

Applications of Nanocomposites and Woodfiber Plastics for Microcellular Injection Molding

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Abstract

The paper reviews the processing advantages and challenges of microcellular injection molding and presents recent research results on applications of nanocomposites and woodfiber-plastic composites as well as new process development for the microcellular injection molding process. In particular, two types of polyamide (PA-6) neat resins and their filled counterparts, such as a PA-6/montmorillonite nanocomposite, a cellulose-fiber-reinforced PA-6 composite, and a hybrid PA-6/cellulose/Wollastonite composite, were injection molded into ASTM test-bar samples with both conventional and microcellular injection molding. These molded samples were then subjected to scanning electron microscope analysis, tensile testing, and impact testing to study how the process conditions and micro-hano-fillers affect the

microstructure and mechanical properties of the microcellular injection molded components. For all the materials studied, the microstructure and the mechanical properties of the molded samples were found to be strongly dependent on the process conditions and presence of the filler systems. Finally, initial results of a novel co-injection molding process that combines the aesthetic and processing advantages of injection molding with the property attributes and benefits of microcellular plastics are presented.

Introduction

Microcellular Injection Molding

Microcellular injection molding (also commercially known as the MuCell process) can produce parts with excellent dimensional stability using lower injection pressure, shorter cycle time, and less material. This process blends “supercritical” fluid (usually nitrogen or carbon dioxide) with polymer melt in the machine barrel to create a single-phase polymer-gas solution. During the molding process, the gas emerges from the melt forming numerous microcells. The size and density of microcells depend strongly on the process conditions and the material system. The typical cell diameter is in the order of 10 to 100 microns. While

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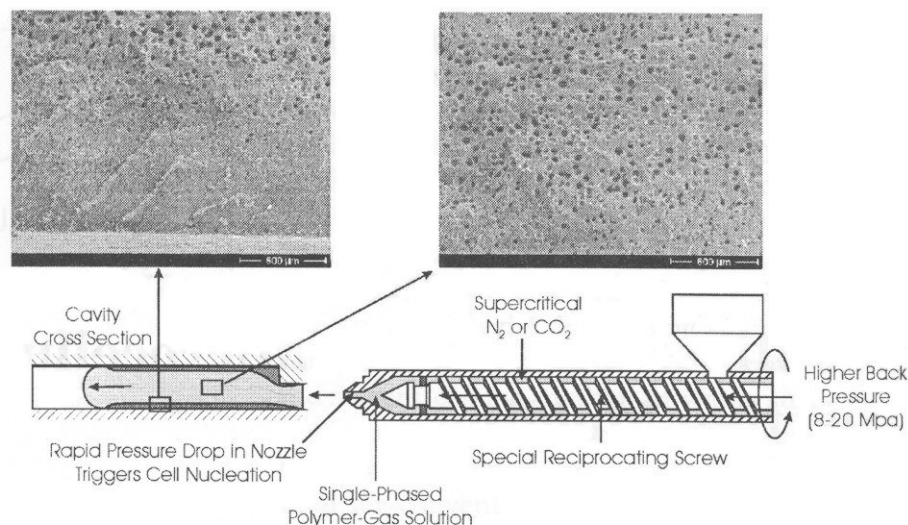
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Figure 1. ~ Schematic of microcellular injection molding machine.



realizing part weight reduction by replacing plastics with gas, the microcells also serve as crack arrestors by blunting crack tips, thereby, enhancing part toughness (1-3). Since the gas fills the interstitial sites between polymer molecules, it effectively reduces the viscosity and the glass transition temperature of the polymer melt. This enables the material be processed at much lower pressure and temperature (1,2) and makes it possible to mold parts with very thin wall thickness (e.g., 0.3 mm). As the gas diffuses out of the microcellular plastic (MCP), the material recovers its glass transition temperature. Further assisted by the endothermic reaction of cell nucleation and growth, the cooling is accelerated and the material vitrifies quickly. Therefore, the process requires much less cooling as compared with conventional injection molding or structural foam injection molding. Finally, internal pressure arising from the foaming eliminates the sink marks and improves the dimensional stability of the molded parts. As a result, little or no packing pressure is needed to pack out the mold. A schematic of the microcellular injection molding machine and the typical microstructure of the molded components is shown in Figure 1. Detailed descriptions of this process can be found in (2,3).

