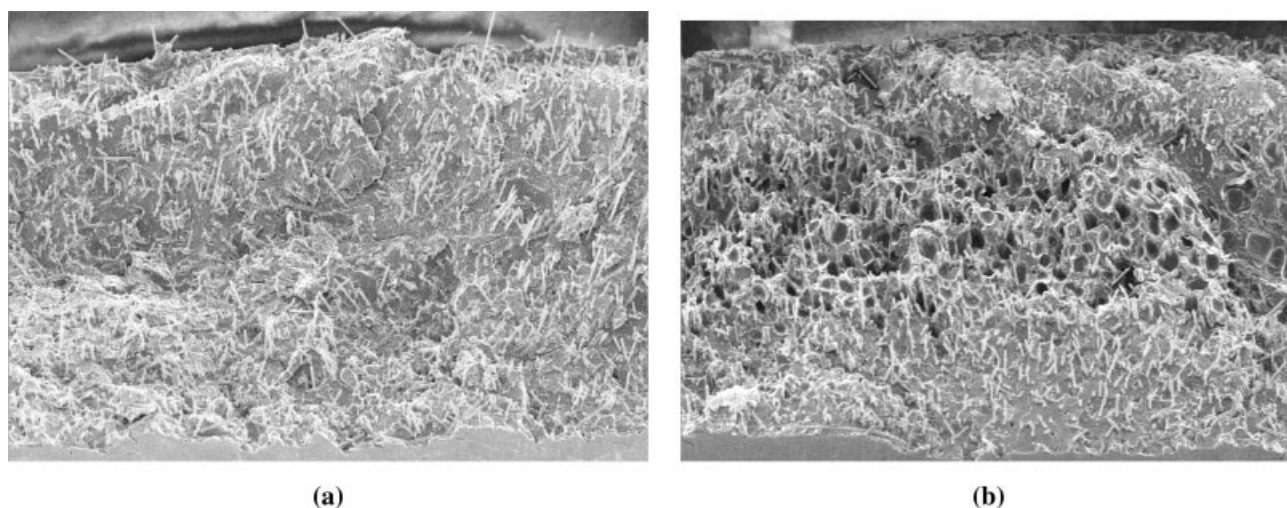
Figure 4 Scanning electron micrographs of the reinforced composite processed at 230°C with (a) 0 wt % CBA and (b) 0.4 wt % masterbatch CBA.

material (0 wt % CBA). Correspondingly, the shear-thinning behavior of the powder-processed samples has already been noted as being only weakly dependent on CBA concentration and more closely resembling the shear-thinning nature of the non-foamed material. For the samples processed with the masterbatch CBA, the extent of fiber breakage diminished with increased concentration, resulting in higher aspect ratio glass fibers in the composite. At the highest concentration of masterbatch CBA, the fiber length distribution more closely resembled the virgin material; the virgin material is differentiated from the nonfoamed material in this work as never having experienced the shear history of the injection molding machine and possessing the longest fiber lengths of all the samples analyzed. For the master-batch-processed samples, the shear-thinning behavior noted in the pressure drop data and viscosity curves was found to increase in a similar manner as the CBA concentration increased.

In the case of samples produced at 270°C, the fiber length distributions shown in Figure 3 presented far less variation and more closely resembled the virgin (unprocessed) resin. We still noticed that samples processed with powder CBA, even at this higher processing temperature, exhibited greater fiber breakage when compared with the masterbatch additive. For example, at 270°C the mean fiber length was found to be 435 μm in our sample processed without CBA, 528 μm for our sample containing 2 wt % master-batch, and 445 μm for our sample containing 2 wt % powder CBA. We observed that temperature significantly influenced the rheology of the material, making differences in viscosity between the samples containing different levels of CBA very small at the higher temperature and correspondingly we noted

that differences in the fiber length distribution became much smaller.

