Applications of Polyamide/Cellulose Fiber/Wollastonite Composites for Microcellular Injection Molding

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Abstract

In this study, a cellulose-fiber-reinforced Polyamide-6 (PA-6) composite, a hybrid composite (PA-6/cellulose/Wollastonite), and the neat PA-6 resin were injection molded into ASTM test–bar samples with conventional and microcellular injection molding. The impact and tensile strengths of molded samples were measured and the Scanning Electron Microscopy (SEM) images were taken at the fracture surfaces. The effects of filler systems and the introduction of microcellular structure on the impact and tensile strengths were studied. It was found that the cellulose fibers and the cellulose/Wollastonite fillers improve the tensile strength and tensile modulus. In addition, the microcellular injection molded neat resin exhibits a higher impact strength than that of the conventionally molded solid part. However, a reduction in tensile strength was observed with both of the filled composites when molded with microcellular injection molding. This could be attributed to microcells at the interface of cellulose fibers and the polymer matrix.

Introduction

Injection molding is one of the widely used plastic processing methods for mass production of complex parts. With its advantages, such as excellent dimensional tolerance, shorter cycle time, and minimal or no post-process finishing required, injection molding accounts for 32% by weight of all the polymeric materials processed [1]. Because of the wide applications and technological innovations, many special injection molding processes have been developed. One of the special injection molding processes, microcellular injection molding (MuCell), blends supercritical fluids (e.g., N_2 or CO_2) with polymer melt to create a single-phased polymer-gas solution. During injection molding, the dissolved gas emerges from the solution creating numerous microcells with diameters ranging between 10 to 100 µm. The size of the cells is generally inversely proportional to the cell density, which are determined by cell nucleation and growth and the amount of gas dissolved in the polymer [1]. The major advantages of this special injection molding process are the weight savings, reduction of material viscosity (thus reduction of injection pressure and clamp tonnage), reduction in processing temperature and the overall cycle time. In addition, internal pressure arising from foaming eliminates the sink marks and the packing requirement while enhancing the dimensional stability of the final part. Further, the microcells introduced act as crack arrestors by blunting the crack tips, thereby, enhancing the part toughness.

Plastics industry has traditionally used talc, calcium carbonate, mica, and glass or carbon fibers to modify the performance of plastics [2]. Approximately about 1.3 million tons of fillers and reinforcements were used in the year 2000. According to [3], wood or other natural fillers were not widely used in plastics industry in the past because of its low bulk density, low thermal stability, and tendency to absorb moisture, although they are renewable resources, lighter materials, less abrasive, and even less expensive. Nevertheless, in the last decade some wood-plastics products have been doing well in attracting awareness and understanding from equipment and additive industries [3]. Wood-plastics materials are currently used for large volume building applications such as plastic lumber because the durability can be increased and the maintenance is reported to be easier. Since the thermal stability of wood fillers is limited, wood can only be used with thermoplastics that melt below the temperature of 200ºC [3]. Particulate form (flour) or very short fibers are the most common forms used in plastics application because of the higher bulk density and the free flowing nature. Low cost, familiarity, and

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availability are also contributing reasons why more companies are trying to use wood fillers in plastics applications. Detailed information on the history, current situation, and outlook of wood-plastic composites in the United States can be found in [3].

Wollastonite is a calcium metasilicate ($CaSiO_3$) that has the theoretical composition of 48.3% CaO and 51.7% SiO_2, but it may contain trace to minor amounts of aluminum, iron, magnesium, manganese, potassium, and sodium. Wollastonite occurs as massive or short prismatic crystals that cleave into massive to acicular fragments [4]. Mostly used in ceramics, paint, and plastics applications, Wollastonite also used in adhesives, friction products (brakes and clutches), joint compounds, metallurgical applications, refractories, and wallboard. In plastics applications, Wollastonite improves the tensile and flexural strengths, reduces the consumption of resins, and improves thermal and dimensional stability at elevated temperatures [4].

