Defect-free replication of polymeric micro structures using novel Ni-PTFE nanocomposite moulds

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KEYWORDS: Nanocomposite mould, defect-free production, micro injection moulding, demoulding force, PTFE nanoparticle

Demoulding defects like pile up plastic deformation and damage has constrained the quality of mass production of plastic micro products, such as microfluidic chips and optical gratings. A high-performance Ni-PTFE nanocomposite mould was fabricated for defects-free demoulding along with quantitative measurement of demoudling force. The Ni-PTFE nanocomposite mould performance was compared with pure Ni mould in terms of demoulding feature integrity, demoulding force, friction, wear and surface adhesion. Results consistently show that Ni-PTFE nanocomposite mould give profound surface integrity of microstructures with significant reduction of demoulding forces under various experiment conditions; the composite mould also displays 38% reduction in friction coefficient, while 5 times extended tool life, much less tool wear and adhesion compared to pure Ni mould. These micro injection moulding processes validated the self-lubrication properties of the Ni-PTFE nanocomposite mould for defect-free production of polymeric micro surface structures.

1. Introduction

Microfluidic chips and micro/nano structured surfaces are ubiquitous in diagnostic, medical and optical applications. Commonly, micro/nano structured nickel moulds by electroforming processes are used to injection mould plastic microfluidic chips, owing to its high precision and high surface finish [1]. However, challenges remain for existing nickel moulds: demoulding distortion & damage of polymer surface structure and limited tool life [2, 3]. When subjected to high pressure and high temperature in micro injection moulding, polymeric micro structure suffers from broken and distorted features due to high adhesion and shrinkage induced friction between mould and polymer interface [4, 5]. This eventually cause problems of microfluidic chip bonding delamination, functional failure of surface, and poor imaging quality for optical use. The associated production yield is reduced with increase of the unit part cost.

We developed permanent self-lubricating long-life micro moulds based on nickel nanocomposites that is reinforced by incorporating WS_2, MoS_2, graphene oxide, and PTFE nanoparticles into the nickel matrix via micro electroforming [6]. Among these nanocomposite formulations, Ni-PTFE demonstrated low friction and enhanced wear resistance, with ease of electrolyte formulation. However, the performance of Ni-PTFE nanocomposite mould when applied in the injection moulding remains unexplored. The demoulding performance, including demoulding force and feature integrity, is critical for the mass production of the polymeric micro devices. In this paper, both Ni and Ni-PTFE mould inserts were fabricated and applied in the micro injection moulding. A precision mould with capability of measurement of demoulding force as well as mould cavity pressure and temperature were developed to quantitively study the demoulding behaviour for nanocomposite mould. A polymer pin was used in the pin-on-disk test to reveal the polymer-mould interaction and examine the mould tool's wear resistance against the polymer material. To further reveal the adhesion between polymer and mould, surface wettability of hot polymer melts on the nanocomposite mould is also characterized.

Our research validates the effectiveness of PTFE nanomaterial composited mould to significantly improve the integrity of surface micro structures. The lubricating mechanism is revealed via in-line demoulding force monitoring under various process conditions, wear test and contact angle measurement. We have established robust correlation between wear test performance and tool life. Finally, this facile and cost-effective method enables creating a reusable, high-resolution mould with low surface energy, ensuring defects-free demolding for the mass production of polymer parts.

2. Experiments

2.1 Injection mould insert fabrication and demoulding monitoring

For characterization of microstructure replication precision and demoulding defects, the star pattern with continuous change of aspect ratio was chosen, where the feature height is 100 μm, and width ranges from 50 µm to 110 µm with aspect ratio covering most of features for microfluidic devices (Figure 1). The fabrication of both the Ni mould insert and Ni-PTFE mould insert involved five procedures as detailed in our previous study [7]. Then the Ni and Ni-PTFE inserts were assembled into an injection moulding for injection moulding.