With regard to the mechanism of fiber breakage, it appears that the two CBA types interacted with the reinforcing agent differently. Both the gas and carrier resin have been shown to lower the shear viscosity of the melt, which would lower the shear stresses transmitted to the fibers during processing and reduce the extent of fiber breakage.[6] The plasticizing effect of dissolved gas in a molten polymer has been repeatedly reported[7,16,18,20,21] (also evident in Fig. 1); however, the fact that fiber breakage occurred to almost the same extent for any concentration of the powder CBA as the nonfoamed sample suggests that the influence of the gas was minor in comparison with the lubricating effect of the carrier resin or possibly there was a synergistic interaction between the gas and carrier. Further experimentation is warranted to improve our understanding of the forces contributing to fiber breakage in the presence of a CBA. However, it is evident from these results that a processor must anticipate differing fiber length distributions in their product based on their selection of CBA.

Density of the molded foam part

The morphology of our reinforced composite foam can be reasonably characterized as a three-layer sandwich structure (i.e., skin – foam core – skin). Scanning electron micrographs revealed that the cellular structure of the molded foams was reasonably uniform across its core layer (shown in Fig. 4). This means that two densities can be used to describe the structure of this foam in our subsequent mechanical analysis, namely a skin density (ρ_s), which is normally assumed to be the solid composite density,

TABLE I
Density and Skin Thickness of the Reinforced Foam Samples

Processing temperature (°C)	CBA (wt %)	Masterbatch			Powder		
		Apparent density (g/cm³)	Skin thickness (mm)	Core density (g/cm³)	Apparent density (g/cm³)	Skin thickness (mm)	Core density (g/cm³)
230	0.4	0.97	1.00	0.79	0.99	1.10	0.80
	2	0.94	0.85	0.80	0.94	0.90	0.79
270	0.4	0.95	0.85	0.82	0.96	0.95	0.80
	1.2	0.93	0.80	0.79	0.94	0.85	0.78
	2	0.92	0.75	0.79	0.92	0.75	0.80

Standard deviation for density, 0.01 g/cm³.
Standard deviation for skin thickness, 0.05 mm.

and a core density (ρ_c), which can be readily calculated using the thickness of the skin (δ_s), and the apparent thickness (δ_a) and density (ρ_a) of the molded part[22]:

$$\rho_c = \frac{\delta_a \rho_a - 2\delta_s \rho_s}{\delta_a - 2\delta_s} \quad (2)$$

Measurements of the skin thickness used in eq. (2) were taken from scanning electron micrographs of samples processed with both CBA types. The variation of skin thickness based on CBA type and CBA concentration as well as processing temperature is summarized in Table I along with the measured apparent density and the calculated core density. The standard deviation for the skin thickness was larger than the density measurement owing to the subjective nature of estimating the thickness of the skin. As observed in the table, both the skin thickness and apparent density decreased with increasing CBA content while the core density remained effectively constant. Overall, the data presented in Table I indicate that there was no significant difference in cellular structure arising from the choice of foaming systems; any minor differences in skin thickness based on the type of foaming agent used did not appear to be reflected in the density data. These results suggest that the carrier resin (present in the masterbatch type CBA but not the powder CBA), while notably affecting the shear viscosity behavior of the polymer, did not alter the mechanisms of foam nucleation or bubble growth for our material system.

Microstructure of the foamed samples

The conclusions drawn regarding comparable cellular structures between the two foaming agents were corroborated by visual characterization of the materials. Figure 5 presents a series of scanning electron micrographs from cross sections of the test specimens (perpendicular to the flow direction) produced under different foaming conditions. These examples detail the core morphology produced at 270°C with

either the masterbatch or powder blowing agent. Cell density values for all samples analyzed by SEM are summarized in Table II. The cell density of the samples produced using either blowing agent showed a small increase in value with increasing CBA concentration, varying at most between 4×10^5 and 7×10^5 cells/cm³. The apparent cell size for the samples was nominally in the range of 60–110 µm for our experiments. Comparison of the cell density based on the CBA type did not reveal a significant difference over the lower concentrations used, the exception being at 2 wt % CBA where the powder consistently produced a higher density. Few examples of coalescence among the grown cells were found, most at the highest concentration of masterbatch CBA used which could explain the difference in cell density noted at this condition compared to the powder CBA. At the lower CBA concentrations studied, the presence of the carrier resin had no observable effect on the structure of the developed foam.