Despite the above-mentioned benefits, microcellular injection molding is not a panacea for all problems with conventional injection molding. The major challenges lie in generating and maintaining the single-phase polymer-gas solution inside the barrel during the plasticating stage and controlling the state of thermodynamic instability

(via temperature and pressure variation) during molding phase to create fine and uniform microcells throughout the part. In terms of up-front costs, the process requires licenses, modifications of the injection system, and an additional supercritical fluid (SCF) injection unit. As with any emerging processes, the processing know-how has yet to be fully established to help the plastics industry materialize the process benefits. Due to the presence of microcells, it may have limited applications with parts that require clarity. The typical swirling pattern on part surfaces due to cell formation could potentially affect the cosmetic appearance while the microcellular structure may adversely affect the mechanical properties of the molded part (4). To eliminate blisters and post-blow, parts molded by the microcellular molding process need to be stabilized for the gas inside the cells to diffuse out and its pressure equalizes with the atmospheric pressure before a secondary operation such as painting takes place.

Nanocomposites

For decades, various types of fillers (minerals, metals, and fibers) have been added to neat polymer resins to form composites that exhibit improved physical and mechanical properties. Recently, nano-sized particles have become available and used as new types of fillers for polymers, leading to an emerging class of high-performance plastic materials - nanocomposites. One of the commonly used nanocomposites is the polymer-silicate nanocomposites, in which the polymer matrix is mixed with nano-clay based montmorillonite (MMT) (5). The nano-clay comes in a powder form

with a mean particle size of 8 μm . Each powder contains thousands to more than a million 10 %, thick platelets, which have a much larger surface area ($\sim 750 \text{ m}^2/\text{g}$) and an aspect ratio (>50) than conventional, macro-sized fillers. Because of the large surface-to-volume ratio and the layer orientation of the nano-fillers, polymer-silicate nanocomposites offer improved stiffness, heat resistance, barrier and flame retardation, and dimensional stability in two dimensions with a relatively small amount of nano-clay ($<10\%$).

Recently, studies by the authors have shown that when a polyamide-6 (PA-6 or Nylon-6) nanocomposite is mixed with the supercritical fluid prior to injection molding, a microcellular part with highly uniform and evenly distributed microcells can be produced. It is believed that the nano-fillers might have served as nucleating sites that promote a huge number of cells initially leading to such a microstructure throughout the molded part, even under a wide range of processing parameter variation. Only with this kind of microstructure can the mechanical properties of microcellular injection molded parts be preserved.

Cellulose Fiber Composites and Microcellular Injection Molding

In the last decade, woodfiber-plastics composite products, being from renewable resources, lighter weight, less abrasive, and, quite often, less expensive, have drawn awareness and interest from equipment and additive industries. However, it is well known that cellulose fibers are temperature sensitive. Therefore, the conventional methods for processing cellulose-filled thermoplastic composites were limited to the use of low-melting commodity thermoplastics such as polyethylene (PE), polypropylene (PP), and poly(vinyl chloride) (PVC). Recently, a novel method of low temperature processing has been developed that enables compounding cellulosic pulp fibers as reinforcements in PA-6 and other high-melting engineering thermoplastics (12). However, when cellulose-filled PA-6 composites are subsequently injection molded, one can see significant "browning" effect on the parts as the processing temperature of PA-6 (around 240°C) causes thermal degradation in the cellulose fibers. Since the microcellular injection molding process allows material to be injected at a lower temperature, efforts were made to explore the processing benefits and property improvements of combining microcellular injection mold-

ing with cellulose-filled PA-6 composite and the hybrid PA-6/cellulose/Wollastonite composite.

