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Pressurized Water Pellets and Supercritical Nitrogen in Injection Molding

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ABSTRACT: In this article, a novel approach to decrease cycle time without compromising part dimensional stability developed in our group is compared with the use of supercritical nitrogen in injection molding. In this new approach, water is pre-pressurized into the polymer pellets containing water carrier particles such as activated carbon (AC), thus no molding equipment modifications are required. Because of its high porosity, AC can trap water inside the particle, thus improving water compatibility with hydrophobic polymers for less water loss during handling and in the barrel during injection molding. After mixing, the polymer with the water carrier, the pellets are batch pressurized with water at a controlled temperature and pressure. The water containing pellets are then fed into the hopper of the injection molding machine. Parts with similar densities were molded and mechanical properties and warpage for both processes compared. It was found that the warpage and mechanical properties of the method presented here are comparable with the use of supercritical nitrogen, which is used in microcellular injection molding. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Typical injection molding involves four stages; starting from filling, packing, cooling, and part ejection. It is well known that the larger parts of the process are the packing and cooling stages, taking up to 75% of the time required to mold a part. The part needs to be mechanically stable and sufficiently cooled before being ejected from the mold. Reducing the needed cooling time to mold a part will have a significant effect on process economics; however, decreasing the cooling time will, in general, adversely affect the dimensional stability of parts. Several special injection molding processes have been developed that produce parts with both improved dimensional stability and lower cycle times.[1] They include microcellular injection molding, gas-assisted injection molding, and water-assisted injection molding. In the microcellular injection molding process, a supercritical gas (usually nitrogen or carbon dioxide) is blended with the polymer melt in the molding machine barrel to create a single phase solution.[2] During the molding process, the gas forms microscale bubbles, improving dimensional stability while decreasing the cycle time without

adversely affecting the mechanical properties of constituent parts.[3] Specific processes based on microcellular injection molding include Mucell, Optifoam, Ergocell, and Profoam.[4] All the above four injection molding technologies use a different method for producing foamed parts that range from a special reciprocating screw and barrel to special gas dosing units in the injection molding unit. Depending on the technology and the material used different foam morphologies may be obtained.

The water- or gas-assisted injection molding process were developed with the objective to improve dimensional stability while reducing part weight and cycle time[5–8]; however, mechanical properties are affected as the final part will have a hollow core. In this process, water or an inert gas (usually nitrogen) is injected into the mold after a partial or full shot of polymer to obtain a full part with a hollow cavity in the center. The injection of water or gas into the core of the polymer melt lowers the temperature of the melt during molding and reduces the heat conduction distance, thus a shorter cycle time can be
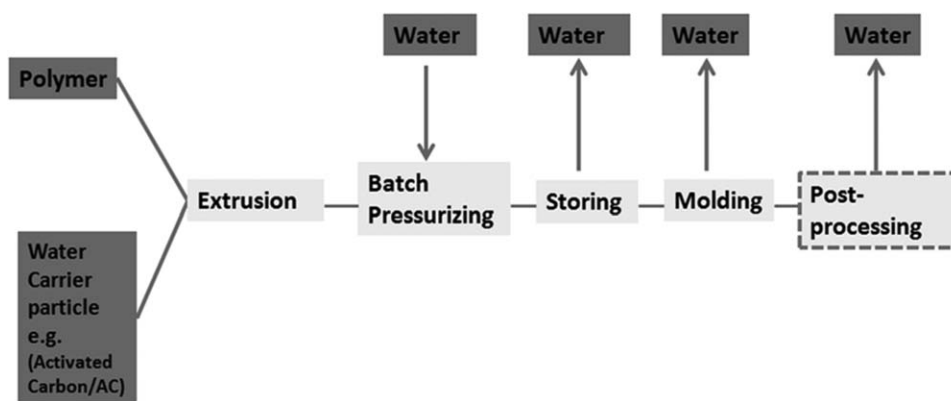
Figure 1. Process schematic of injection molding of water containing polymer.

achieved. All the above processes require special equipment or mold modifications.