The similarity in the foam structure evolved by the two CBA types (masterbatch and powder) allowed our discussion with regards to mechanical properties in the subsequent section, to be more closely related to the influences of the CBA composition. The similarity in cell geometry produced between the two CBA means that the differences in the mechanical test results may be related to material properties of the constituents in the blowing agents and do not need to make consideration for differences in tensile stress distribution during testing. A final note important to the mechanical properties was that the interfacial adhesion between fiber and matrix was not notably altered by use of either CBA; both foamed and nonfoamed samples of our composite exhibited good wetting of the fibers in the scanning electron micrographs, with no voidage surrounding the reinforcing agent.

Tensile properties

Figure 6 shows the influence of CBA type and processing temperature on the tensile modulus of the
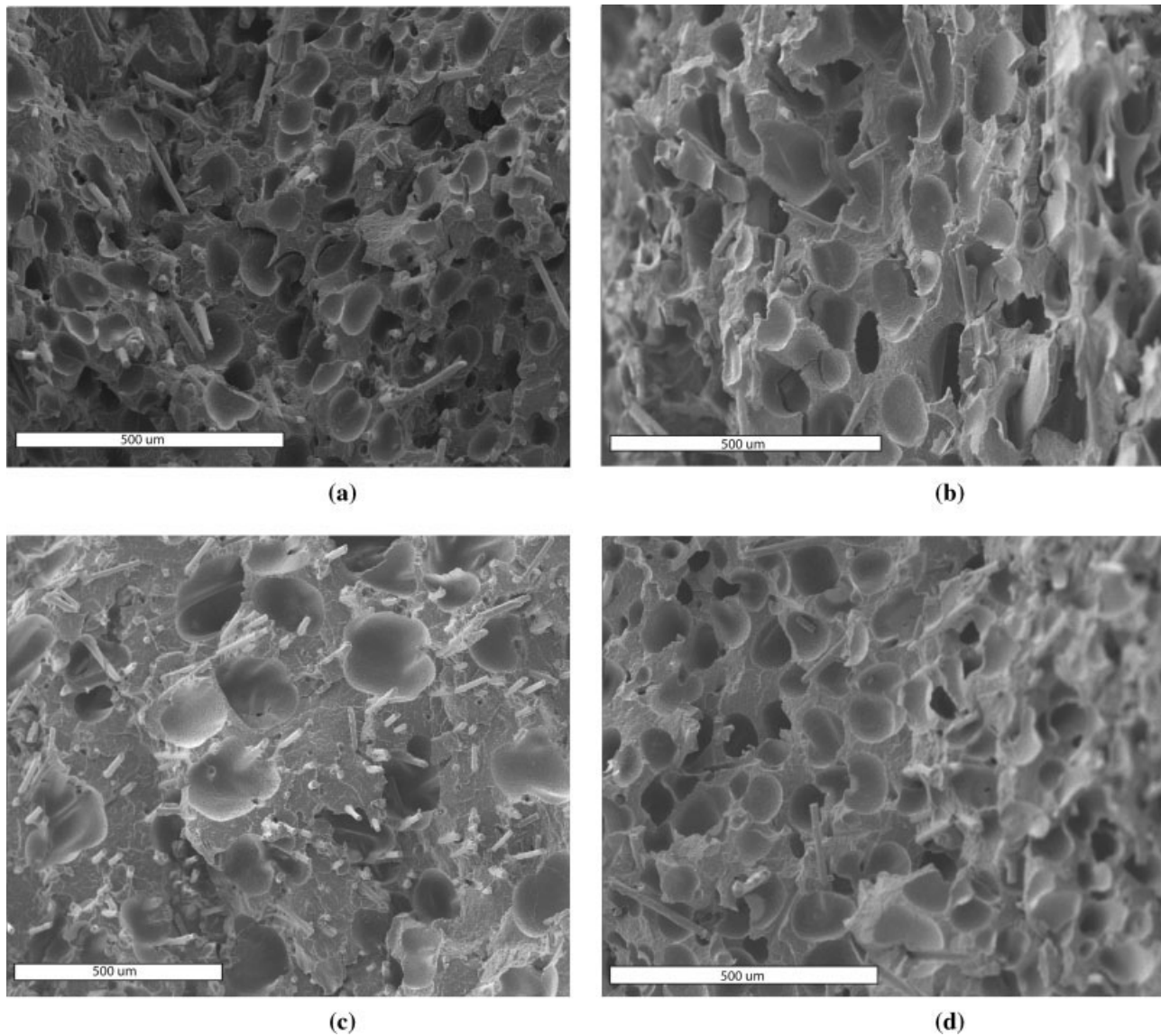
Figure 5 Core morphology observed by SEM of the reinforced polypropylene foam processed at 270°C, at CBA concentrations of (a) 0.4 wt % MB, (b) 2 wt % MB, (c) 0.4 wt % PD, and (d) 2 wt % PD (where MB represents the masterbatch CBA and PD for the powder CBA).