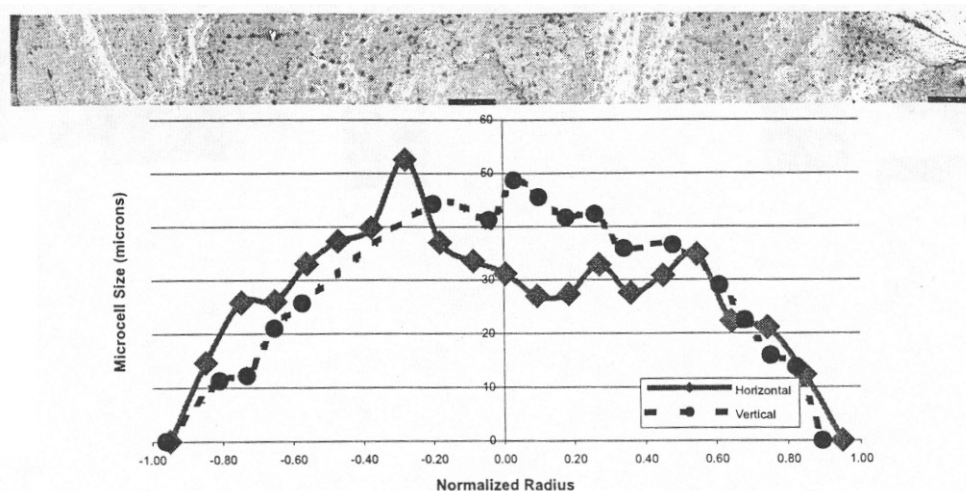
Research Objectives

The objectives of this study are to evaluate the processing benefits of applying nanocomposites and cellulose fiber composites for microcellular injection molding as well as to study the effects of filler systems and key processing parameters on microstructure and part quality of the resulting microcellular injection molded components. In addition, efforts have been made to develop a novel co-injection molding process that combines the aesthetic and processing advantages of injection molding with the property attributes and benefits of MCPs.

Experimental Set-up, Material Systems, and Analysis Procedures

A 150-ton TOYO injection-molding machine and an Arburg 55-ton two-color, co-injection molding machine (both with MuCell capability) were employed for the molding experiments. Nitrogen gas was used as the physical blowing agent in the experiments as it tends to generate finer microcells in injection molded parts. Experiments were performed based on several design of experiments (DOE) fractional orthogonal design matrices (4,6,9). Based on the DOE, ASTM D638 tensile samples were molded at various supercritical fluid (SCF) levels, melt temperatures, shot sizes, melt plastication pressures (MPP), and injection speeds. The rationale of using DOE is to understand the effects of various processing parameters on the microstructure and mechanical properties of the molded samples with relatively less molding trials. Two different types of PA-6 base resins with different filler systems, e.g., polymer-silicate polyamide (PA-6) nanocomposites, cellulose-filled PA-6 composites, and their neat-resin counterparts were employed to study the effect of using micro-/nano-scaled fillers as nucleating agents to control the size, density, and distribution of microcells. The molded samples were then subjected to scanning electron microscope (SEM) testing, transmission electron microscope (TEM) testing, x-ray diffraction analysis (XRD), tensile testing, impact testing, and dynamic mechanical analysis (DMA). Detailed descriptions of these DOE matrices and more complete test results can be found in other papers presented elsewhere (6-8).

Figure 2. ~ (Top) A “composite” SEM micrograph. (Bottom) Averaged cell sizes in two perpendicular directions across the diameter of the spruce.



Microstructure of Microcellular Injection Molded Parts

The microstructure of microcellular injection molded parts depends on many factors, such as the number of nucleation sites (homogeneous versus heterogeneous nucleation), process conditions (e.g., SCF level, pressure drop rate, etc.), strength and molecular structure of the matrix, as well as growth and coalescence of microcells during molding. **Figure 2, top** is a “composite” SEM micrograph showing the microstructure of a neat PA resin at a cross section of the spruce near the machine nozzle. Several SEM micrographs were combined to show the change of cell size and distribution across the diameter of the spruce. The measured microcell sizes in two orthogonal directions are plotted in **Figure 2, bottom**. Microcells of varying sizes can be found throughout the cross section except near the part surface where there is a thin, non-cellular polymer skin layer (typically in the order of hundreds of microns). The reason for the solid skin layer could be attributed to the gas diffusion near the part interface and the growth of the gas cell being hampered by the rapid cooling of the material near the surface. A mathematical model that takes into account the temperature/pressure histories of polymer melt during cooling and the cell growth of supercritical gas has been developed to predict the solid layer thickness and cell size distribution (8).