A novel approach has been developed to decrease cycle time and improve dimensional stability while not affecting the mechanical properties, much like microcellular injection molding. The developed approach differs from the traditional water-assisted injection molding in that the water is pre-pressurized into the polymer pellets containing water carrier particles such as activated carbon (AC). It is well known that AC is a form of processed carbon that has a very large surface area available for adsorption as a result of extremely high porosity.[9–11] AC can trap water inside the particle, thus improving water compatibility with hydrophobic polymers, reducing water loss during handling and in the barrel during injection molding. The schematic of the process is shown in Figure 1. After mixing the polymer with the water carrier, the pellets are batch pressurized with water at a controlled temperature and pressure. The pressurized pellets are then dried at ambient conditions to eliminate the excess surface water and obtain the desired water content. The water containing pellets are then fed into the hopper of the injection molding machine. Thus no molding equipment modifications are required[12] because the physical blowing agent (water) is readily available inside the pellets. Parts with similar densities were molded and mechanical properties, surface roughness, and warpage for both processes were compared. The effect of packing pressure on part warpage was also measured. The new approach was initially developed using thermoplastic polyolefin, (TPO) however, because this material does not lend itself to microcellular molding; in this work, we also used polystyrene (PS) for a better comparison. For clarity, Table I shows a comparison between the new approach, microcellular injection molding, and regular injection molding.

EXPERIMENTAL

Materials and Compounding

Two polymers were used for this study, TPO (ATX889NYX NATURAL) from Lyondellbasel with a melt flow index of 30 g/10 min (230°C/2.16 kg) and 3100 general purpose crystal PS from INEOSNOVA. The AC (Spartan Series) was obtained from Carbon Resources Company, which is produced from high-quality coconut shell carbons with an average particle size of 7 μm. Compounding was done using a twin screw extruder equipped with a pelletizer die (Leistritz ZSE-27; $D = 27$ mm; $L/D = 40$). The temperature zones of the extruder barrel were kept at 160°C in the feed zone and 180°C at the die tip. The extruder was typically run at 100 rpm. The 0.5 wt % of particle level was selected to not affect the mechanical properties of TPO or PS.

A custom-made pressure and temperature vessel was used to pressurize water into pellets after compounding. The pellets were submerged in warm water ($\sim 50°C$) using a stainless steel bucket and placed inside the vessel at a set pressure and temperature; 0.52 MPa and 95°C, respectively. The time inside the vessel determined the water content of the pellets. The water content was measured with an HR83 Halogen Mettler Toledo, which uses the weight loss on drying technique (LOD). The water content of each material was measured before injection molding. Water was not pressurized into the AC particles before compounding because most of the water would evaporate during the extrusion process. Mixing wetted AC particles with polymer pellets to get a uniform mixture would also be a problem during the compounding process.

Because materials were not injection molded on the same day and water retention differs depending on the ambient

Table I. Comparison Between the Use of Supercritical Nitrogen and Pressurized Water with the Regular Injection Molding Process

Method	Equipment modification	Silver stripes	Sink marks	Warpage	Mechanical properties	Void size (μm)
Regular injection molding	No	No	Yes	Yes	Good	No
Supercritical nitrogen	Yes	Yes	No	No	Only slightly affected	3–100
Pressurized water	No	Yes	No	No	Good	500

Table II. Summary of Parameters Used in the Experiments

Method	Injection speed (cm/s) high/low	Injection pressure (MPa) high/low	Packing pressure (MPa) high/low	Rotational speed (cm/s) high/low	Nitrogen pressure (MPa)	Material
Supercritical nitrogen	10/5	206/137	3.45/0.69	38/12.7	3.5	PS
Pressurized water	10/5	206/137	3.45/0.69	38/12.7	N/A	PS/TPO

conditions and resin used, water content before injection molding was different for TPO and PS. In this study, the water content in the TPO pellets was approximately 0.26 wt %, and the water content in the PS pellets was approximately 0.31 wt % for most of the experiments except for the results shown in Figures 13 and 14, where the water level was approximately 0.4 wt %. For industrial use, the desired water content can be controlled by storing the pellets at a controlled temperature and humidity before molding. Data to be able to select the desired initial water value as a function of pressurizing parameters and pellet storage conditions are being developed. In the case of PS, when no water carrier (AC) was used, the maximum amount of water that we were able to obtain was 0.1 wt %, thus justifying the need of a water carrier particle. Note that if the water level was larger than 0.4 wt %, although resulting in a larger cycle time reduction, tended to produce parts with lower mechanical properties and water drops were visible on the surface of the mold cavity after each injection molding cycle. However, water levels below 0.1 wt % did not provide significant reduction in cycle time. The level of water chosen between 0.2 and 0.4 wt % did not produce water droplets in the mold or molding equipment. For completeness of analysis, the following samples were molded:

- without water to represent regular injection molding;
- nitrogen SCF to represent microcellular foam;
- water only to represent our method; and
- water and SCF to represent a combination of both methods.

