Packing parameters effect on injection molding of polypropylene nanostructured surfaces

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PACKING PARAMETERS EFFECT ON INJECTION MOLDING OF POLYPROPYLENE NANOSTRUCTURED SURFACES

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Abstract

In today´s industry, applications involving surface patterning of sub-µm to nanometer scale structures have shown a high growth potential. To investigate the injection molding capability of replicating sub-µm surface texture on a large scale area, a 30x80 mm^2 tool insert with surface structures having a diameter of 500 nm was employed. The tool insert surface was produced using chemical-based-batch techniques such aluminum anodization and nickel electroplating. During the injection molding process, polypropylene (PP) was employed as material and packing phase parameters (packing time, packing pressure) were investigated. The replicated surface topographies were quantitatively characterized by atomic force microscopy using specific three-dimensional surface parameters and qualitatively inspected by scanning electron microscopy. Results showed that the degree of replication from the tool to the polymer part was mainly influenced by packing pressure level and distance from the gate.

Introduction

Replication technologies are the most widely used techniques when producing micro- and nano-structured surface textures [1]. The establishment of periodic nanometer features and the fabrication of nanoscale geometries is challenging the development of nanotechnology-based products such as high density data storage supports, micro/nanofluidic systems for Lab-on-a-chip (LoC) applications (e.g. for sequencing of genomes, high throughput screening, point of care diagnostics and cell-culturing), and surface calibration standards in the sub-nanometer dimensional scale range. Moreover, nanoscale patterning can influence the physical property of a surface such as wetting behavior, hydrophobicity, hydrophilicity, self-cleaning, transparency, etc [2-4]. Proposed techniques for the preparation of three dimensional nanoscale features by means of rapid prototyping methods such as PDMS casting, laser milling, micro machining [5-7] or adoption of clean room based silicon processes [8] as e-bean lithography and nano imprinting lithography are often employed [9,10]. These methods suffer from serious drawbacks when it comes to cost-effective industrial application especially when larger areas than a few square cm^2 have to be fabricated. On the other hand, nano structuring of polymer materials using the injection molding process would result in high throughput and cost effective manufacturing due to short cycle times. However, the employment of the injection molding process involves a wide range of polymers with different characteristics enabling different replication qualities and therefore optimization experiments should be carried out to ensure a high degree of replication. The comparison of the structure between the mold geometry and the final workpiece geometry is used as a measure of the replication quality. Typical challenges for accurate comparisons and optimization are the definition of suitable measurands and the precise relocation of the measuring points on different samples.

The potential of obtaining mass-production of multi-scale (i.e. from macro- down to sub-µm scale) large polymer areas by using injection molding and large-area nano structured tools is enormous [11]. To evaluate critical factors affecting replication quality of molded sub-µm surface topographies on a large scale, a 30x80 mm^2 nickel tool produced by aluminum anodization and subsequent nickel electroplating was employed. The effects of packing phase conditions (packing pressure, packing time) combined with the distance from the gate were investigated using atomic force microscopy (AFM) and scanning electron microscopy (SEM). A specific relocation procedure was developed to ensure high measurement repeatability and reliable replication assessment.

Nano structuring of mould inserts

Preparation of nanometer-sized structures to pattern the mold used for polymer replications was made via anodizing of an aluminum (Al) substrate. The anodic porous alumina fabricated by the anodic oxidation of aluminum created a self-organized structure similar to a nanohole array. Prior the anodising process, the 99.5% Al substrate was treated by mechanical and electrochemical polishing to achieve a more attractive oxide film on the sample surface. Between these two surface preparation steps, the aluminum substrates were annealed below the melting point (at 500ºC for three hours) to obtain a larger grain size and to eliminate residual stresses from previous manufacturing operations. The anodizing process was

carried out in a phosphoric acid electrolyte with constant temperature of 0°C for 24 h at 195 V. The fabricated compact alumina pore structure was then dissolved in etchant solutions containing H_3PO_4 (35 ml/liter) + CrO_3(20g/liter) at 85°C which does not attack the Al. A first nickel seed layer was deposited by physical vapor deposition (PVD) in order to enhance the corrosion resistance of the obtained nano structures and to promote the deposition of a thick nickel layer. The nickel electroplating process parameters were optimized to avoid potential problems such as high surface roughness, pitting, poor adhesion and high internal residual stresses. After completion of the nickel electroplating step, the Al substrate was dissolved by chemical etching (60g/l of NaOH at 65°C for 24h) and the nickel master nano structured pattern is revealed.

