

High-rate Manufacturing of 3D Products with Nanostructured Surfaces

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ABSTRACT

Injection molding permits manufacturing of complex three-dimensional polymer products with nanostructured surfaces in less than 30 seconds. New work has explored the practical limits of feature size during injection molding. Surfaces with a range of nano and submicron-scale structures were molded from amorphous and semicrystalline thermoplastic polymers having a range of molecular weights, flow promoters and related additives, and loadings of nanoparticulate fillers. Replication of the surface features was correlated with the polymer chain length (molecular weight), additive mobility, and filler loading.

Key words: injection molding, nanostructured surfaces

1. INTRODUCTION

Nanostructured surfaces impart additional functionality to relatively thick polymer parts. These nanostructured surfaces impart new adhesive, frictional, wetting, self-cleaning, and other properties the parts. Injection molding enables high-rate manufacturing of these parts with nanostructured surfaces. As shown in Figure 1a, the main wall of the part is filled with polymer melt during the injection stage of the injection molding process. The nano-scale features on the part's surfaces, however, resist filling. These features typically are filled during the packing stage of the injection molding process (Figure 1b). High pressures (100-150 MPa) applied to the melt force the melt into the nanoscale features. Then the features and main wall of the part are solidified and the part is ejected from the mold (Figure 1c).

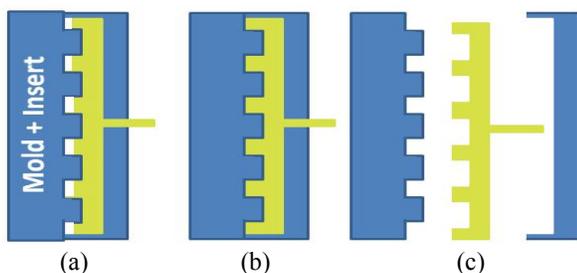


Figure 1. Injection molding of polymeric parts with nanostructured surfaces: (a) filling of the mold with polymer melt, (b) "packing" to complete filling of the features, and (c) part ejection after melt solidification. The typical cycle time is less than 30 seconds.

Molds for injection molding are machined steel plates, but most tooling inserts with the nanoscale features are fabricated using lithography and etching techniques. Insert substrates

include silicon wafers, silicone (e.g., polydimethylsiloxane), photoresist, polymer films like polyimide, and metals like steel. Features sizes depend on the exposure methods, with UV exposure, extreme UV exposures, and E-beam exposures providing features as small as 157 nm, 13 nm, and 10 nm, respectively. Often patterned silicon and photoresist substrates are electroformed to create more durable metal tooling. Submicrometer-sized features can etched directly into steel, but grain size affects the quality of the features. Polymer tooling has been produced by embossing a polymer film with an etched silicon master [1]. Polymer tooling often is coated with metal to enhance durability and cleanliness (Figure 2). Anti-stiction coatings added all tooling substrates improve filling and part ejection.

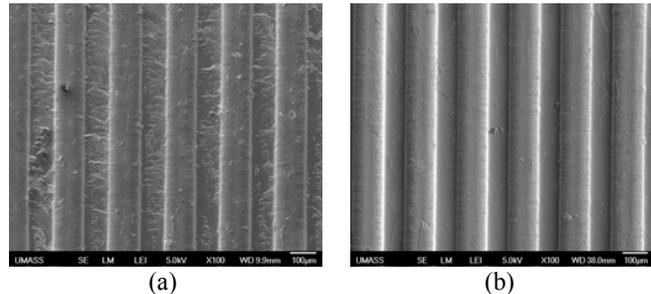


Figure 2. Polymer tooling insert with (a) no metal coating after 100 injection molding cycles and (b) with metal coating after 1000 injection molding cycles [2].

New work has explored the practical limits of feature size during injection molding. Surfaces with a range of nano and submicron-scale structures were molded from amorphous and semicrystalline thermoplastic polymers having a range of molecular weights, flow promoters and related additives, and loadings of nanoparticulate fillers. This work examined the effects of tooling design, material properties, and processing on the replication surfaces with nano and submicron-scale features.

2. EFFECT OF TOOLING DESIGN

The design of the tooling inserts affects replication of the nanostructured surfaces. As shown in Figure 3, features created with negative tooling do not always replicate as well as those created with positive tooling [3]. Polymer melts are not easily forced into the depressions in the surface of the negative tooling. This poorer replication is not associated with the trapping of air in the depressions. Most tools are vacuum vented, which removes the air before melt is injected into the mold. As illustrated in Figure 4, depth ratios are similar with and without vacuum venting; vacuum venting only improves

the sharpness of the molded features [4]. The replication of negative tooling depends on the temperature of the melt, the temperature of the mold surface, and the pressure applied to the melt. Greater pressure is required to fill smaller features. Higher temperatures, which slow solidification, also enhance replication. Feature spacing also affects filling, with spacing-to-feature size ratios of 1:1 providing the best replication [5]. With narrower and wider spacing of the negative features in the tooling, insufficient filling pressure and non-uniform heat transfer, respectively, adversely affect feature replication [5].

