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Master Thesis

On the demolding of micro-structured surfaces for medical applications

by

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submitted to

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Affidavit

Affidavit:

I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume.

Datum (Tobias Struklec)

Acknowledgment

This thesis was written in course of a research project focusing on the demoldability of micro structured polymer devices at Sony DADC Austria AG.

Werner Balika brought me to the team of engineers currently working with various medical applications. This helped me to investigate the different applications regarding their demoldability. I want to thank him for supervising my work at Sony DADC. His advice, experience and attention to detail encouraged me to work systematically for scientific as well as industrial standards.

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Last but not least, I want to thank my family and friends for all the support I got during my studies at the University of Leoben.

Abstract

This thesis is a theoretical study on the demolding of micro structured polymer surfaces in hot embossing and injection molding. Many replication problems, e.g. ripping or deformation of the micro structure, can affect the final part quality. These problems arise due to the lack of understanding the underlying mechanisms. Therefore, demolding force was introduced as a representing value for the demoldability of micro structured surfaces. Subsequently, the mechanisms for demolding are studied leading to an overview of main influencing factors. These – geometry, material, mold and process – are studied regarding their impact on demoldability. Furthermore, this thesis tries to link these influencing factors to the demolding problems as well as to the local physical mechanisms, i.e. adhesion, friction and stress distribution. Based on this theoretical background the design of the microstructure for a test chip is discussed, taking into account the theoretical study. The specifications for this test chip try to minimize secondary influences, like hindered shrinking of the micro structures due to geometrical inhibition. Additionally, a test plan is devised to examine the correlation of different coatings to the demolding force. This will allow selecting appropriate coatings for different processes and should give insight into the interactions of different polymers with different metal based or fluorine based coatings.

Kurzfassung

Diese Arbeit ist eine theoretische Studie zum Thema Entformen von mikrostrukturierten Oberflächen im Heißpräge- und Spritzgussverfahren. Derzeit entstehen viele Probleme bei diesen Anwendungen, wie zum Beispiel das Abreißen von Rippen oder die Verformung der Mikrostruktur. Die zugrunde liegenden Mechanismen sind noch nicht ausreichend untersucht. Deshalb wurden in dieser Arbeit die Entformungsmechanismen genauer untersucht und daraus ein Überblick über die wichtigsten Einflussfaktoren zusammengestellt. Diese Einflussfaktoren - Geometrie, Material, Werkzeug und Prozess - wurden hinsichtlich ihrer Auswirkungen auf die Entformbarkeit analysiert. Für jeden dieser Aspekte versucht diese Arbeit die Einflussfaktoren nicht nur mit dem Entformungsvorgang, sondern auch den lokalen physikalischen Mechanismen, wie Adhäsion, Reibung und der Spannungsverteilung in Verbindung zu bringen. Auf Basis dieses theoretischen Hintergrundes wurde ein Test-Chip entwickelt. Die Spezifikationen für diesen Test-Chip sollen sicherstellen, dass sekundäre Einflüsse, wie zum Beispiel die Schrumpfbehinderung durch die Geometrie der Mikrostrukturen, so gering wie möglich bleiben. Nur so kann sichergestellt werden, dass die geplanten experimentellen Versuche reproduzierbar sind. Zusätzlich wurde ein Testplan entwickelt, um die Korrelation von verschiedenen Beschichtungen mit der Entformungskraft zu untersuchen. Die Durchführung dieses Testplans soll nicht nur die Auswahl geeigneter Beschichtungen für verschiedene Prozesse ermöglichen, sondern auch einen Einblick in die Wechselwirkungen der verschiedenen Kunststoffe mit unterschiedlichen metall- oder fluorbasierenden Beschichtungen geben.

Contents

1 Introduction and objectives

The trend of modern lab-analysis in life science and medical applications focuses more and more towards “lab-on-a-chip technologies”. These life-science applications try to get as many features as possible on an even smaller space [*3*, *17*, *31* and *37*]. Therefore, the expectations for these applications increased continuously and are still increasing today. Not only the geometry of the channel (micro-geometry) but also the geometry of the polymer part (macro-geometry) is getting more and more precise, subsequently the dimensional tolerances for the polymer applications are going down. By now tolerances of only a few micrometers are desirable. Additionally, these applications are in medical services which impose many restrictions. These restrictions limit not only the variety of materials to choose from but also affect the processing, since almost no additives or enhancements may be used. The resulting injection molding process is seldom ready for large scale production [*9*]. This thesis tries to improve the current injection molding system. In particular, it focuses on the demolding and demoldability of micro structured surfaces. The interaction of structured polymer surfaces with the surface of the mold has yet to be investigated thoroughly. Still, the interaction leads to different kinds of problems, like structures that may rip in the demolding process. These interactions might also induce bending of the chip, or inhibit demolding altogether.