To characterize the demoulding force, a load cell to measure the ejection force is embedded behind the ejector plate to characterize the demoulding force, which includes the forces required to eject the macro-substrate and micro structures, where micro structure dominate the demoulding forces. The pressure of the mould cavity is also measured to with mould cavity temperature/pressure sensor to indicate compression applied by polymer melts during moulding process to reflects the potential adhesion between polymer and mould. This is related to mechanical interlocking and chemical reactions at interface. All data is collected with Kistler COMO system.

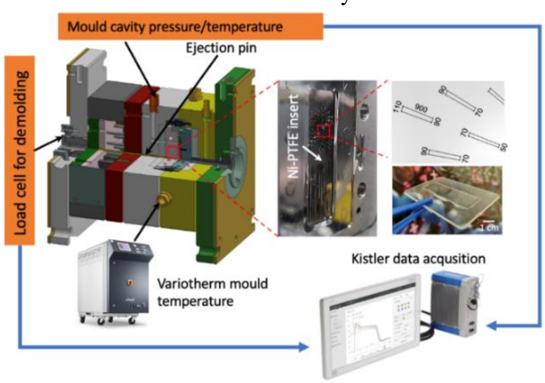

Fig. 1 Injection moulding system with mould designed with load cell for demoulding forces and cavity pressure/temperature measurement, where the Ni-PTFE insert is embedded into motion half of the mould.

2.2 Injection moulding and sample characterization

Both amorphous and semicrystalline polymers were chosen to validate the performance of Ni-PTFE nanocomposite mould, including Polypropylene (PP, Sabic, 83MF10), Cyclic Olefin Copolymer (COC, TOPAS, 8007), and Polymethyl methacrylate (PMMA, ALTUGLAS VSUVT). The glass transition temperatures (T_g) for COC and PMMA are 78 °C and 95 °C, respectively, while the heat deflection temperature for PP is 85 °C. This study specifically investigates the influence of mould temperature and injection velocity on demoulding behavior, as they determine the pressure applied when hot polymer is injected into mould, affecting adhesion between polymer and mould insert (Table 1). Additionally, the variotherm system is applied for COC and PMMA, which is often used to assist the filling of micron or submicron size features [7], where the mould temperature is increased above the T_g of polymer during filling of the mould cavity and subsequently decreased below the T_g of the polymer to ensure the solidification of the polymer. Ten samples were collected to ensure consistency.

Table 1 Injection moulding parameters for three polymers.

Materials	Injection velocity (mm/s)	Mould temperature (°C)
COC	75	40, 50, 60, 70, *85/30
	75, 125, 175, 225	60
PP	75	40, 50, 60, 70
	75, 125, 175, 225	60
PMMA	75	50, 60, 70, 80, *100/40
	50, 75, 100	60

*(warm circuit/cold circuit temperatures in variotherm)

After injection moulding, the polymer parts and the mould inserts were examined using scanning electron microscope (SEM) (Hitachi Topdesk 4000) to scrutinize the structural integrity. Energy dispersive X-ray spectroscopy (EDS) was performed for the element analysis of the injection-moulded COC components. A polymer pin made of COC was used in a pin-on-disk test (ISC200PC) against moulds with a normal load of 1 N and sliding time of 10 minutes for friction and wear characterization. Polymer melt contact angle measurements were conducted using COC polymer melt at a temperature of 210 °C utilizing a drop shape analyzer (Krüss DAS100E) to characterize polymer-mould adhesion.

3. Results and discussion

3.1. Feature integrity and demoulding behaviour

In general, all polymer parts produced from Ni mould shows different levels of demoulding defects, whereas the polymer parts injection moulded from Ni-PTFE mould demonstrates intact structural integrity with good surface quality. With a mould temperature of 70 °C, PP component shows slight pile-up defects along the sidewall of the micro channels when produced from Ni mould, while the one from Ni-PTFE mould shows no defects (Figure 2). Such defects are not so obvious due to higher materials shrinkage from crystallization and less molecular interaction between PP and Ni, causing less damage, as the demoulding force is much smaller than amorphous polymer (Figure 5).