To demonstrate the effect of process conditions on the microstructure of the molded parts, **Figure 3** shows some representative SEM micrographs near the center of the test bar sample for microcellular PA nanocomposite samples molded under

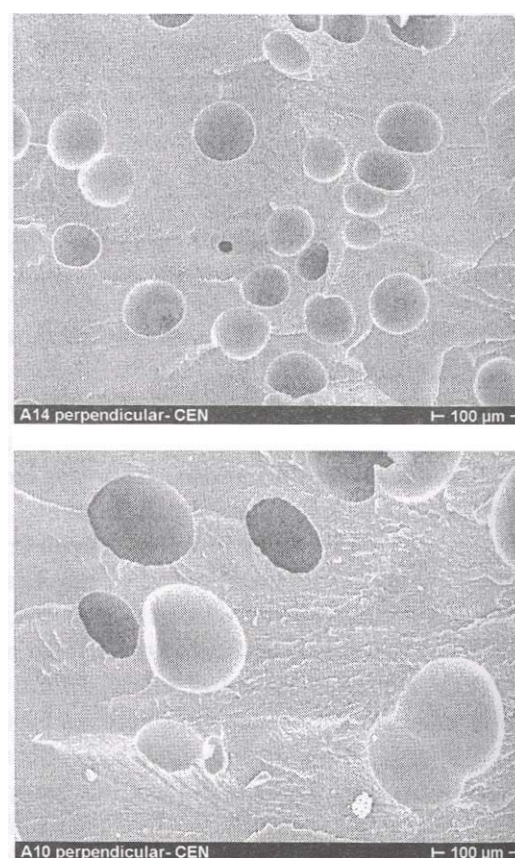


Figure 3. ~ SEM micrographs of the microcellular PA 6 nanocomposite molded under different process conditions, which result in different cell sizes and densities.

different conditions. The results obtained so far indicate that variations in process parameters, such as melt temperature, SCF level, injection speed and pressure, and shot size, can drastically affect the cell size, density, and distribution and, hence, the strength and the quality of the injection-

molded parts. In general, the cell size strongly depends on the shot size and moderately decreases with increasing SCF level, injection speed, and MPP, and increases with melt temperature, whereas the cell density is generally inversely proportional to the cell size. Since the effects of process conditions are intertwined in the DOE designs, further studies with refined DOE and different material systems are needed to develop guidelines of optimal processing windows to effectively control the microstructure of the molded parts.

In the past, significant research has been carried out on controlling the cell size and cell density of microcellular parts using micro-scaled fillers. One of the on-going studies by the authors focuses on the effect of nanoclay fillers (as in polymer-silicate nanocomposites) on the microstructure of microcellular PA-6 components (6,9). The study shows that, at higher weight reductions (e.g., 20% or higher), the presence of exfoliated nanoclay platelets can increase the density of cells by one order of magnitude and reduce cell-size significantly. For example, **Figure 4** compares the SEM micrographs of the microcellular injection molded PA nanocomposite and its neat resin counterpart. The samples were molded under the same process conditions at 20 percent weight reduction. The micrograph for the nanocomposite shows a near “ideal” microstructure with highly uniform and evenly distributed microcells. This result suggests a feasible way of using nanoclay to effectively control the nucleation and growth of microcells.