foamed composite. The two samples processed in the absence of blowing agent exhibited the highest tensile modulus due to their relatively high densities. The samples produced with varying content of the blowing agents showed a rapid loss in stiffness with decreasing material density, whereas processing temperature appeared to have much less influence on the tensile modulus than previously observed for the nonfoamed samples. The change in stiffness due to CBA concentration (either powder or masterbatch type) was anticipated due to the reduction in volume fraction of the glass fibers and matrix resin within the final composite[10]; however, the fact that the rule of mixtures does not satisfactorily explain the trend indicates that the relationship was not simply additive. Comparing the performance of the two foaming

agents, it appears that the powder CBA consistently produced foamed parts possessing a higher modulus (by $\sim$ 8% at the highest additive concentration) than did the masterbatch CBA for similar apparent

TABLE II
Cellular Density of Reinforced Foams

Processing temperature (°C)	CBA content (wt %)	Masterbatch (10^5 cells/cm^3)	Powder (10^5 cells/cm^3)
230	0.4	4.5	4.8
	2.0	5.1	7.4
270	0.4	5.5	4.1
	1.2	6.3	5.8
	2.0	6.6	7.1

Measured standard deviation, 5.7×10^4 cells/cm^3.
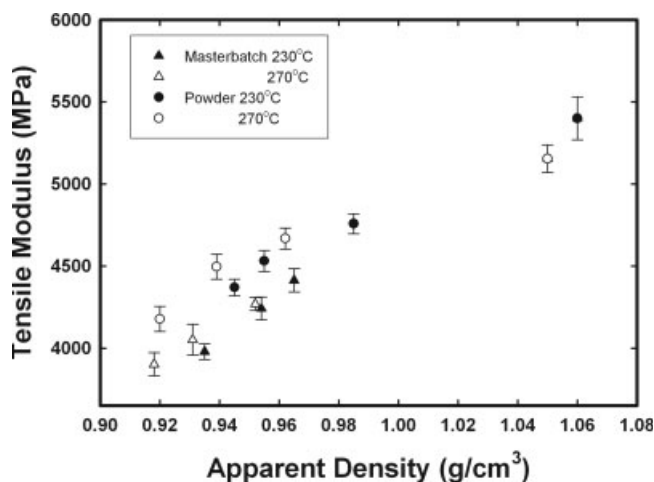
Figure 6 Variation of Young's modulus under tensile testing with respect to apparent density for reinforced foam samples produced under all examined conditions using the low pressure injection molding process.

density. The difference in modulus noted at any given CBA concentration between the two CBA types corresponded to the differences noted in either the skin thickness,[7,23] fiber length distribution,[10,11] or material composition; the foam structure was not considered to be a significant factor in the difference in modulus found since the estimated core density remained effectively constant between the two CBA types. The contribution of these factors (i.e., skin thickness, fiber length distribution, and material composition) on the modulus was further analyzed.

