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Crystalline polycarbonate articles fabricated by hot powder compaction

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The feasibility of a novel method is demonstrated by producing crystalline polycarbonate with a defined shape from polycarbonate for the first time.

Injection molding is the most common method for producing thermoplastic parts. In the case of polycarbonate, however, this process generally gives rise to amorphous (rather than crystalline) solids. This is because polycarbonate (PC) crystallizes extremely slowly (i.e., with a crystallization half-time of 12 days) and so can be regarded as an amorphous polymer for practical purposes.[1] PC articles made by injection molding have an exceptional combination of transparency and toughness, but their amorphous nature means that they are prone to stress cracking by organic liquids such as acetone, they have low scratch resistance, and they have limited service temperatures (i.e., below the glass transition temperature, T_g, of 150°C).

As an alternative fabrication method for PC parts, polymer powder compaction—based on powder metallurgy (PM)—has thus been attempted.[2–5] PM is an established industrial fabrication process (e.g., for production of automotive gears) in which a metal powder is placed in a die cavity. Compaction at ambient temperature is then used to compress the powder and produce a 'green compact.' The green compact is subsequently hot-sintered in a furnace (just below the melting temperature) to produce the final article in the desired shape. The earliest attempts at mimicking the PM process with polymers, however, were not particularly successful.[2] For example, articles produced via cold (i.e., ambient temperature) compaction of amorphous PC powder expanded and cracked when they were used above the T_g.[6]

In our work,[7] we have thus studied the feasibility of using hot powder compaction (HPC) to fabricate crystalline PC parts. The tool set required for HPC is similar to that for PM, but for the case of polymers, the die and punches must be heated (i.e., heat and pressure have to be applied simultaneously to the polymer powder to achieve proper consolidation).[8] Indeed, we have previously demonstrated that HPC can be used to convert highly crystalline polyethylene terephthalate (PET) powder into a crystalline PET part.[8] In addition, we were able to discharge the PET articles hot (i.e., at the compaction temperature) from the die. HPC of semicrystalline polymers may thus be a feasible process, but it has not yet been developed as a full-scale industrial fabrication method.

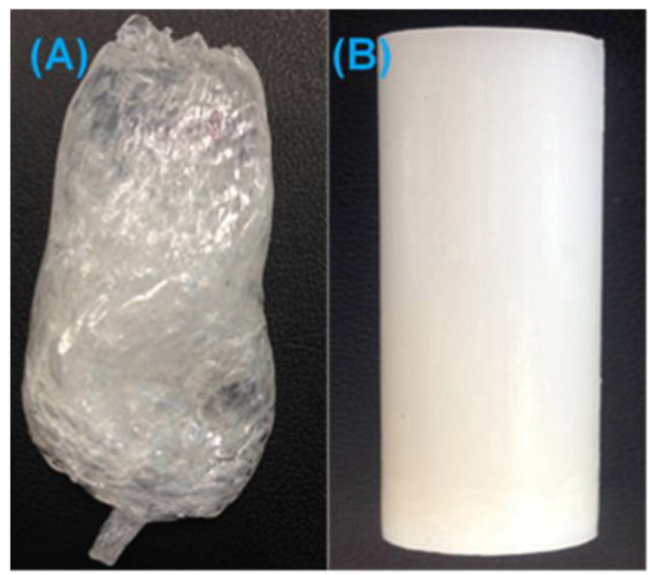

Figure 1. *(A) Amorphous polycarbonate (PC) extruded as an irregular blob. This sample was produced by hot powder compaction (HPC), i.e., above the glass transition temperature, in a rheometer and then discharged without cooling. (B) Crystalline PC powder that was optimally compacted at 210°C into a cylinder and discharged without cooling.*

If amorphous PC powder is subjected to HPC above the T_g and discharged without cooling, it extrudes—see Figure 1(A)—as an irregular viscous, molten blob. In our novel HPC approach for the fabrication of crystalline PC samples, it is necessary to first make a crystalline PC powder. Amorphous PC can be crystallized by immersing it in either

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acetone or super-critical carbon dioxide.[9] In our method we thus converted the amorphous PC powder to a crystallized powder by immersing it in acetone (at a crystallinity of about 20%). The powder particles before and after crystallization from the acetone are shown in Figure 2.

The onset of melting for our crystalline PC powder occurred at about 210°C. We thus conducted HPC of the powder at this temperature in a capillary rheometer. This device acts like a single-sided punch (piston for applying pressure) and die system (barrel), and the net shape that is produced is a cylinder (diameter of 10mm). The cylinder we produced from the crystalline PC powder and that we discharged at 210°C is shown in Figure 1(B), from which it can be seen that the sample was translucent and had a smooth finish. To our surprise, despite the low crystallinity, there was no sticking in the barrel and the surface did not exhibit any damage. A differential scanning calorimeter (DSC) analysis of our fabricated cylinder confirmed that its crystallinity (see Figure 3) was about the same as the initial powder. The cylinder thus represents the first time that a crystalline article with a defined shape has been made from PC.

We compared the properties of our crystalline PC articles (i.e., made via HPC) with injection-molded PC articles. For example, we find that the Rockwell M hardness of an HPC-produced crystalline PC sheet was 63.3, compared with 26.2 for an amorphous, injection-molded PC sheet. In addition, the HPC parts were immune to surface etching and stress cracking induced by acetone, and their dissolution time (in methylene chloride) was longer than for the injection-molded samples. The HPC items also did not change dimension or shape at high temperatures (i.e., above the T_g and up to the crystallization temperature). Furthermore, HPC of the crystalline PC powder at 180°C produced a similar cylinder. In this case, however, the consolidation was incomplete, as evidenced by the appearance of grain boundaries and voids (see Figure 4).