It was also found that the nanoclay helps to facilitate gas dissolution into the polymer melt and, thus, increase the level of weight reduction (9). More specifically, the maximum achievable weight reduction with the neat PA resin is 25 percent, beyond which molding problems will occur with the excessive SCF inside the injection barrel. However, a 31 percent weight reduction could be obtained with its nanocomposite counterpart. Moreover, the addition of gas also helps to further disperse the nanoclay platelets in the polymer-gas solution, according to the XRD data with PA-6 nanocomposites (6). Evidently, multiple, synergistic benefits can be realized by combining microcellular injection molding with nanocomposites. Table 1 summarizes the general effect of process conditions and fillers on the cell size and mechanical properties of microcellular injection molded

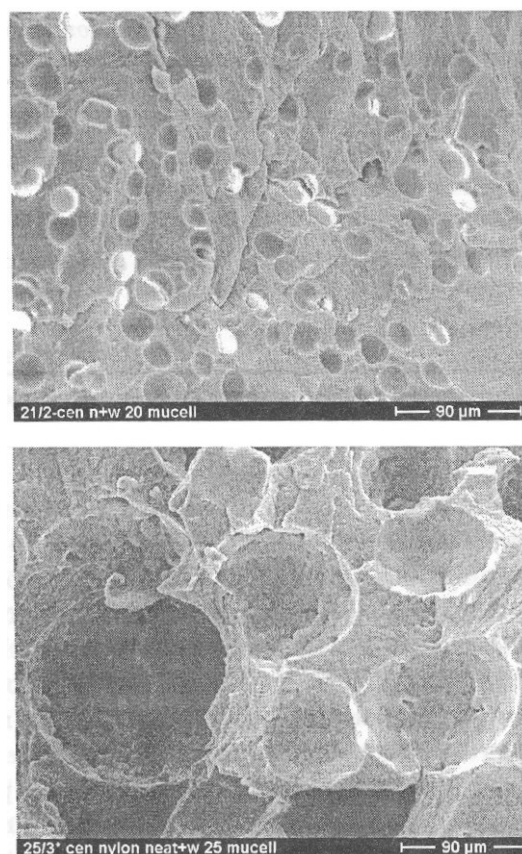


Figure 4. ~ SEM micrographs of the microcellular PA 6 nanocomposite (top) and neat PA 6 resin (bottom) molded under the same process conditions. Effect of nanoclay fillers on the cell size and density can be seen.

parts. The exact behavior will undoubtedly depend on the individual material and process conditions used.

Mechanical Properties of Microcellular Injection Molded Parts

The mechanical properties are closely related to the microstructures and the weight reductions obtained by the presence of gas (4,10,11). This section discusses the effects of process conditions and filler system on the tensile, weld-line, and impact strengths of microcellular injection molded parts.

Tensile Strength

A number of materials systems, namely, PA-6 nanocomposites, PA-6 neat resins, PA-6 with 28 wt. % wood cellulose fibers, PA-6/cellulose/Wollastonite composite, polycarbonate (PC), have been employed to study the tensile strengths of the microcellular injection molded parts and compared with those of solid parts. For the materials systems studied, the addition of gas tends to bring

Table 1. ~ General effect of process conditions and fillers on the cell size and mechanical properties of microcellular injection molded parts.^a

Control variables	Dependent variables			
	Cell size	Tensile strength	Impact strength	Weld-line strength
Melt temperature	increase	decrease	decrease	increase
SCF level	decrease	increase	inconclusive	inconclusive
Injection speed	decrease	increase	increase	increase
MPP level	decrease	increase	increase	inconclusive
Shot size	decrease	increase	increase	increase
Micro-/nano-fillers	decrease	increase	decrease	inconclusive

^a Dependent variable increases/decreases with increasing control variable, I: Inconclusive based on the available data.

about a reduction in the ultimate tensile strengths and the ductility/brittleness depends on the process conditions used (**Fig. 5**). The presence of the reinforcing fillers, on the other hand, improves tensile strength. For instance, tensile strengths in nanocomposites and cellulose-filled composites are higher than those observed with neat-resin samples (6,7). Based on testing results, higher shot sizes and MPP, which increase the amount of polymer in the component, increase the tensile strengths. The SCF levels and melt temperatures also have an important effect on the tensile strengths. The highest tensile strengths for PA 6 resins have been observed at the highest levels of shot size, MPP, injection speed, and SCF level and at the lowest level of melt temperature.