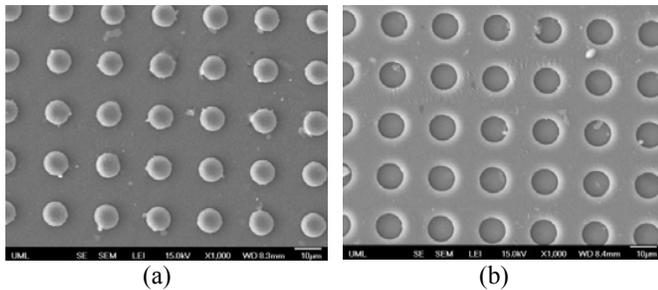


Figure 3. Copolyester block copolymer features injection molded from electroformed nickel tooling with (a) negative and (b) positive features [6].

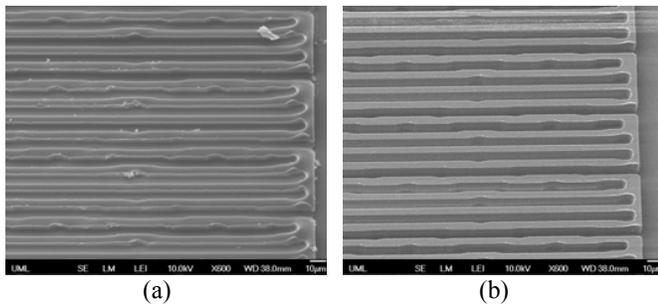


Figure 4. Polystyrene features injection molded (a) without vacuum venting and (b) with vacuum venting [4].

In contrast, polymer melts can flow around the projections in the surface of positive tooling. The positive tooling features, however, can block flow of the polymer melt. For example, with 17, 40, and 84- μm -wide-channels, channels with near perfect depth ratios of 0.99 were obtained when the positive tooling features were aligned in the direction of polymer flow or had an angle opened in the direction of flow [5]. Significantly poorer replication of the channel depth occurred when the tooling projections were aligned perpendicular to the flow front or when the channel projections had no angle opened to the oncoming flow front [7].

These effects become more pronounced as the tooling features become smaller and higher or deeper. As shown in Figure 5, the depth ratio - i.e., the ratio of the feature height in the part to the feature depth in the negative tooling - decreased with increasing tooling aspect ratio. Since most tooling inserts fabricated using lithographic techniques have a constant depth, the feature width or diameter is varied to produce features with variable aspect ratios (AR) - i.e., the ratio of the feature depth to the feature width or diameter. In Figure 5, near complete

replication of the 900-nm-wide trenches was achieved because these features were relatively shallow (AR \sim 0.30:1). In contrast, the 100-nm-wide features with aspect ratios of 1.25:1 showed depth ratios of about 0.10.

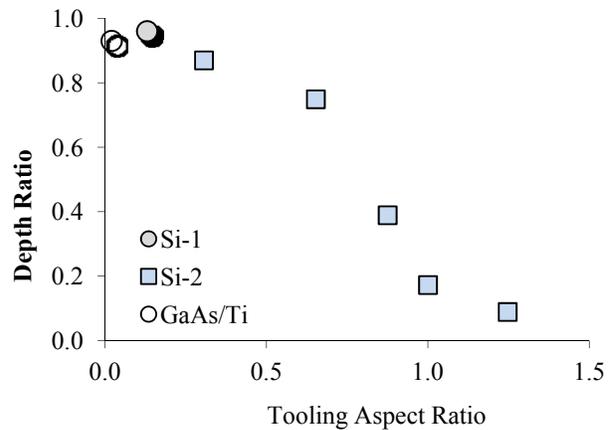


Figure 5. The effect of tooling aspect ratio on the depth ratios achieved in polycarbonate features injection molded from silicon (Si-1 and Si-2) and titanium-coated gallium arsenide (GaAs/Ti) tooling inserts.