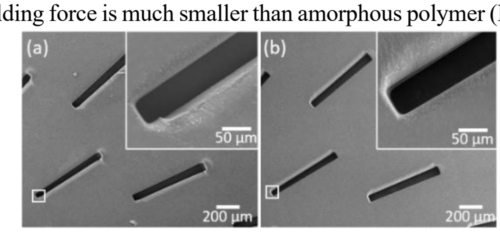

Fig. 2 Surface morphology of injection moulded PP from Ni mould (a) and from Ni-PTFE mould (b) with a mould temperature of 70°C.

COC produced from Ni mould showed sever feature damage at a corner at 70 °C, and this demoulding failure was more severe when variotherm system was applied, as a higher mould temperature (85 °C) was used, which can cause higher adhesion and is reflected by higher demoulding force (Figure 5a). Obviously, the COC components moulded from Ni-PTFE mould at both temperatures have micro features with sharp edges (Figures 3 b and d) without material piled up, where the demould force measured is significantly lower compared to that under pure Ni mould. The EDS result confirmed that no PTFE particles were adhered onto the injection moulded COC chips.

PMMA shows the similar behavior to COC, where severe friction and adhesion-induced damage were observed on the part surfaces produced from Ni mould. Specifically, with variotherm system, severe polymer pile-up and broken edges were found on the polymer structure. Pile-up is a plastic deformation, causing mainly by materials shrinkage induced friction and adhesion deformation. The breakage is attributing the brittle nature of PMMA itself. In comparison, when Ni-PTFE mould was applied, all PMMA components show well-defined micro structures with excellent surface quality without any pile-up and breakage, and the demoulding force is also well reduced (Figure 4).

Additionally, due to high adhesion force, solidified PMMA part was stuck into the micro structure of the pure Ni mould under the variotherm condition (Figure 4e). This demoulding failure can cause contamination to Ni mould, and reduce the production efficiency, as the injection moulding process must be terminated and the adhered PMMA has to be removed carefully. In conclusion, these results confirmed the profound performance of Ni-PTFE mould when applied for both amorphous and semicrystalline polymers.

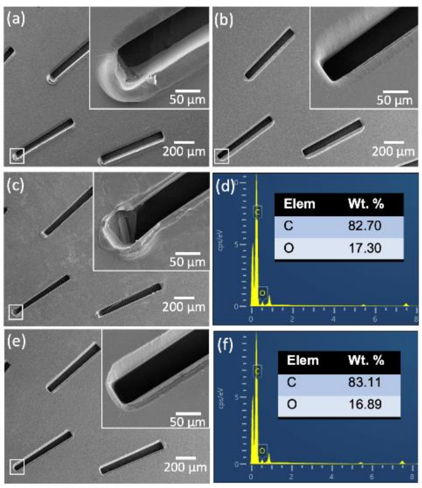

Fig. 3 Surface morphology of injection moulded COC from Ni mould with a mould temperature of 70°C (a), and from Ni-PTFE mould (b); with a mould temperature of 85/30°C from Ni mould (c) and Ni-PTFE mould (e); (d) and (f): the EDS analysis from image (c) and (e).

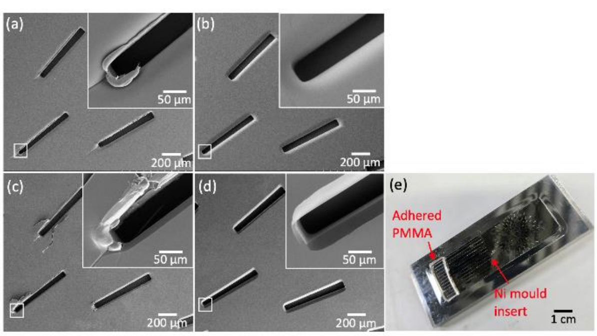

Fig. 4 Surface morphology of injection moulded PMMA from Ni mould with a mould temperature of 50°C (a), and from Ni-PTFE mould (b); with a mould temperature of 100/40°C from Ni mould (c) and Ni-PTFE mould (d); (e) image of PMMA adhered to pure Ni mould insert after demoulding at mould temperature of 100/40°C.