To understand how the two CBA were affecting the stiffness of the material, it was necessary to remove the contributions of the foam, i.e., density, cell density, cell size, and skin thickness, from our mechanical data. Further tensile measurements were made with select samples prepared with the appropriate CBA type and concentration but now completely filling the mold cavity and applying a packing pressure of 70 MPa. Density measurements and microscopic observations of the new test specimens confirmed that these new samples did not exhibit a foam structure. The average density of the nonfoamed samples was 1.056 $\pm$ 0.007 g/mL. Tensile measurements for these nonfoamed samples containing either of the two CBA are shown in Figure 7. The differences in stiffness caused by varying the CBA concentration for a particular processing temperature appear to be largely dependent on the material composition alone; fiber length was not considered a significant factor for reasons that are discussed later in this section. The powder CBA had a small reinforcing effect on the modulus; at 230°C the 2% rise in the average tensile modulus observed at the highest CBA level lies within the error of measurement, but at 270°C the 4% rise in value

could be considered significant. Since at 2 wt % CBA the inorganic filler content would be only 0.5 wt % in the molded part, the difficulty in seeing its reinforcing behavior within the composite is understandable. For the masterbatch CBA, a significant 3% reduction in modulus was observed at the highest concentration for both processing temperatures. The fact that the same concentration of inorganic filler was found in these samples as with those processed with the powder CBA indicates that the carrier resin had a dominant influence on the stiffness of the composite (at least with regard to contributions made by the residuals making up the foaming agents). The differences in the modulus observed among the nonfoamed samples in Figure 7 appeared to account for the different rate at which the tensile modulus decreased in Figure 6 as related to CBA type.

Since the nonfoamed samples in Figure 7 were processed in the presence of the CBA, the rheology and consequentially the resulting fiber length distribution of the system should have remained similar to that already measured for our foamed parts (Fig. 3) when identical CBA content and type was used (acknowledging some minor increase in fiber breakage to a comparable extent for all samples which may be attributed to the mold packing). With this consideration in mind, the trends in the tensile modulus for the samples in Figure 7 appear to reflect those expected based on the composition of the CBA added rather than fiber length. A high modulus inorganic filler is expected to increase the modulus of the final material while a lower modulus polymer like the carrier is expected to lower the modulus of the final material. The fact that the trends in Figure 7 adhere to our expectations for the CBA-filled composites
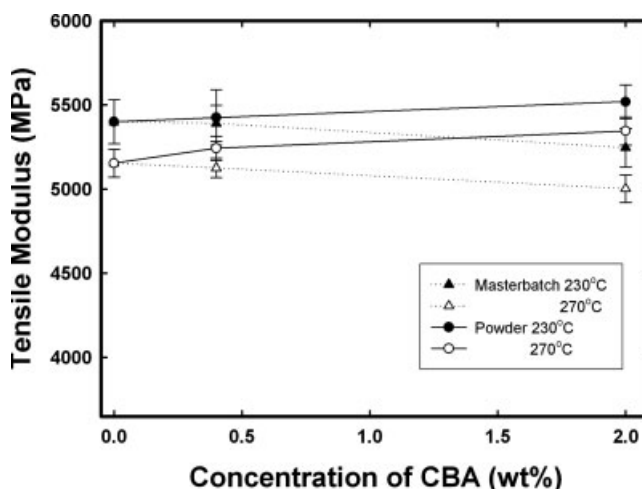
Figure 7 Variation of Young's modulus under tensile testing with respect to the concentration of blowing agent used in producing reinforced foam samples without a foam structure by using a conventional injection molding process that included a packing stage.

indicates that the variance in fiber length found in Figure 3 based on CBA type did not observably affect the stiffness of the final part; with longer fiber lengths as those found in samples processed with the masterbatch CBA, it would be expected that the tensile modulus would increase rather than decrease with increased concentration of the foaming additive if the attribute of fiber length was dominant.