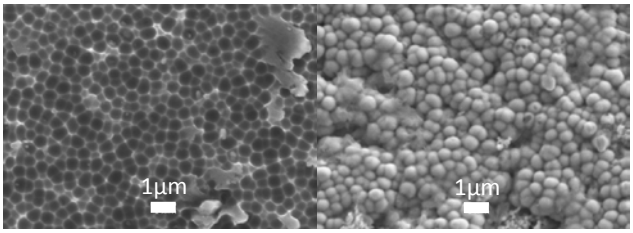

Figure 1: SEM images of replications steps. Left: Al substrate after oxide layer dissolution Right: electroplated nickel insert surface.

Experimental nano injection molding

Nano-structured polymer replicas over an area of 30x80 mm^2 were produced by injection molding. To evaluate the influence of process parameters on the replication of nano scale structured surface, a statistically designed set of experiments was carried out. The investigation aimed at characterizing the replication quality from the master geometry to the thermoplastic polypropylene substrate and to understand the filling behavior of the melt along the entire test sample length. Two different process parameters were varied in order to determine their influence on the surface replication:

- Packing pressure: P(pack);
- Packing time: t(pack).

Surface characterization was made at four different distances from the gate position. A full-factorial design has been carried out performing 2^2=4 molding experiments (varying packing pressure and packing time between two levels). Maximum and minimum values of the two selected process parameters were taken into account due to machine capability and process feasibility.
In particular:

- The minimum level of packing time (2 sec) was the minimum time that allowed effective shrinkage compensation and dimensional stability.
- The maximum level of packing time (4.5sec) was set taking into account optimized stable weight of the samples as well as no flash in the part and overfilling of the mold cavity.
- Packing pressure was set as 15% and 40% of the maximum injection pressure measured by the machine.

Process parameters particularly related to the filling phase were set considering machine capability, material physical properties and process feasibility. Melt temperature was chosen as a balanced value to avoid material degradation, and premature solidification during the filling of the cavity. The mold temperature was set in order to allow successful part demolding, complete cavity and short cycle time. Finally, high injection speed was selected to enhance replication and it was limited by the capability of the machine.

Table 1: Process parameters

Process parameters	Values
Melt Temperature [^oC]	208
Mold Temperature [^oC]	38
Injection Speed [mm/s]	350
Maximum Injection Pressure [MPa]	180

Polypropylene (PP-INSPIRE-H712-52RNA) was used as polymer substrate. PP was selected for its good replication capability even at relatively low mold temperatures. The injection molding process was carried out using Ferromatik K60 machine with a reciprocating screw of 35 mm diameter.

Measurement strategy and results

Critical dimensions of the molded replicas are in the 100 nm-range; it is therefore necessary to have an accurate estimation of the replication quality, preferably with a single-digit nanometer resolution. In most cases, the degree of replication assessment is focused mainly on the specific ratios between width and height of features. Real surfaces, instead, develop by nature in the three dimensional space. 3D description and analysis of surfaces represent a more realistic approach to characterize and visualize 3D data, and this can be achieved at sub-µm scale by 3D AFM measurements and subsequent image processing. It is also important to provide information about the geometrical form of micro structure elements and their spatial distribution in order to understand the surface phenomena.