Injection Molding

Injection molding was done using a 100 ton Battenfeld co-injection molding machine (HM 100/350H/350H), which is also capable of foam molding with supercritical nitrogen. The mold consisted of a 16.2 cm square flat plate with 3.85 mm cavity thickness. In all molding experiments, melt temperature (205°C), mold temperature (27°C), back pressure (3.4 MPa), and packing time (10 s) were held constant. Nitrogen pressure of 3.5 MPa was used for foam molding. Table II summarizes the parameters used for all experiments.

Testing

The flat plate warpage was measured following ASTM D1181. The setup is shown in Figure 2. The part was attached to a steel flat plate using a screw. At each corner, the height and thickness were measured using a dial indicator and calipers, respectively. The warpage of each part was obtained as the average value of the difference between each respective height and thickness measurement. After the warpage measurements, flexure mechanical testing samples were cut according to the layout shown in Figure 3 using a band saw. Mechanical test (ASTM D790 for Flexural) was done on the cut samples using an INSTRON testing machine (model 5565). Eight flexure samples, four from each part, were used to obtain an averaged data point. Surface roughness and density were measured at the middle of each sample on the completion of the mechanical test. Surface
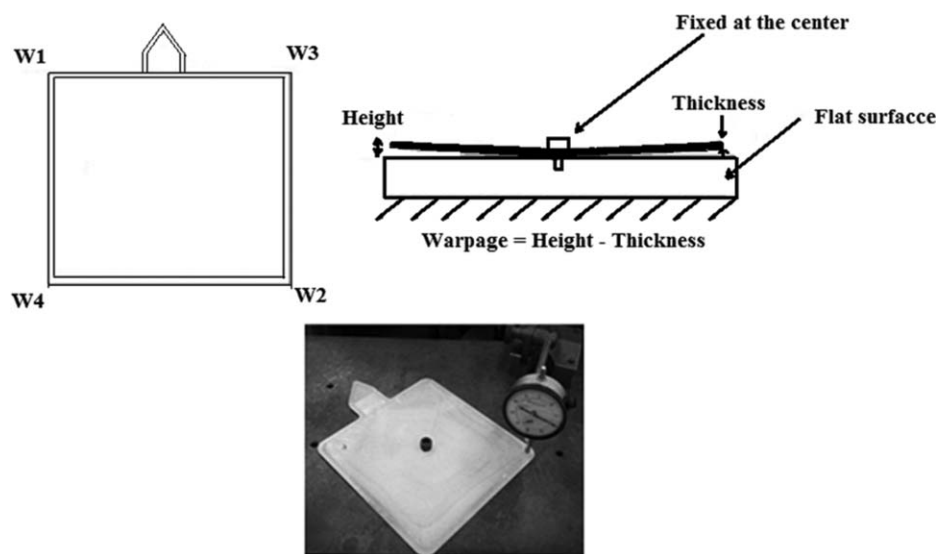

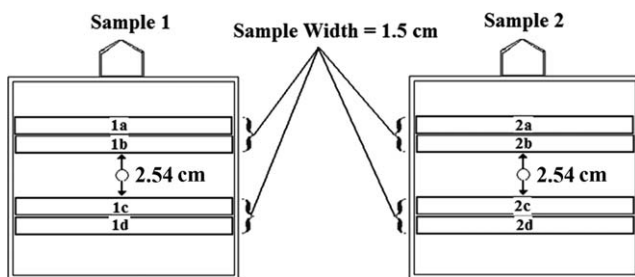**Figure 2.** Flat plate mold and warpage measurement.

Figure 3. Flat plate sample testing.

roughness was obtained using an optical profilometer (Veeco Wyko NT9100). Part volume measurements were obtained by subtracting part weight submerged in water from its actual weight and dividing the result by the density of water. Density measurements were obtained by dividing the mass by the obtained volume.