Impact Strength

The impact test results with solid nanocomposites and cellulose-filled composites show that the addition of micro-hano-scaled fillers reduces the impact strength of the filled materials. However, with microcellular injection molding process, an improved toughness has been observed with the nanocomposite as well as the neat PA resins (**Fig. 6**). Nevertheless, the impact test results with microcellular, cellulose-filled composites exhibit comparable or lower impact strengths compared with its solid counterparts (7). Such a reduction of impact strength is probably due to the presence of microcells at the interface between the cellulose fibers and the reinforcing cellulose fibers (**Fig. 6**). Recall that the fillers (e.g., nanoclay or cellulose fibers) could serve as nucleating sites (a phenomenon known as heterogeneous nucleation) that promote cell nucleation and growth at the polymer-fiber interface. For nanocomposites, the size of the nanoclay platelets is at least two orders of magni-

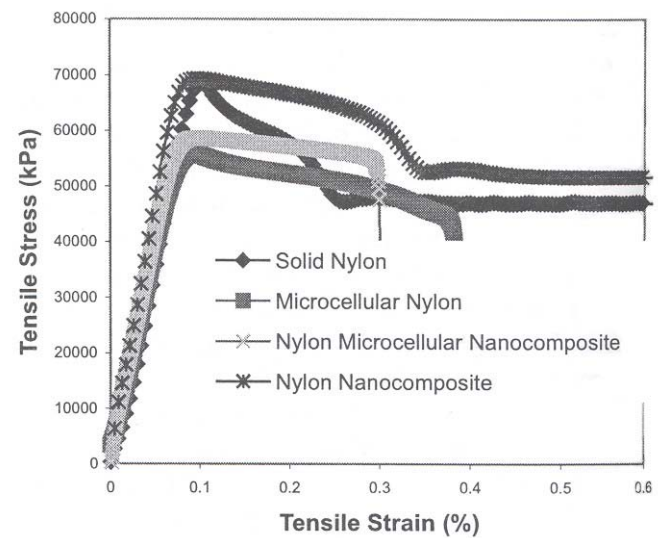


Figure 5. ~ Tensile stress-strain curves for different samples.

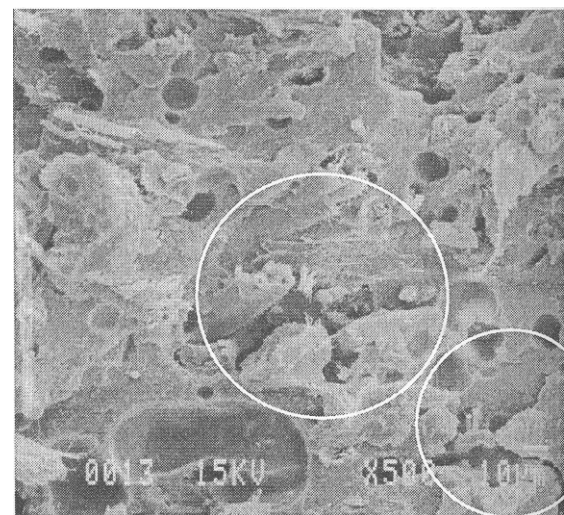


Figure 6. ~ SEM micrograph of microcellular PA-6/cellulose fibers composite showing microcells surrounding the fibers.