When melt can flow directly into the features, filling occurs during the injection stage. Most melt, however, does not flow directly into the tooling features because this design leaves an undesirable gate vestige amid the molded features. Instead, melt typically flows across the features and fills the main wall of the part. The melt hesitates at the features - i.e., it stops flowing into the features - during filling. The hesitation allows cooling of the melt front and creates the whitish caps on the features (shown in Figure 6). This cooler melt must be forced into the features by the high pressures of the packing stage. The degree of hesitation and cooling increase as the size of the feature decreases. As a result, the filling smaller features requires melt high pressures.

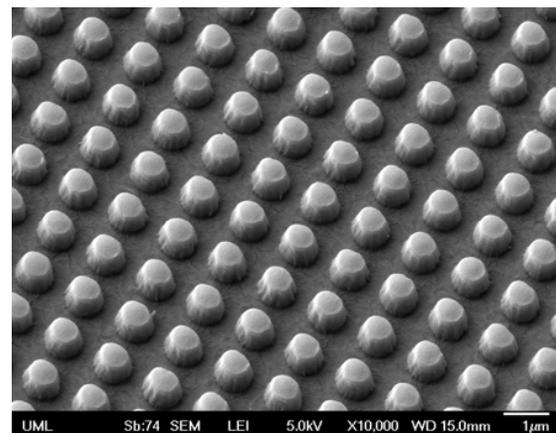


Figure 6. Replication of 1- μm -diameter negative tooling features by indirect flow of the polymer melt. Hesitation occurred with indirect (impingement) flow, creating the whitish caps on the features [8].

Feature replication can be improved by controlling the heat transfer through the tooling inserts. Rapid cooling of the tooling surface - and solidification of the melt at the surface - prevents complete replication of features. When nickel tooling inserts (which have a thermal conductivity of ~91 W/m-K) are in direct contact with the water-cooled steel mold, the melt in the features solidifies within 1 second. This rapid cooling produces features with low depth ratios and poor edge definition. There are three basic strategies for overcoming this problem: (1) increasing mold temperature, (2) insulating the tooling insert from the water-cooled mold, and (3) varying the mold temperature during the molding cycle.

Increasing the temperature of the mold slows the cooling, allowing the melt to solidify more slowly. This slower solidification provides better feature replication. Increases in mold temperature, however, are limited by the depression of the polymer's glass transition temperature within 20-nm of the mold surface. With higher mold temperatures, this melt does not solidify and is dragged along the features' surfaces during part ejection. As shown in Figure 7, this melt is detrimental to feature definition. During injection molding trials with several amorphous polymers (e.g., polymethylmethacrylate, polycarbonate, polystyrene, and cyclic olefin copolymer) [9], the critical mold temperature, T^* , was at least 15°C below the polymer's bulk glass transition temperature, T_g (Table 1). To eliminate the effects associated with the layer of melt at the tooling surface, mold temperatures were set at or below T^* .

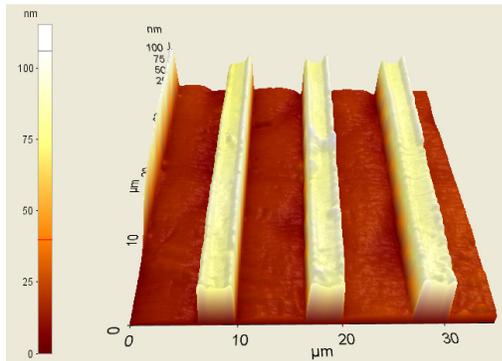


Figure 7. Still-molten polycarbonate at the mold surface is dragged along the feature surfaces during part ejection. This melt reduces the sharpness of the features' edges.

Material	T^* , °C	T_g , °C	T^*-T_g , °C
COP	65	80	15
PS	80	97	17
PMMA	80	107	27
O-PC	---	144	---

Table 1. Critical Mold Temperature for Selected Polymers [9]

Retarding heat transfer by insulating tooling features from the water-cooled mold also slows cooling and increases the melt solidification time. As shown in Figure 8, inserting a 600- μ m-thick polymer sheet between the tooling insert and the

mold wall increased the solidification time from 1 second to 14 seconds. With smaller and higher aspect ratio features, longer solidification times improve the depth ratios and provide significant improvements in definition of the feature edges. Similar insulating effects occur when using polymer-based tooling inserts. The polymer substrate retards heat transfer and the metal coating on the polymer tooling insert is too thin to affect the solidification time.