RESULTS

Injection Molding/TPO

Flat plate parts were molded using 41 s, 36 s, 31 s, and 26 s cycle time by varying the cooling time. A reduction in cooling time increased the warpage of the molded part. The flat plate's minimum required cooling time changed depending on the material used and was dictated by three defects: warpage larger than 0.9 mm (regular injection molding), sprue breakage (parts with supercritical nitrogen), and swelling around the sprue area (parts with pressurized water). Parts molded with TPO + 0.5 wt % AC showed warpage larger than 0.9 mm at a 26 s cycle time. Parts molded with TPO + 0.5 wt % AC + N_2 resulted in sprue breakage during demolding at a 26 s cycle time. Parts molded with TPO + 0.5 wt % AC + 0.26 wt % water showed swelling around the sprue area during demolding at a 21 s cycle time. Figure 4 summarizes the effect of water and supercritical N_2 on warpage for TPO + 0.5 wt % AC. It is shown that a small water percent content (0.26 wt %) has a greater effect on warpage than supercritical nitrogen allowing for demolding at a lower cycle time (26 s), which was possible only with water. The combination of supercritical nitrogen and a small water percent content further reduced warpage, but its
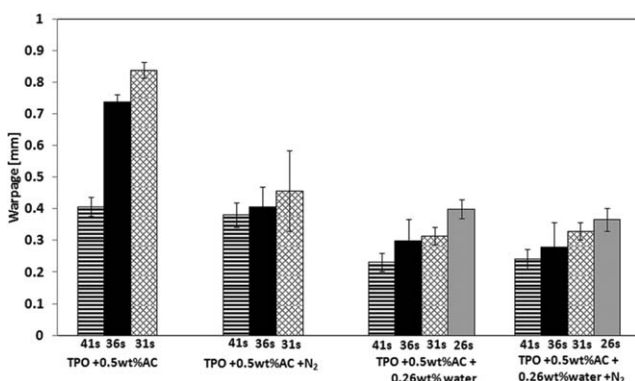

Figure 4. Effect of pressurized water and/or supercritical nitrogen on warpage for TPO.
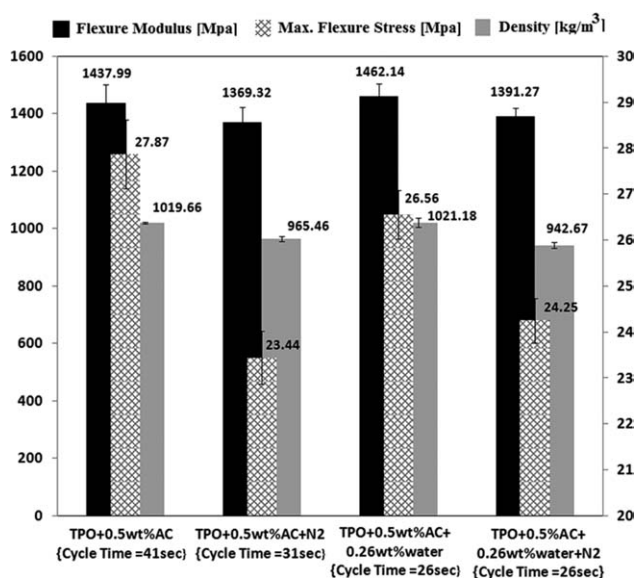

Figure 5. Mechanical properties and density for TPO + 0.5 wt % AC + 0.26 wt % water.

effect was insignificant. The reduction in warpage is probably due to the presence of bubbles, which help avoid nonuniform shrinkage by releasing molding stresses. The acceptable level of warpage will depend on the part function. What is clear is, there is an inverse correlation between cycle time and part warpage, for example when molding without water and or nitrogen, if you keep the part in the mold for 41 s, the warpage is about 0.4 mm, on the contrary if you demold at 31 s, the warpage value is increased to above 0.8 mm. These values are decreased using nitrogen or water. For example, if the acceptable warpage is 0.4 mm, we can demold in 26 s if we use water vs. 41 s without water.
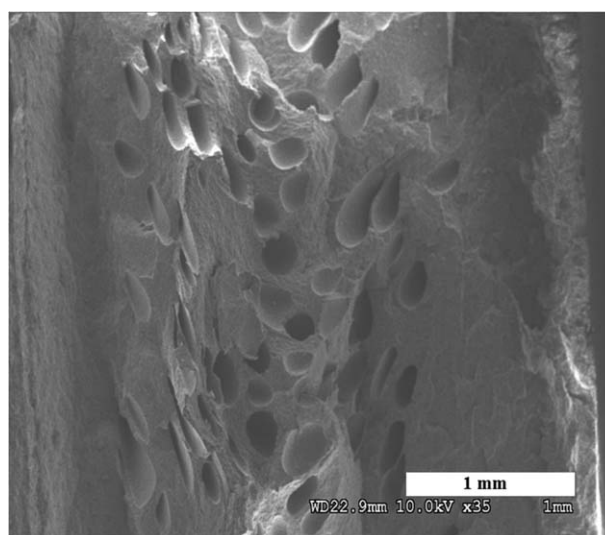