An extensive literature investigation is the main part of this thesis. This will provide a basic knowledge of the demolding phenomena that have already been investigated. On this basis, an overall picture is given that allows for this problem to be tackled in a systematic manner in future projects. This shall lead to an improvement for upcoming production lines where the attained experience may help to reduce the number of defective goods during the injection molding process and thereby facilitating competitive molding for micro structured applications, e.g. lab-on-a-chip applications.

2 Manufacturing of medical applications

2.1 Medical applications

Medical is a term used to describe every tool or auxiliary tool that has contact either directly to the patient, e.g. a syringe, or indirectly, e.g. a blood container. The term medical also states that all of these “parts” need to be approved to ensure they cause no harm or influence tests. In America this is commonly done by the Food and Drug administration (FDA) which provides a good index for medical applicability.

Polymer based applications are strictly regulated. Besides the polymer type (monomer) every used additive is relevant for the approval process. Table 1 and Table 2 show a material study by Usama [*37*] and point out which polymers are feasible for micro injection molding and molding of microstructures. These two lists will later be the basis for the material choice in this thesis.

Table 1: List of amorphous polymers used for micro-injection molding based on the research of Usama [37].

Polymer	**Full name**
PMMA (acrylic)	Polymethylmethacrylate
PC	Polycarbonate
PSU	Polysulfone
PS	Polystyrene
COC / COP	Cyclic olefin (co)polymer
PPE (PPO)	Polyphenylene oxide
PEI	Polyetherimide
PAI	Polyamide imide
MABS	Methylmethacrylate acrylonitrile-butadiene-styrene
SAN	Styrene acrylonitrile
SBS	Styrene-butadiene-styrene
ABS	Acrylonitrile-butadiene-styrene

Table 2: List of semi-crystalline polymers used for micro-injection molding based on the research of Usama [37].

Polymer	Full name
LCP	Liquid crystal polymer
PP	Polypropylene
PE	Polyethylene
POM (acetal)	Polyoxymethylene
POM-C	Polyoxymethylene (carbon filled)
PBT	Polybutyleneterephtalate
PBT-HI	Polybutyleneterephtalate (filled with 15% glass fibre)
PA 6 (nylon)	Polyamide 6
PA 12	Polyamide 12
PA 12 C	Polyamide 12 (carbon filled)
PVDF	Polyvinylidene fluoride
PFA (teflon)	Perfluoroalkoxy
PEEK	Polyetheretherketone
PLA (polyester)	Polylactic acid (polylactide)

These strict regulations and a thorough testing process lead to long time to market times. This makes it hard to enter a well established or saturated market. There are two similar fields for medical application that remain significant especially for competitors on this market. Both have a growing demand and are scientifically of great interest. The scientific interest comes from the small basic knowledge regarding small scale structures and the ways they can be produced.

2.1.1 Disposables

Disposable often refers to point-of-care devices that are meant for one use only. Most commonly it is an experiment that can be performed in a test tube. The goal of these applications is to receive a consumer good that brings the lab to the patient allowing a fast diagnostic process. An example would be a lab on a chip urine test that no longer requires for the urine to be send to a laboratory and for the patient to wait unnecessarily long for the results. A similar example would be a test for the blood type that can be carried out at home. Both of these examples can be realized as a micro fluidic application.

Figure 1 is an example of a micro fluidic application. The function of this chip is to dilute a sample in a buffer solution. Both of these (buffer and sample) are provided by two of the three wells on the left side of the chip. They are mixed and travel along the separation channel. Overflowing or unneeded sample will flow into the waste chamber to ensure the separation process is not influenced. In the detection area the desired quantity is measured, e.g. light absorption to measure the amount of a given substance in the sample.

These applications can be distributed in a large quantity with a common price range of a single digit euro number. The demand is estimated to be several millions for individual application. Every one of these chips needs to assure functionality. To provide functionality the tolerances of the design are very slim, making it a challenge to realise all applications in terms of polymer processing.