In order to comply with these requirements, the surface characterization was based on the evaluation of two 3D surface amplitude parameters:

- Surface roughness Sa defined as the arithmetic mean of the absolute of the height within the defined evaluation area (1) [12];

- Hybrid parameter Sdr describing both amplitude and spacing properties of the surface defined as the ratio of the increment of the interfacial area of the scale limited surface within the definition area [12]. This parameter can be defined as the percentage of additional area contributed by the textured surface compared to an ideal plane equal in size to the measurement region (2).

$$S_a = \frac{1}{MN}\sum_{K=0}^{M-1}\sum_{l=0}^{N=1}\left|z(x_k, y_l)\right| \qquad (1)$$

$$S_{dr} = \frac{\left(\sum_{K=0}^{M-2}\sum_{l=0}^{N-2} A_{kl}\right) - (M-1)(N-1)\delta x\delta y}{(M-1)(N-1)\delta x\delta y} 100\% \qquad (2)$$

Atomic force microscope (AFM) has been employed to scan across the surfaces using an open loop instrument having a measuring volume of 200 µm x 200 µm x 10 µm. Surfaces have been measured in contact scanning mode. A pilot study was performed in order achieve optimal set up, considering influencing factors as scan speed and force finally set at 15 µm/s 10 nN respectively. The final measuring set up considered possible implementation in a production environment where trade-off between accuracy, precision of measuring results and especially scanning time are very relevant [13]. Measuring areas of 15 µm x 15 µm with 2048 x 512 pixels in the fast scanning directions (i.e. X) and slow scanning direction (i.e. Y) respectively were scanned with the calibrated instrument on both nickel master and polymer replicas. As far as the relocation was concerned, specific procedures were applied to ensure that the same corresponding areas were measured on different samples. Accurate relocation was ensured by the sample stage (responsible of keeping the sample in place during each measurement) and the linear encoder mounted on the X-axis of the coordinate measuring machine stage on which the AFM is mounted [14]. The uniform scanning signals of the linear incremental encoder enabled measuring steps with a resolution of 1 nm. Once the movable stage was aligned with the center of the rectangular sample geometry the Y coordinate of the coordinate measuring machine was locked. Only the Z-axis (allowing the AFM probe to approach the different surfaces) and the X-axis (allowing measurement repositioning over the different surfaces) were moved.

Measurement reproducibility based on the experimental set-up was tested. The nickel master was measured and then removed from the movable stage. After 24 hours, the nickel master was mounted again in the movable stage. The repeated surface measurement proved the effectiveness of the applied relocation procedure. Measurement analysis made with scanning probe image processor software (SPIP) [15] showed the same image reconstruction for the two different measurements (see Figure 2). Standard deviation calculated between Sa average values of three repeated measurements at the same spot on the two different days was equal to 0.4 nm.

The AFM was calibrated with optimized setting parameters and subsequently employed to perform 3 measurements on both nickel master and PP replicas at each spot (see areas 1, 2, 3 and 4 in Figure 3), representing different distances from the gate. Average of both Sa and Sdr values are reported in Table 2, 3, 4 and 5.

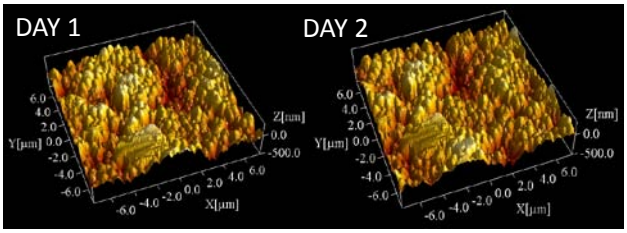

Figure 2: Same evaluated area scanned by the AFM in two different days.

An investigation using scanning electron microscopy (SEM) was performed (see Figure 8), in order to qualitatively assess the replication accuracy. SEM images were aligned with the same criteria used for the AFM measurements. Reference lines close to the gate area were used as origin for the SEM software to realign and move the scanning position to the desired evaluation areas.

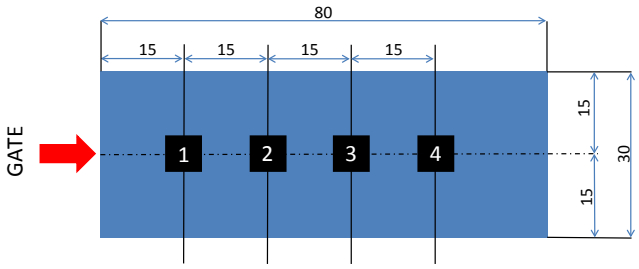

Figure 3: Layout of the measuring strategy performed on both nickel master and polymer replicas.