Figure 6. SEM micrograph showing the foam morphology of TPO injection molded with supercritical nitrogen taken 2 cm away from the sprue of the flat plate part.
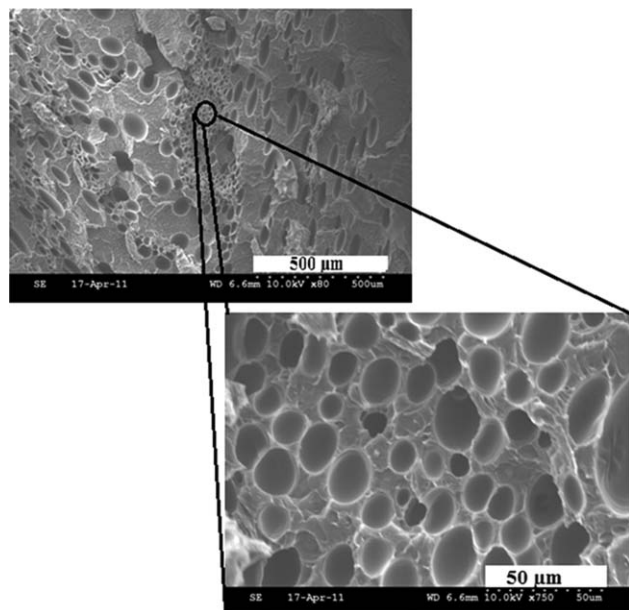
Figure 7. SEM micrograph showing the foam morphology of PS injection molded with supercritical nitrogen taken 2 cm away from the sprue of the flat plate part.

Figure 5 shows the mechanical properties and density for TPO + 0.5 wt % AC without water, with 0.26 wt % water and with supercritical nitrogen molded at the lowest cycle time possible that was established as explained before. The parts molded with supercritical nitrogen resulted in lower mechanical properties compared to parts molded with water containing pellets because of most likely a greater decrease in part density. Figure 6 shows the foam morphology obtained for TPO injection-molded parts with supercritical nitrogen. Because of the low viscosity of TPO at the molding temperature, the small bubbles coalesce into larger bubbles (average size 400 μm) resulting in a nonmicrocellular foam sample. In the next section, we compare our process
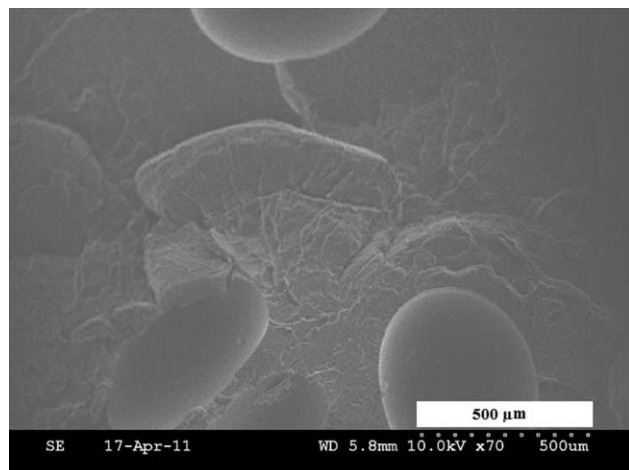

Figure 8. SEM micrograph showing the foam morphology of PS + 0.5 wt % AC + 0.31 wt % water taken 2 cm away from the sprue of the flat plate part.
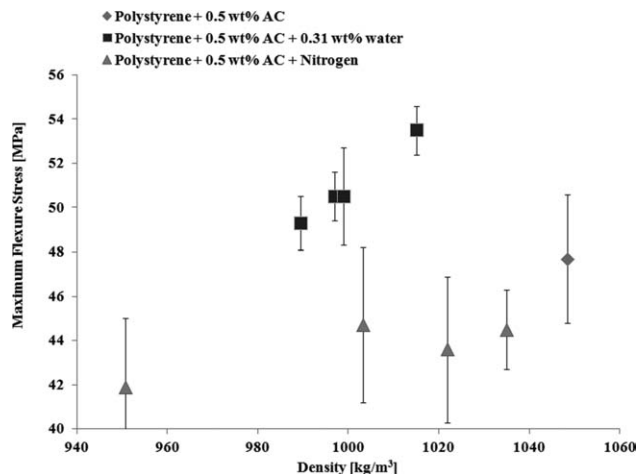

Figure 9. Effect of pressurized water and nitrogen on maximum flexure stress at 41 s cycle time.

with the supercritical nitrogen process, using PS, because it gives more uniform foam morphology with smaller average cell size, as a result of its larger viscosity at molding temperatures, which is due to the phenyl group, avoiding the small bubbles to coalesce into larger bubbles.