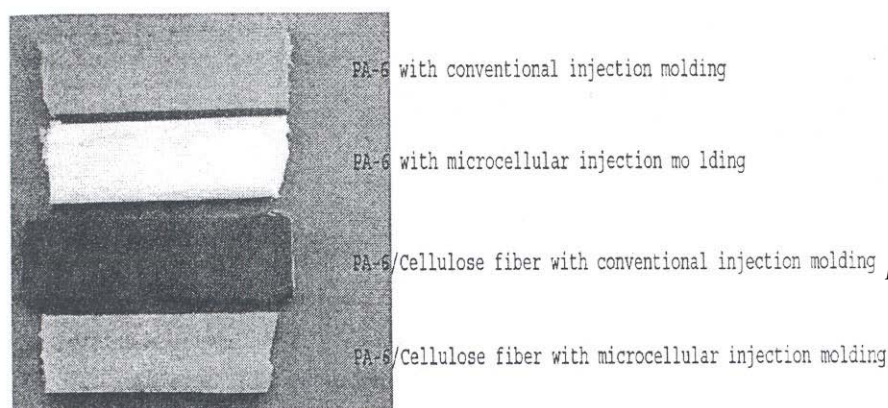


Figure 7. ~ Browning effect of injection molded cellulose-filled PA-6 parts.

tude smaller than that of the microcells (Fig. 3). Hence, the material properties in the polymer matrix are hardly affected by the microcells. Nevertheless, this is not the case with the cellulose-filled composite, for which the microcells and diameter of cellulose fibers (~20 microns) are of comparable sizes. When the fibers are separated from the polymer matrix by the microcells as shown in Figure 6, the reinforcing effect of fibers reduces. Accordingly, the impact strength decreases.

Weld-Line Strength

As a result of less material usage, absence of high packing pressure, and lower processing temperature, the weld-line strength of microcellular components is lower than its solid counterparts and is significantly dependant on the process conditions (4). In particular, the weld-line strength of microcellular injection molded components increases with increasing melt temperatures, shot-size, and injection speed and is weakly dependant on the SCF level. Optimizing the process conditions can minimize the adverse effects of weld-lines on the part performance and surface appearance.

Experimental Results with Cellulose-Fiber-Reinforced PA-6 Composite

When the experiments were being conducted with cellulose/PA-6 and PA-6/cellulose/Wollastonite composites, color changes in various sample sets were observed. With the conventional injection molding process, the solid neat PA-6 sample exhibits a colorless, translucent appearance. However, with microcellular injection molding, the sample color changes to white-opaque - presumably due to the increased light scattering caused by the presence of micro-scaled bubbles

(Fig. 7). On the other hand, the virgin raw cellulose/PA-6 composite pellets are originally a light cream color. When the cellulose/PA-6 composite is conventionally molded, the color of the material turned dark brown, suggesting some degree of thermal degradation of the wood cellulose fibers due to high processing temperature with PA-6. Note that the natural cellulose fibers can only be used with thermoplastics that are processed below 200°C. When the cellulose/PA-6 composite is processed with microcellular injection molding, temperature setting at Zone 3 was reduced from 232° to 216°C and the molded samples exhibit a much lighter-brown color (Fig. 7). The light-brown color of the microcellular cellulose/PA-6 composite sample may suggest a reduction in thermal degradation, since a lower processing temperature was employed. Nevertheless, the presence of microcells can also contribute to the lightening of the color.

It was also found that the cellulose fibers and the cellulose/Wollastonite fillers improve tensile strength and tensile modulus. In addition, the microcellular injection molded neat resin exhibits higher impact strength than that of the conventionally molded solid part. For the microcellular injection molded composites, the impact strength-to-weight ratio was comparable to those of the conventionally molded solid part. Due to the presence of microcells within the microcellular injection molded samples, a reduction in tensile strength was observed with both of the filled composites and neat resin. A fractographical study reveals that some of microcells were formed at the interface of cellulose fibers and the polymer matrix, which could have a significant effect on the mechanical properties of the molded parts. A detailed