3.2. Demoulding force and process characteristics

The demoulding behaviour of polymer materials is well related to friction and adhesion between polymer-mould interface, where shrinkage induced localized pressure can cause normal pressure for high friction, while mechanical interlocking and chemical affinity/reaction induces adhesion. PP as a semicrystalline material has higher shrinkage rate and lower modulus and higher elongation, enables less tendency of damage. Compared to amorphous polymers, e.g. COC and PMMA, the cavity pressure is much lower, leading to less adhesion from process and less deformation from material properties. For PMMA and COC, obvious plastic deformation occurs. All cavity pressure does not change much for COC when mould temperature is increased from 40 °C to 85 °C/40°C, where demoulding force varies (Figure 5). This indicates less effect from melt adhesion. For PMMA, the cavity pressure increases at high temperature conditions, but demoulding force is overall decreasing except for the situation of variotherm condition. This is related to polymer and mould thermal expansion, where at higher temperature, the difference is less. For the situation of increasing the injection velocity, the cavity pressure is consistently increased (Figure 5). However, the demoulding forces do not change much. This means the effect of process conditions on demouding is less profound compared to the materials shrinkage induced friction and their resist to plastic deformation. It is obvious that PP is much easier for demoulding compared to COC and PMMA. PMMA under various process conditions shows higher demoulding forces, indicating higher friction and adhesion.

Significantly, when the Ni-PTFE composite mould is used, although the cavity pressures are increased, the demould forces are consistently decreased. This is a significant result to show that our nanocomposite mould can really minimize the surface damage of features at various process conditions.

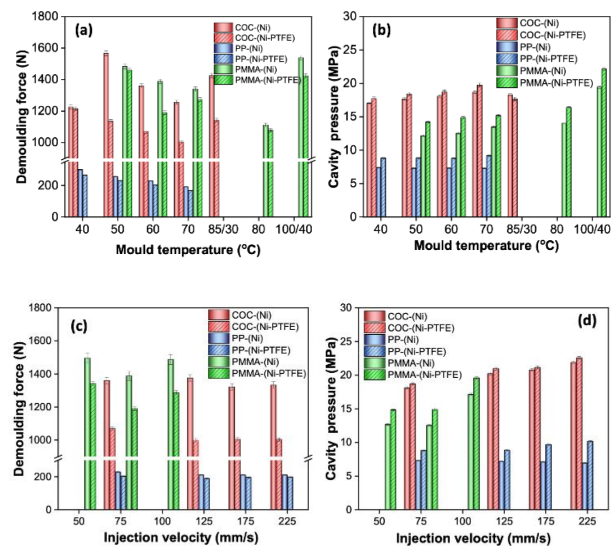

Fig. 5 The relationship between demoulding force and cavity pressure with mould temperatures and injection velocities: (a) and (b) under mould temperature, and (c) and (d) under different injection velocity.

3.3. Mould tool surface characteristics and tool life

After injection moulding for more than 1500 cycles, both pure Ni mould and Ni-PTFE nanocomposite mould were examined using SEM. Broken edge was found on the 50-µm-wide feature on the Ni mould, whereas the Ni-PTFE mould remains intact with no polymer contamination or damage. PTFE nanoparticles were found on the nanocomposite mould surface, which contributes to the lubrication properties of such mould (Figure 6).

Figure 7a shows the coefficient of friction (COF) of two moulds when sliding against COC. The mean COF has been reduced by 38% from 0.45 for Ni to 0.28 for Ni-PTFE. This indicates the improved lubrication properties of the Ni-PTFE nanocomposites. Moreover, the stable wear starting time increased 5 times from 101 s for Ni mould to 524 s for Ni-PTFE mould. This result represent that Ni-PTFE mould has significantly extended tool lifetime, as less adhesion would occur when contacting with polymer material. This result was further supported by the surface wettability test, as Ni mould has a contact angle (CA) of 81° when contacting with COC melt, whereas Ni-PTFE mould has a CA of 98° in the same experimental condition, owning to its lower surface energy and higher hydrophobicity (Figure 7a). The microhardness was increased from 200 Hv for Ni mould to 460 Hv for Ni-PTFE mould, which would contribute to the enhanced wear resistance (Figure 7b).