Materials and Experiments

Three materials systems were employed in this study, namely, (1) a neat PA resin (Ashlene™ 829L), (2) a wood cellulose-filled PA-6 composite (composite-1), and (3) a PA-6/cellulose/Wollastonite composite (composite-2). The neat resin used is a low viscosity, lubricated, basic PA-6. Highly purified, bleached chemical cellulose fibers made from southern hardwoods (TerraCel™ 10J) were used as fillers for the filled composites. With uniformly high cellulose content and low extractable content, this material has excellent thermal stability in temperature ranges, suitable for engineering thermoplastic such as PA-6. The average fiber diameter is ~20 microns and the average fiber length is ~0.85 mm, which makes the L/D ratio of 40-50. Composite-1 consists of 28 wt% cellulose fiber/72 wt% PA-6 and composite-2 consists of 20 wt% cellulose fiber/20 wt% wollastonite/60 wt% PA-6 [5].

A 150-ton TOYO injection-molding machine was employed for the molding experiments and N_2 gas was used as the physical blowing agent. The molding experiments were done based on similar process conditions for comparison purposes. The only major difference between the conventional and microcellular injection molding processes is that the Zone3 temperature used in microcellular injection molding is lower in order to reduce the thermal degradation of the reinforcing cellulose fibers. A total of six sample sets were produced, namely:

- Solid neat PA-6 resin
- Microcellular neat PA-6 resin
- Solid composite-1
- Microcellular composite-1
- Solid composite-2
- Microcellular composite-2

The composite materials were compounded on a 32 mm co-rotating Davis Standard twin-screw extruder using low-temperature processing methods that have been described [6].

Standard ASTM tensile tests (ASTM D638) and notched and un-notched impact tests (ASTM D256) were performed with these samples sets. In addition, SEM micrographs were taken at the fracture surfaces to examine the microstructure and the fracture mechanism.

Experimental Results

Color Change

When the experiments were being conducted, noticeable color changes in various sample set were observed (cf. Fig. 1). With the conventional injection molding process, the solid neat PA-6 sample has 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. On the other hand, the color of conventionally molded composite-1 (i.e., cellulose fiber-reinforced composite) sample became dark brown, while its microcellular sample exhibits a light-brown color. Since the raw composite-1 pellets are in a light cream color, the dark-brown color of the conventionally molded parts demonstrates some degree of thermal degradation ("browning") of the wood fibers due to high processing temperature with PA-6. The light-brown color of the microcellular composite-1 sample, on the other hand, may suggest reduced degradation, since a lower processing temperature was employed (Zone3 reduced from 210°C to 187°C). However, presence the microcells can also contribute to the lightening of the color. More studies are needed to determine the actual cause of the color changes.

Tensile Strength

The tensile tests were conducted according to ASTM D 638 standards. Figures 2 and 3 plot the data points of tensile strength and tensile modulus for all the six sample sets. For the tests, four to six test bar samples from each sample sets are tested. From the figures, one can see that when wood cellulose fibers and/or Wollastonite mineral are introduced, the maximum

tensile stress and the tensile modulus increase noticeably. However, the tensile properties of the microcellular injection molded samples decrease compared with their conventional solid counterparts. The best tensile strength is achieved using conventional injection molding process with PA-6/wood cellulose fibers/ Wollastonite composite whereas the solid PA-6/Wood cellulose fibers composite exhibits the highest tensile modulus.

Impact Strength

The impact tests were done using Izod impact tests that satisfy the ASTM D256 standard for notched and un-notched samples. Figure 4 plots the notched experimental results for all six material sample sets. Despite the large data scattering, microcellular injection molded PA-6 exhibits the best impact strength, which is consistent with many previous studies (see, e.g., [7]). However, contrast to the neat-resin data, both of the composite materials processed by microcellular injection molding process result in either comparable or lower impact strength compared with their solid counterparts processed by the conventional injection molding process. Such an unexpected result will be explained in the following section using the SEM micrographs at the fracture surface.

SEM Micrographs

Using SEM, the microstructures of the samples were analyzed. Figures 5 and 6 show how the microstructures of the microcellular injection molded PA-6 differ from conventional injection molded PA-6. Microcellular injection molding method introduces microcells with the sizes ranging from 1 to 60 μm.