Statistical analysis and discussion

The statistical analysis of the measuring results was performed by evaluating Sa and Sdr 3D surface amplitude parameters.

Statistical analysis results are shown in the format of the main effects plot for the two mentioned output (see Figure 4 and 5).

It is possible to observe that higher packing pressure improves the replication of the structured surface with mean value of Sa similar to the one measured on the nickel insert surface. The polymer melt, due to the high injection speed, is able to reach the end of the mold before freezing, whereas material shrinkage in the middle area of

the sample determines poor replication quality. Mean Sa value are also comparable to the one measured on the insert at the gate position being this the last part of the sample to solidify and where pressure is maintained higher for a longer time. Main effects plot of the Sdr output show an influence of the different packing time on the textured surface replicated on the polymer substrate. The material shows the tendency to deform during ejection due to incomplete cooling (increasing the percentage of additional area from an ideal flat surface) on the master surface for short packing time.

In addition, the main effects plots of standard deviations (Figure 6 and 7) show the measurements reliability over the whole design of experiments, with Sa and Sdr standard deviations in the range of 0.2-11 % and 2-20% respectively.

Table 2:Sa measurements values of both nickel stamper and polymers replicas at different packing time and same packing pressure of 23 Mpa.

	Nickel insert Sa [nm]	**PP Sa [nm]**	
		t(pack) = 2.0 s	**t(pack) =4.5 s**
		P(pack) = 23 Mpa	**P(pack) = 23 Mpa**
Position 1	95.0	108.1	46.3
Position 2	79.9	39.1	80.2
Position 3	89.6	55.5	56.9
Position 4	116.7	84.2	104.6

Table 3: Sa measurements values of both nickel stamper and polymers replicas at different packing time and same packing pressure of 57 Mpa.

	Nickel insert Sa [nm]	**PP Sa [nm]**	
		t(pack) = 2.0 s	**t(pack) =4.5 s**
		P(pack) = 57 Mpa	**P(pack) = 57 Mpa**
Position 1	95.0	121.3	110.7
Position 2	79.9	101.0	75.9
Position 3	89.6	106.5	82.3
Position 4	116.7	106.0	103.9

Table 4: Sdr measurements values of both nickel stamper and polymers replicas at different packing time and same packing pressure of 23 Mpa.

	Nickel insert Sa [nm]	**PP Sdr [%]**	
		t(pack) = 2.0 s	**t(pack) =4.5 s**
		P(pack) = 23 Mpa	**P(pack) = 23 Mpa**
Position 1	33.1	10.3	0.7
Position 2	13.9	2.1	3.7
Position 3	24.2	4.5	2.6
Position 4	14.4	10.8	7.6

Table 5: Sdr measurements values of both nickel stamper and polymers replicas at different packing time and same packing pressure of 57 Mpa.

	Nickel insert Sa [nm]	**PP Sdr [%]**	
		t(pack) = 2.0 s	**t(pack) =4.5 s**
		P(pack) = 57 Mpa	**P(pack) = 57 Mpa**
Position 1	33.1	19.6	7.6
Position 2	13.9	9.3	7.4
Position 3	24.2	8.1	6.5
Position 4	14.4	6.0	7.8

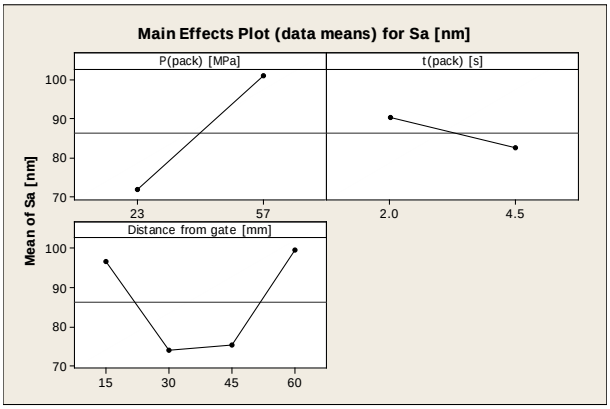

Figure 4: Main effects plot of Sa.