Finally, we would like to examine how the foam structure evolved by the use of either CBA affects the elastic modulus of the molded part; whether the mechanical behavior shown is more than simply a response to changing the volume fraction of components making up the material. To make this evaluation, empirical mechanical models are useful. The most commonly applied empirical model for the modulus of elasticity[2,23,24] of high-density foams is

$$E_f = E_s \left(\frac{\rho_a}{\rho_s} \right)^2 \qquad (3)$$

where E_f and E_s are the Young's moduli for the foamed and solid composite, respectively. The model is intended for uniform foams rather than the integral skin structure possessed by our samples. Throne[2] proposed the use of a modified form of eq. (3) to account for the skin:

$$E_f = \phi E_s + (1 - \phi) \left(\frac{\rho_a}{\rho_s} \right)^2 E_s \qquad (4)$$

where ϕ is the volume fraction of the skin making up the sample. Both models make use of the mechanical properties of the solid polymer in their calculations which in our case differs based on the concentration and composition of CBA additive. Using the tensile modulus determined for the sample without the inclusion of CBA (i.e., 0 wt % CBA) in eq. (3) yielded poor agreement, underestimating the stiffness by as much as 40%. The stiffness values measured for those nonfoamed specimens in Figure 7 were more appropriate as E_s in these models, now including the differences in material composition attributed to the CBA. The results of the calculations are shown in Figure 8. The integral skin model of eq. (4) overestimated the modulus by as much as 15% for the powder and 19% for the masterbatch-processed samples. The simpler square-power model of eq. (3) intended for uniform foam showed much better agreement with the experimental data, with a 2% difference observed for either powder or masterbatch CBA-processed samples. The fact that the square-power model fits the experimental data well suggests that the variation in elastic modulus for these reinforced thermoplastic foams based on CBA concentration was primarily influenced by the volume displaced by the gas phase rather than being
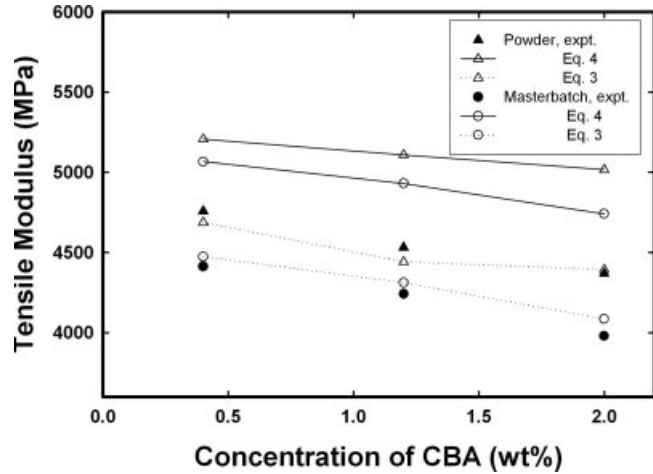

Figure 8 Comparison of the tensile modulus determined experimentally for the reinforced polypropylene foam with respect to two different empirical models for high-density foams.

sensitive to variation in the skin thickness found between the use of either CBA type.

CONCLUSIONS

The processability, morphology, and mechanical properties of a glass-fiber-reinforced polypropylene were examined based on the type of CBA chosen to foam the composite. The implications of this choice have been shown, in this article, to be small but certainly not insignificant for a processor. In terms of processability, the masterbatch type CBA was found to yield lower shear viscosity at any concentration when compared with the powder type CBA. The lower shear viscosity was found to significantly affect the resulting fiber length distribution measured in the molded samples. Longer fibers survived to the mold cavity as the concentration of the masterbatch CBA was increased, while in the case of the powder CBA the distribution of lengths more closely resembled those processed in the absence of a foaming agent. With regard to morphology, both CBA types yielded equivalent uniform high-density foam structures when the concentration of active ingredients critical to foaming was kept the same. The tensile modulus was measured for the different samples due to its ready application to empirical models. This mechanical property was shown to be affected by the choice of CBA used to foam the material; though this dependency did not occur to be due to the fiber length distribution. Rather, it was surmised that the carrier resin in the masterbatch additive and the inorganic particulate generated the differences in tensile modulus observed—these differences were as large as 8% at the highest concentration of CBA used.

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