The microstructure of the solid and microcellular PA-6/cellulose fiber composite shown in Figs. 7 and 8 reveal that some bubbles occur at the interface between the cellulose fibers and the polymer matrix. That is, compared to the one processed by conventional injection molding (Fig. 7), there are voids at fibers surroundings in Fig. 8 and Fig. 9. As reported in [8], cell nucleation tends to take place at the interface between the polymer and the additives (i.e., the fibers) – a phenomenon called heterogeneous nucleation. Since the purpose of the cellulose fibers is to enhance the material performance, these voids may offset the fiber reinforcing functions significantly. This is why in the mechanical tests microcellular injection molded composites tend to have lower strengths.

Conclusion

The conclusion of this research can be drawn from two different points of view: the material and the process. From the material aspect, solid PA-6 has highest impact strength but lower tensile strength compared to PA-6/cellulose fiber and PA-6/cellulose fiber/Wollastonite composites. As for the process point of view, microcellular injection molding results in better impact strength compared to conventional injection molding process for neat resin as the microcells introduced in the process act as crack arrestors. However, for composite material with fibers or mineral, microcellular injection molding does not yield improvements in tensile or impact tests due to the presence of microcells around the fibers.

Acknowledgements

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Figure 1 Sample color changes when microcellular injection molding process is used.

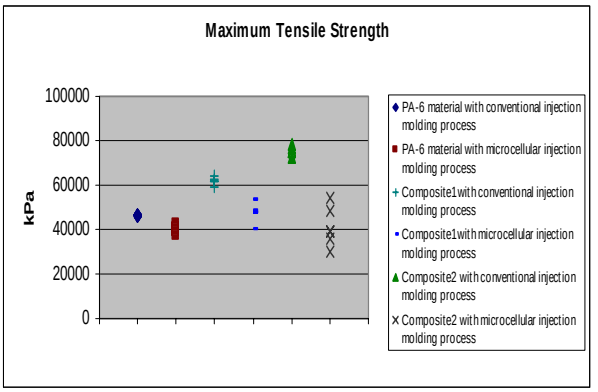

Figure 2 Maximum tensile strength data for solid and microcellular PA-6, PA-6/cellulose fiber composite, and PA-6/cellulose fiber/ Wollastonite composite.

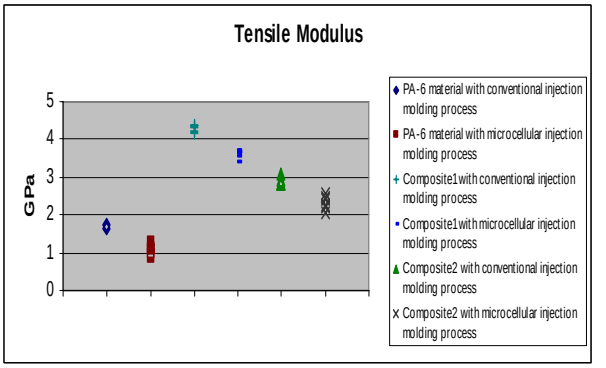

Figure 3 Tensile Modulus of elasticity for solid and microcellular PA-6, PA-6/cellulose fiber composite, and PA-6/cellulose fiber/ Wollastonite composite.

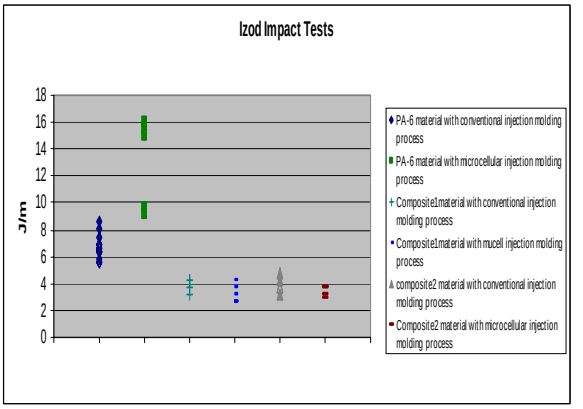

Figure 4 Notched Izod impact test results for solid and microcellular PA-6, PA-6/cellulose fiber composite, and PA-6/cellulose fiber/ Wollastonite composite.