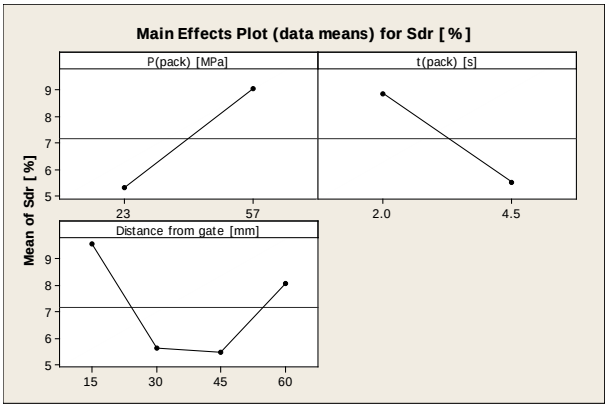

Figure 5: Main effects plot of Sdr.

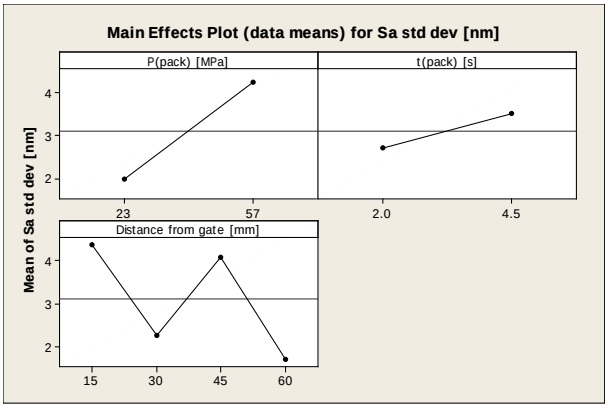

Figure 6: Main effects plot of Sa standard deviation.

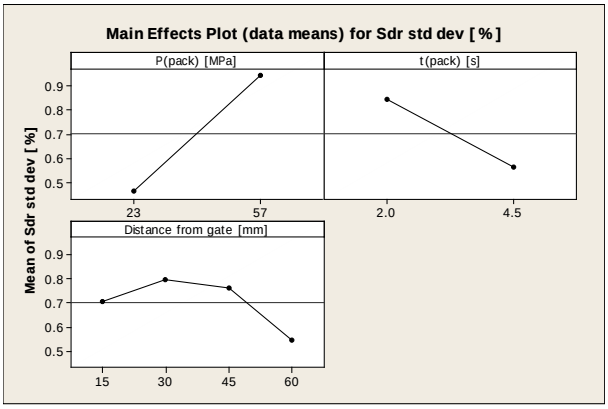

Figure 7: Main effects plot of Sdr standard deviation.

Conclusions

Replications of nano scale textured nickel surface on PP substrates produced by injection molding were analyzed. Tools were fabricated by applying a bottom-up batch-chemical process based on the creation of sub-µm structures by aluminum anodization and subsequent nickel electroforming. Replication qualities of polymer surfaces were characterized by analyzing amplitude (Sa) and hybrid (Sdr) 3D surface parameters. For this purpose an AFM was used. Tool and polymer surfaces were inspected by high resolution imaging obtained from scanning electron microscopy. Statistical data analysis was used to investigate how process conditions influence the measured variation of the characterized polymer nano structured replicas. Factors having a significant effect on the replication amplitude have been found to be the packing pressure and the distance from the gate location for both Sa and Sdr. Minor effect of packing time was observed for the amplitude parameter Sa which showed a smaller effect than the spatial parameter Sdr.