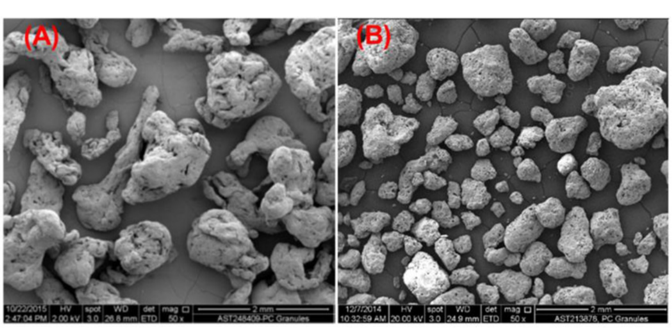

Figure 2. *Scanning electron microscope (SEM) images of (A) amorphous PC powder and (B) PC powder crystallized from an acetone solution. Scale bars mark 2mm.*

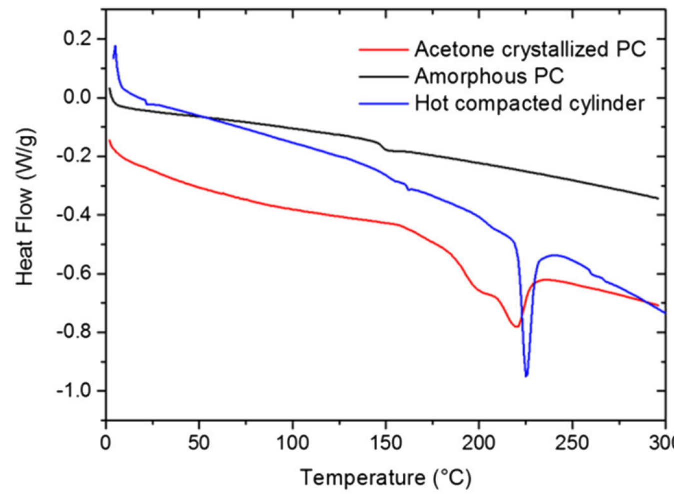

Figure 3. *Differential scanning calorimeter analysis results for amorphous PC powder, PC powder crystallized from an acetone solution, and the HPC-produced (at 210°C) PC cylinder.*

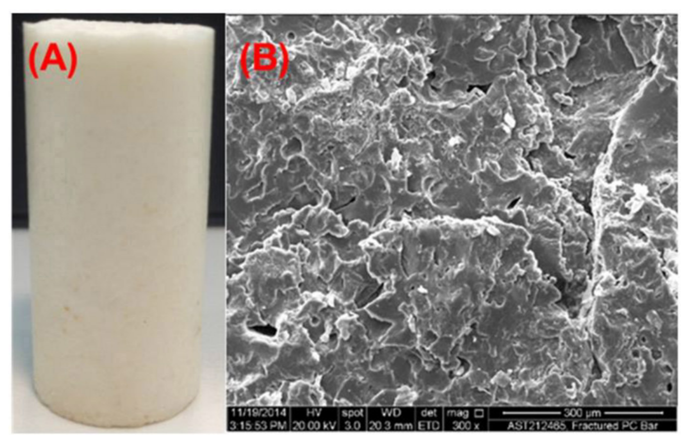

Figure 4. *(A) Cylinder of acetone-crystallized PC powder that was produced via HPC at 180°C and discharged without cooling. (B) SEM image of the same sample, in which voids and grain boundaries (caused by under-consolidation) can be seen. Scale bar marks 300µm.*

There are some problems associated with HPC compared with injection molding. For instance, there is some limitation to the complexity of the part that can be produced. That is, as much complexity as desired can be achieved in the plane of the part (the surface being compressed), but the complexity can only be increased three or four times in the thickness direction. Furthermore, HPC works best for

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semicrystalline rather than amorphous polymers, whereas injection molding is suitable for both types of material. Overall, however, the operational requirements for HPC of polymers are more favorable than for injection molding. For example, HPC can generally be conducted below the melting temperature of the polymer. In contrast, for injection molding, the material needs to be heated to about 30–50°C above its melting temperature. In addition, the part can be discharged at the compaction temperature in HPC and so no cooling of the mold is necessary. Powder compaction therefore represents an energy-saving approach. Moreover, no sprues and runners are required for HPC, and thus virtually no waste materials are produced. In cases where the polymerization produces a powder, the direct use of the reactor polymer is possible with HPC.

In summary, we have demonstrated that HPC is a viable fabrication process for semicrystalline polymer parts. Some process adaptions (i.e., temperature and pressure combinations) may be required, however, depending on the polymer. In addition, the required tools are the current limitation to full-scale development of this technique (i.e., PM tool sets are unsuitable for polymers because they are used for cold powder compaction). For HPC of polymers, however, the die and punches need to be heated and insulated, but these have yet to be developed. In our ongoing work we are thus looking for manufacturers to develop heated and insulated tooling with which we can produce delicate parts (such as gears) via hot powder compaction. In particular, the die and punches need to be carefully designed to minimize thermal gradients. With the right tooling in place, HPC can become a viable industrial fabrication method.

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