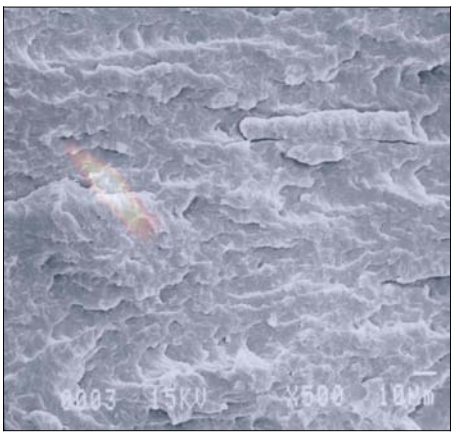

Figure 5 SEM micrograph of conventional injection molded PA-6.

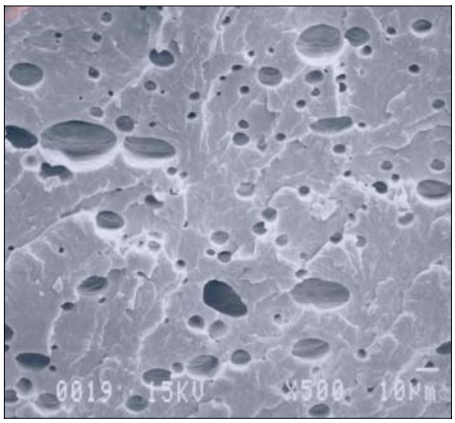

Figure 6 SEM micrograph of microcellular injection molded PA-6.

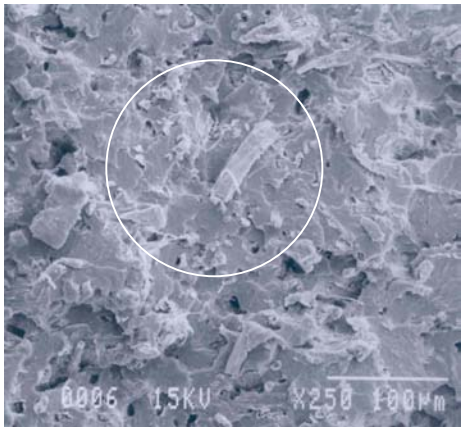

Figure 7 SEM micrograph of conventional injection molded PA-6/cellulose fibers composite.

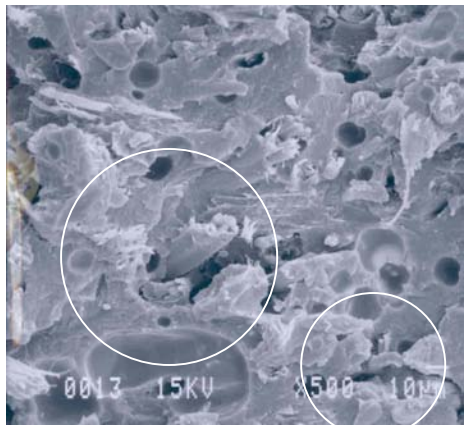

Figure 8 SEM micrograph of microcellular injection molded PA-6/cellulose fibers composite showing voids around the fibers.

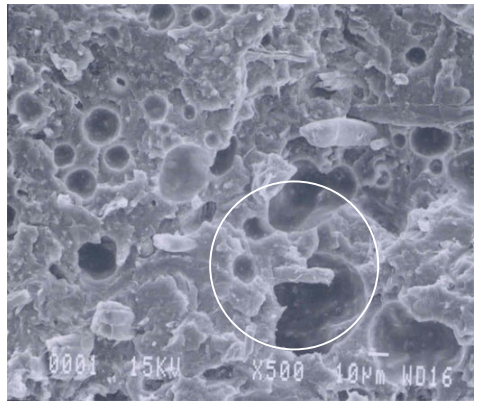

Figure 9 SEM micrograph of microcellular injection molded PA-6/ cellulose fibers/Wollastonite composite showing voids around the fibers.