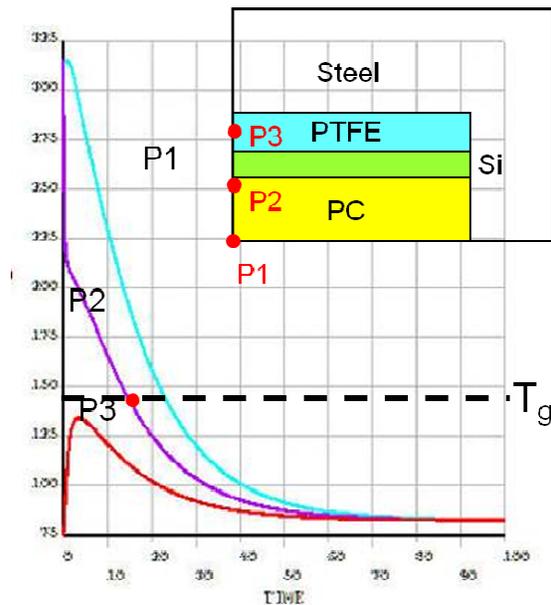


Figure 8. Inserting a 600- μ m-thick polymer sheet between the tooling insert and the mold wall increased the solidification time at the polymer surface (P2) from 1 second to 14 seconds [10].

Filling the features at very high mold temperatures and then rapidly cooling the melt also improves feature replication. The melt remains hotter during the injection and packing stages. The rapid cooling quickly solidifies the features and reduces cycle time. Filling at high temperatures is achieved by (1) temporarily turning off the cooling water, (2) using two sets of water lines with two different temperatures, and (3) heating the mold surface using induction, electrical heater cartridges, and infrared radiation.

Overall, controlling heat transfer becomes more critical as the features become smaller and have higher aspect ratios.

3. EFFECT OF MATERIALS

Amorphous thermoplastics, including polystyrene, polymethylmethacrylate, polycarbonate, and cyclic olefin polymers (COC, COP) solidify gradually and exhibit similar shrinkage in the microfeatures and the macroscale parts. Semicrystalline thermoplastics, however, solidify more rapidly, making micro and nanofeature replication more difficult. The surface features also show shrinkage that is unpredictable and usually much greater than observed in macroscale parts. With amorphous polymers, replication of feature depths or heights

depends on melt viscosity, whereas replication of feature details, like the bottoms of microfluidic channels, improves with longer solidification times [11].

With amorphous and semi-crystalline polymers, lower viscosity melts provide better replication. The polymer chains, however, "assemble" along the mold wall and significantly affect filling for features narrower than 10 μm [12]. The assembled polymer chains also increase the melt viscosity at the mold wall compared to the bulk viscosity of the melt, η_b [12]. The viscosity, η , is related to the polymer's radius of gyration, R_g , using

$$\eta = \eta_b \left[1 + \xi \left(\frac{R_g}{D} \right)^2 \right] \quad (1)$$

where D is an external characteristic length (e.g., the feature width) and ξ is an empirical non-dimensional constant. For very narrow (140-nm-wide) features, Srirajpinyo [9] showed that depth ratios decreased with increasing radius of gyration of the polymer (Table 2). Therefore, the overall size of the polymer seems to limit feature replication.

Polymer	M_w , g/mol	R_g , nm	η_b , Pa-s	DR, %
PMMA	61,340	3.9	203	91
O-PC	22,050	6.5	61	80
PS	123,600	14	333	62

Table 2. Effect of Polymer Size on Replication [9]

With block copolymer thermoplastic elastomers, feature replication, especially depth ratio are influenced by hard and soft segment content in the elastomer, and not by viscosity as occurs with thermoplastics [13]. Feature definition (i.e., the shape of the molded feature relative to the feature shape in the tooling) also seems to depend on hard segment content of the elastomers. Softer thermoplastic elastomers - i.e., systems with lower hard segment content - have exhibited better feature definition, but have required lower melt and mold temperatures for injection molding [13-14]. In contrast, thermoplastic vulcanizates, which as dynamically vulcanized blends of rubbers like EPDM and thermoplastics such as polypropylene, contain rubber domains with diameters of about 3 μm . Although deformable, these domains seem to hinder replication of features smaller than 10 μm [15].

Low molecular weight species, such as additives and residual monomer, limit replication, particularly for smaller sized features. The high shears stresses during injection molding force these low molecular weight species to the interface between the melt and mold wall. They deposit on the mold wall and create defects in subsequent parts.

Replication in thermoplastics improves with high melt temperatures, high mold temperatures, and high pack pressures. The high temperatures, however, increase shrinkage, particularly in semi-crystalline polymers. Higher pressures also reduce polymer mobility, and thus, increase melt viscosity.

This effect seems to limit replication in smaller features.

CONCLUSIONS

Replication of the nanostructured surfaces appears to be limited by polymer chain length (molecular weight), the mobility of low molecular weight species like additives, and by increases in melt viscosity associated with high melt pressures and "assembly" of polymer chains along the mold wall. Tooling design also influences this replication.

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