Injection Molding/PS

More uniform foam morphology was obtained by using PS instead of TPO in the injection molding with supercritical nitrogen. As a result, a better comparison on part warpage, cycle time, and mechanical properties between the use of supercritical nitrogen and pressurized water containing pellets in injection molding was obtained based on parts with similar part density. Figure 7 shows the foam morphology for PS injection-molded parts with supercritical nitrogen, and a close up to the center section of the molded part that consists of a uniform network of bubbles ranging from 10 to 15 μm in diameter. For pressurized water containing parts, the foam morphology is composed of bubbles in the range of 100 to 500 μm, as shown in Figure 8. Depending on the injection molding parameters, the obtained
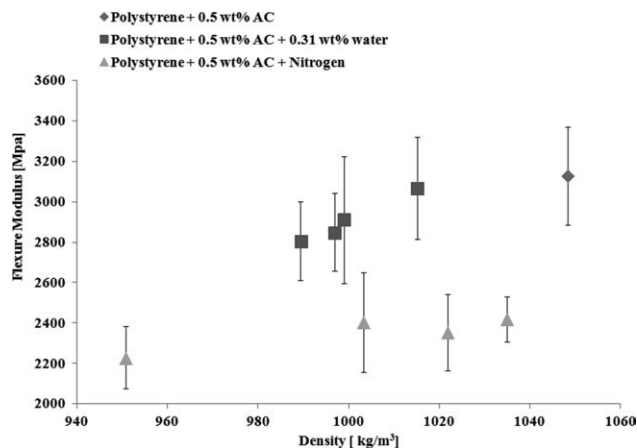

Figure 10. Effect of pressurized water and nitrogen on flexure modulus at 41 s cycle time.
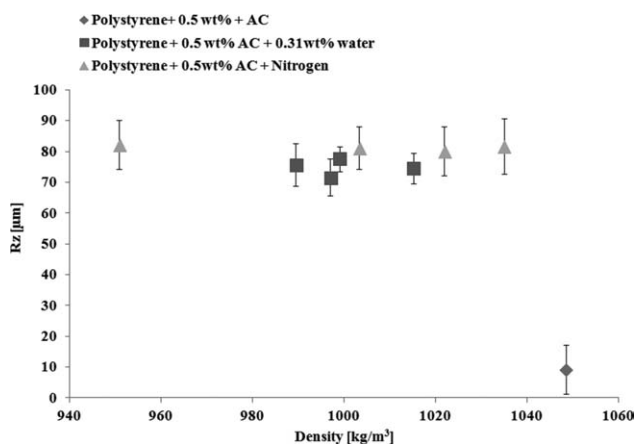
Figure 11. Effect of pressurized water and nitrogen on surface roughness $[R_z]$ at 41 s cycle time.

Figure 13. Effect of pressurized water and nitrogen on warpage at 41 s cycle time.

density results for the case of supercritical nitrogen ranged from 950 to 1020 kg/m³, and 990 to 1015 kg/m³ for pressurized water containing parts. Mechanical properties, surface roughness, and warpage measurements were obtained from both injection molding methods shown in Figures 9–13. In all cases, the cycle time was kept constant at 41 s. For reference, we also show the results obtained from a typical/solid injection-molded part. Supercritical nitrogen injection-molded parts showed a decrease of 10% in maximum flexure stress and a decrease of 25% in flexure modulus compared with the solid injection-molded part. Pressurized water injection-molded parts showed a decrease of 10% in flexure modulus but showed similar maximum flexure stress results to the solid injection-molded part.