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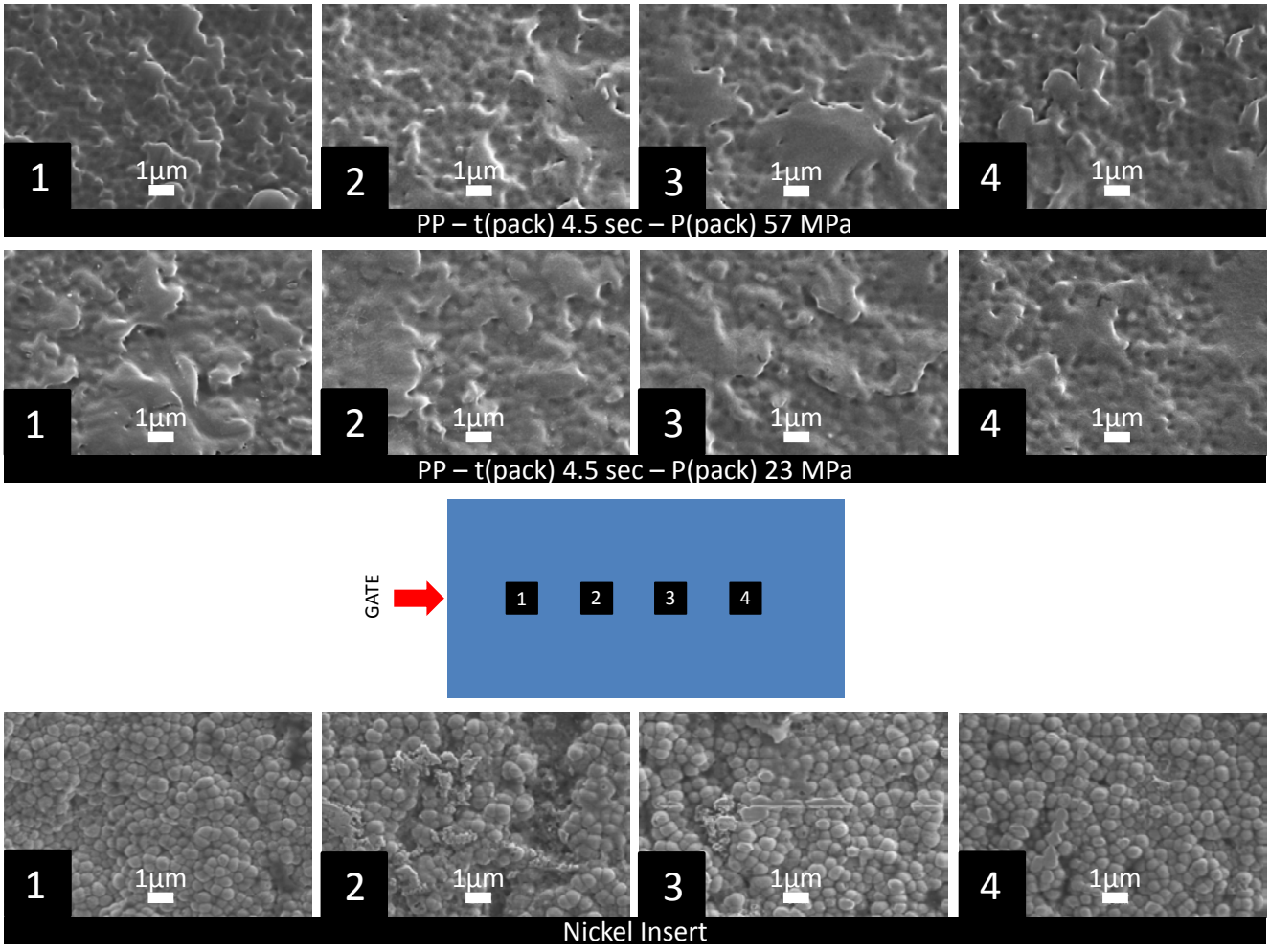

Figure 8: SEM images of nickel surface texture (bottom) and PP injection molded polymer substrates at same packing time of 4.5 sec and different packing pressure (top). Numbers indicate positions of the taken images. Reference points coordinates correspond to those performed in the measurement strategy, (see Figure 3).