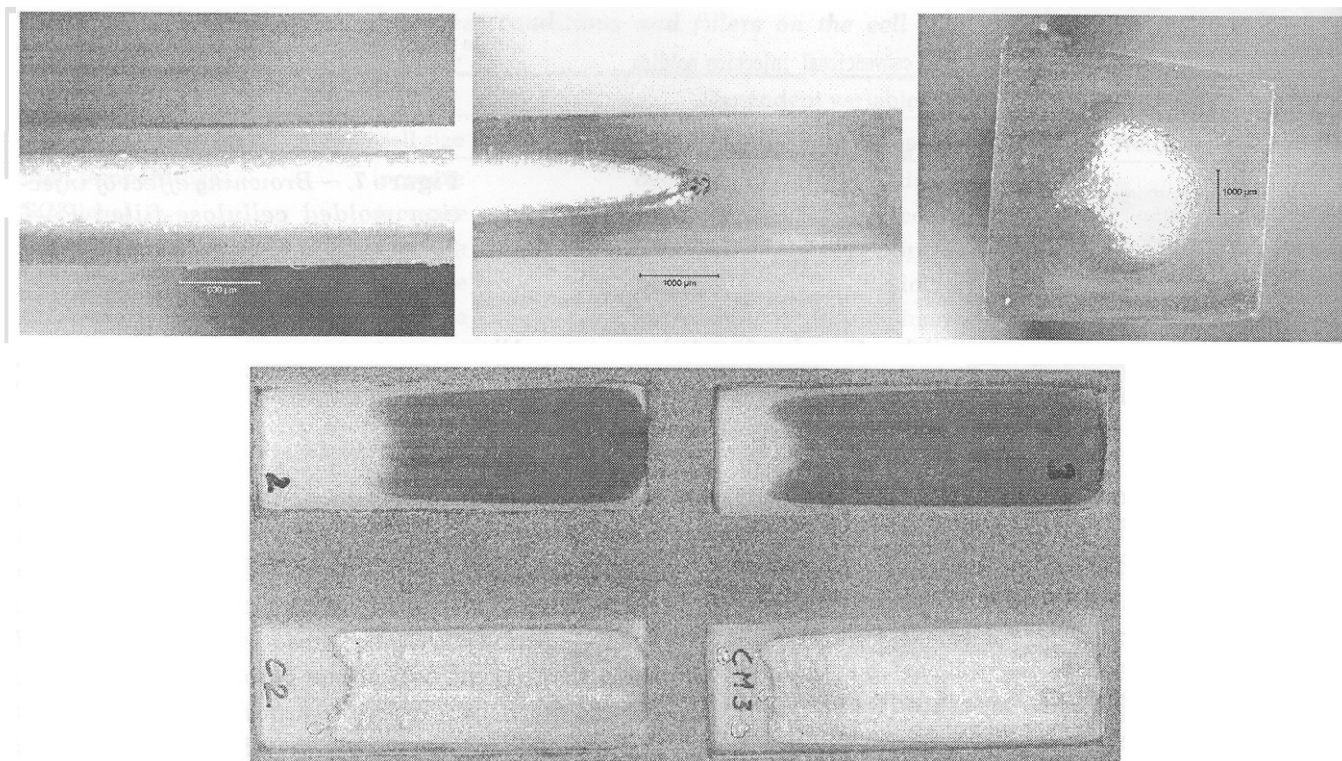


Figure 8. ~ (Top) Pictures of the cross sections of a co-injection molded part that contains a microcellular PS core sandwiched by clear, solid PS skin layers. (Bottom) Comparisons of microcellular co-injection molded parts and conventional co-injection molded parts (with red colored pigment).

discussion of the experimental results can be found in (7).

Microcellular Co-Injection Molding

By integrating solid plastics with MCPs via co-injection molding, synergistic benefits can be realized. Further, this process is a perfect candidate for recycling of post-consumer plastics. **Figure 8** shows pictures the cross sections at the runner and cavity and the top view of a co-injection molded part that contains a microcellular polystyrene (PS) core sandwiched by clear, solid PS skin layers. Initial experimental results suggest that the resulting foamed microstructure strongly depends on the skin-to-core switch-over time and the variation of pressure inside the cavity. Ideally, this microcellular co-injection molding process enables components with class “A” surfaces and lightweight microcellular cores to be molded while eliminating the swirling patterns typical of microcellular injection molded parts on the surfaces.

Conclusions

The process conditions and micro-hano-scaled fillers have great influences on the microstructure

and, thus, the mechanical properties of microcellular injection molded components. In addition, initial results of a novel co-injection molding process, which has potential in producing parts with class “A” surfaces while reducing part weight, were presented.

Acknowledgments

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