Both injection molding methods gave similar surface roughness results with average roughness depth (R_z) and average surface roughness (R_a) values 800% and 600% larger than the solid part. Because the cycle time was kept constant at 41 s, the warpage results from both methods were similar and almost did not vary across the different obtained densities. But, both methods
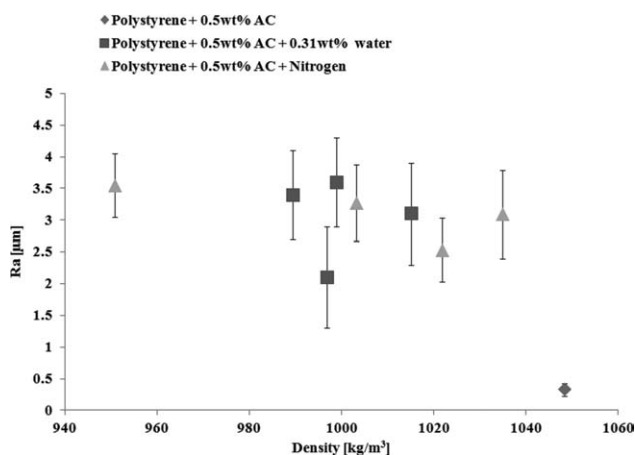
reduced part warpage by 200% when compared with the solid part.

To better show the influence of pressurized water and supercritical nitrogen on warpage, flat plate parts were molded using 41 s, 36 s, 31 s, and 26 s cycle time by varying the cooling time and using the injection molding parameters that resulted in similar part densities of approximately 1000 kg/m³ from both methods. Figure 14 summarizes the results, we can see that a small water percent content (approximately 0.4 wt % for this set of experiments) has a greater effect on warpage than supercritical nitrogen allowing for demolding at a lower cycle time (26 s), which was possible only with pressurized water containing pellets. At a 26 s cycle time, flat plate parts injection molded using supercritical nitrogen broke across the middle during demolding. For parts without water or nitrogen, if molded at 31 s, the sprue brakes when trying to eject the part.

Figure 15 shows the effect of packing pressure on warpage for a 41 s cycle time by using packing pressures of 3.45 MPa and 0.69 MPa. A reduction in packing pressure resulted in 14% warpage increase for the solid part and did not affect the warpage of supercritical nitrogen injection-molded parts. In the case of pressurized water containing pellets, a decrease in packing

Figure 12. Effect of pressurized water and nitrogen on surface roughness $[R_a]$ at 41 s cycle time.
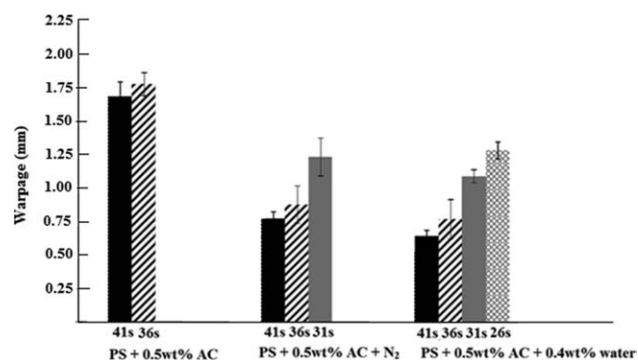

Figure 14. Effect supercritical nitrogen and pressurized water containing pellets on part warpage compared with the warpage of a solid part.
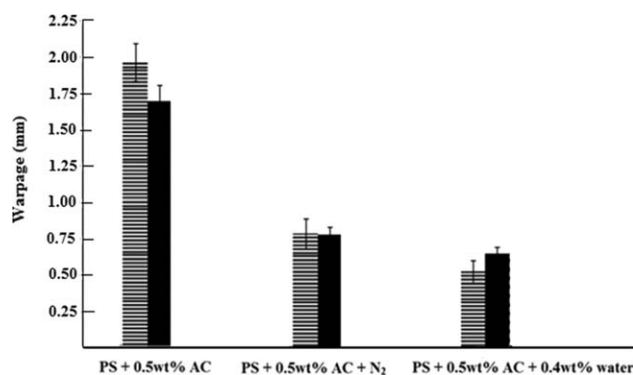
Figure 15. Effect of packing pressure on warpage for the 41 s cycle time [0.69 MPa (dash bar) vs. 3.45 MPa (solid bar)].

pressure resulted in a 20% reduction in warpage. Decreasing the packing pressure below 0.69 MPa will result in a short shot. Reducing the packing pressure allowed an increase in bubble growth, which decreased warpage.