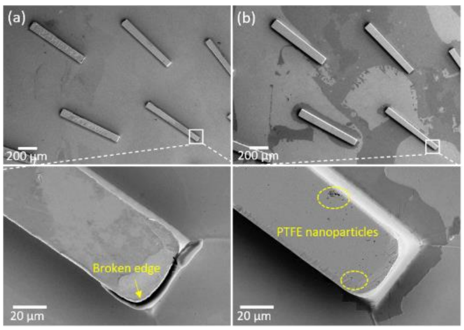

Fig. 6 Surface morphology of moulds after injection moulding: (a) Ni mould, and (b) Ni-PTFE mould; the micro features have a width of 50 μm and a height of 100 μm in the subfigures.

After the pin-on-disk test, the wear track on both moulds were characterized under SEM. Figure 7c shows the wear track with a width of 628 μm on the Ni mould, with continuous polymer transfer layer detected. Grooves were also developed during the sliding of polymer pin, due to the low wear resistance of Ni mould. In comparison, the Ni-PTFE mould shows excellent wear resistance against the polymer material, with only small and individual polymer debris detected on its surface. These results further validate the improved lubrication properties and wear resistance of Ni-PTFE mould. Such properties contribute to the low demoulding force and defects-free demoulding of polymeric components even under different experimental conditions, as measured by demoulding forces.

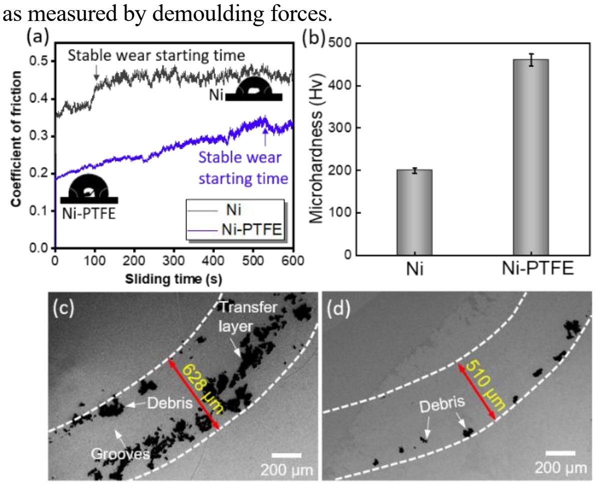

Fig. 7 Coefficient of friction of mould surfaces against the COC pin and the COC melt contact angle on the mould surfaces (a); microhardness of two moulds (b); wear morphology of Ni mould (c) and Ni-PTFE mould (d) after the pin-on-disk test.

4. Conclusions

A study of Ni and Ni-PTFE nanocomposite mould for replication of surface microstructure by micro injection moulding was conducted. The demoulding behavior from both moulds with features from 50 μm to 100 μm with continuous variation of aspect ratio from 2 to 1 was studied quantitatively. Experiments consistently validate that Ni-PTFE nanocomposite mould showed profound demoulding performance with less feature damage and maintains high level feature integrity against both amorphous and semicrystalline polymers. Instead, pure Ni mould causes a significant feature plastic pile up and damage. Our friction measurement using COC materials indicated 38% reduction in friction coefficient, while 5 times extended tool life compared to pure Ni mould insert in-terms of wear. In addition, our tool track analysis and contact angle measurement further validate that Ni-PTFE composite has significant less adhesion compared to pure Ni mould. This paper paves the way towards defects-free injection mould of surface microstructures based on a high-performance Ni-PTFE nanocomposite mould.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support from China Scholarship Council (CSC), the Science Foundation Ireland (SFI) (No. 22/RP-2TF/10466 and 20/FIP/PL/8741) and Enterprise Ireland (CF-2021-1635-P).

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