DISCUSSION

The use of pressurized water pellets for injection molding was originally developed using TPO resin because of the interest of our industrial collaborators. However, TPO did not provide a good comparison with the use of supercritical nitrogen. TPO is mostly a blend of PE, PP, block copolymer polypropylene BCPP, and rubber. The PP and PE components of the blend constitute the "crystalline phase", and the rubber gives the "amorphous phase". Foam that forms in the amorphous phase breaks easily creating bigger bubbles.[13] As a consequence, the foam morphology obtained (Figure 6) consisted of many large bubbles (average cell size 400 μm) that decreased the mechanical properties of the part.

Unlike TPO, PS has a higher viscosity because of its phenyl groups enabling PS foam to maintain its form and impede the combination of small bubbles into one large bubble. Injection-molded parts of PS with supercritical nitrogen resulted in a foam morphology consisting in cell size ranging from 10 to 100 μm (Figure 7). Compared with supercritical nitrogen, the use of pressurized water pellets formed very few large bubbles (~ 500 μm) that did not affect the mechanical properties of the part. Thus mechanical properties for both processes were similar. When tested in tension, mechanical properties of the pressurized water process tend to be about 90% of the solid injection-molded part.[14]

The use of supercritical nitrogen or pressurized water allowed for the reduction of the minimum required packing pressure to mold a good part with no sink marks or shrinkage. A reduction in packing pressure resulted in a decrease in maximum flexure stress for the solid PS + AC parts. Therefore, PS + AC + water foamed parts had a higher maximum flexure stress than that of the solid PS + AC parts.

Despite the advantages of cooling time reduction and dimensional stability, the surface characteristics associated with supercritical nitrogen and pressurized water molded parts, such as

unique flow marks referred to as silver strikes, is one of the main drawback associated with these two methods.[15] This drawback may limit the application of the processes to surface critical parts. We are in the process of evaluating process parameters that will minimize these imperfections.

Part warpage, caused by differential shrinkage of material in the molded part, creates residual stresses. Residual stresses act on a part similarly to external applied stresses. If the residual stresses induced during molding are high enough to overcome the structural integrity of the part, the part will warp or crack on ejection from the mold.[16] Part warpage is mainly caused by the following factors: low packing pressure, short packing time, or short cooling time. Supercritical nitrogen and pressurized water-molded parts showed similar reduction in warpage when compared with a typical/solid-molded part. In both processes, warpage is decreased because of the presence of bubbles, which contribute to releasing the internal molding stresses.

The decrease in cycle time that is possible with either supercritical nitrogen or pressurized water processes will depend on the level of warpage permissible. The acceptable level of warpage will depend on the part function. What is clear is, there is an inverse correlation between cycle time and part warpage, for example when molding without water and or nitrogen, if you keep the part in the mold for 41 s, the warpage is about 0.4 mm; on the contrary, if you demold at 31 s, the warpage value is increased to above 0.8 mm. These values are decreased using nitrogen or water. For example, if the acceptable warpage is 0.4 mm, we can demold in 26 s if we use water vs. 41 s without water. Some of the cooling time reductions are due to the heat absorbed when either nitrogen or water change phase; however, the amount of heat absorbed is not very large.[14]

CONCLUSIONS

In this article, two injection molding approaches are compared: the use of supercritical nitrogen and the use of pressurized water containing polymer pellets. Experimental measurements were obtained from parts over a possible specified density range allowing for a fair comparison. Both approaches were conducted on the same injection molding machine. Results showed that a small water percent content has a greater effect on warpage than supercritical nitrogen when using a Battenfeld injection molding machine. Both injection molding methods gave similar surface roughness results with R_z and R_a values 800% and 600% greater than the solid part. Three point bending mechanical testing results showed a decrease in flexure modulus for both methods, but only pressurized water containing parts had similar maximum flexure stress results to the solid injection-molded part. The use of water pellets also allows the injection-molded part to be ejected earlier compared with supercritical nitrogen. Deciding the best process setting would be a compromise between the cycle time and warpage.

Future Work

An alternative approach to microcellular injection molding that does not require any equipment modifications is being developed. An additive which is compounded with the thermoplastic pellets that are then injection molded is being used. The

additive is produced by an in-situ polymerization of polyaniline (PANI) onto a water carrier particle such as Halloysite-Clay (HC), where HC is naturally exfoliated because of its tubular shape and uniform surface charge.[17] PANI has the function of adsorbing both water and CO_2 gas. Previous to injection molding, the plastic pellets pre-mixed with additive microparticles are pressurized with water/CO_2 in a batch process under controlled pressure and temperature.

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