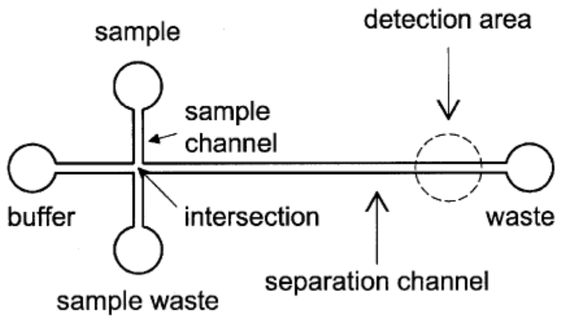

Figure 1: Setup and functioning principle of a disposable lab-on-a-chip system for capillary electrophoresis [17].

2.1.2 Life science applications

The goal of life science products is not necessarily to be a consumer product unlike disposable point-of-care applications. Life science is mostly used for scientific purposes. This means in most cases it is enhanced equipment for research purpose. An example here would be the analysis of the genome on a chip. In this case the application would use a patterned structure to generate a homogeneous DNA distribution. The price range is usually higher then for disposable applications and simultaneously has a lower demand that rarely exceeds half a million.

Both applications have in common that they try to miniaturize current applications to perform more and more tests on a single chip, which subsequently makes the name "lab on a chip" evident.

Polymers are an ideal basis for these applications because the pressure to account for new innovations is high. This means rapid prototyping, short time to market and a low manufacturing and material price are necessary. Polymer replication offers all of these options.

2.2 Replication of micro structured surfaces

To produce micro structured polymer devices in large numbers, replication methods are used. This means a negative of the desired design is manufactured and replicated over and over again. The negative for polymer processing is called "stamper" which is used to carry the pattern that is replicated in the polymer. This stamper can be manufactured in a variety of ways including micromachining from silicon, LIGA (Lithographie, Galvanoformung und Abformung; Lithography electroplating and molding) and machining using a CNC micro-milling tool (for making larger features).

Table 3 is an overview of existing stamper fabrication methods and an evaluation of different aspects like availability or cost.

For the manufacturing of a certain micro structure (see chapter 5.1) a suitable manufacturing technology has to be chosen. Generally three dimensional structures and undercuts are hard to manufacture. Important is the choice of geometry because wet silicon etching is inferior to LIGA, and is limited in the freedom of design. Micro milling (mechanical micromachining) on the other hand can be used for almost any design but has a minimum feature size defined by the size of the drill. Regarding design, only the LIGA technology would fulfill all necessary requirements. Unfortunately, its excessive cost and low availability make it unfeasible for stamper manufacturing. Most promising is the optical lithography and electroforming method where all needed structures can be achieved with comparably low cost and good availability.

Table 3: Overview on existing master fabrication methods [2].

Technology	Choice of geometry	Minimum feature size	Height	Total surface area	Aspect ratio	Lifetime	Cost	Availability
Wet silicon etching	-	+	0	++	-	+	+	++
Dry silicon etching	+	++	+	++	+	-	0	+
Optical lithography and electroforming	+	++	+	++	0	+	0	0
Laser ablation and electroforming	++	+	+	-	+	+	-	-
LIGA	+	++	++	-	++	+	--	--
Mechanical micromachining	+	0	+	+	0	++	-	-
μ-EDM (Electric discharge machining)	-	0	+	-	+	++	-	-

An alternative to replication methods that require a stamper or other form of negative is available as well. The technology uses a thermo active polymer resin that is located on a plane surface. A focused light beam cures the polymer at desired positions. This creates a hardened three-dimensional construct of any desirable design. Although this process allows for almost any structure to be manufactured, it is limited due to large production times, small areas and high cost.

Therefore, the common industrial used processes for replication are “injection molding” and “hot embossing”.

2.2.1 Injection molding

Injection molding is a manufacturing process used for producing parts mostly from thermoplastic polymer materials in large numbers. The polymer material is fed into a heated barrel. In the barrel the polymer is transported by a screw leading to the nozzle. During transportation, the heat of the barrel and the shear strain are mixing and melting the polymer. The retracting screw doses a defined amount of polymer in front of the closed nozzle.

Figure 2 illustrates the injection molding process starting with the closing of the mold (1. Mold Closing). The forward motion of the screw forces the polymer melt into a mold cavity (2. Filling). Once the cavity is filled, a holding pressure is maintained to compensate for material shrinkage (3. Packing-holding). This is done to ensure a sufficiently good molding of the structured area. In the cavity the polymer cools down and hardens in the form of the mold cavity (4. Cooling). Parallel to the cooling, the screw again doses material to prepare for the next shot. Once the part is cooled down, the mold opens and the part can be ejected (5. Mold Opening). Then the cycle starts again with the closing of the mold. A common injection molding cycle time is only a few seconds up to a few minutes.

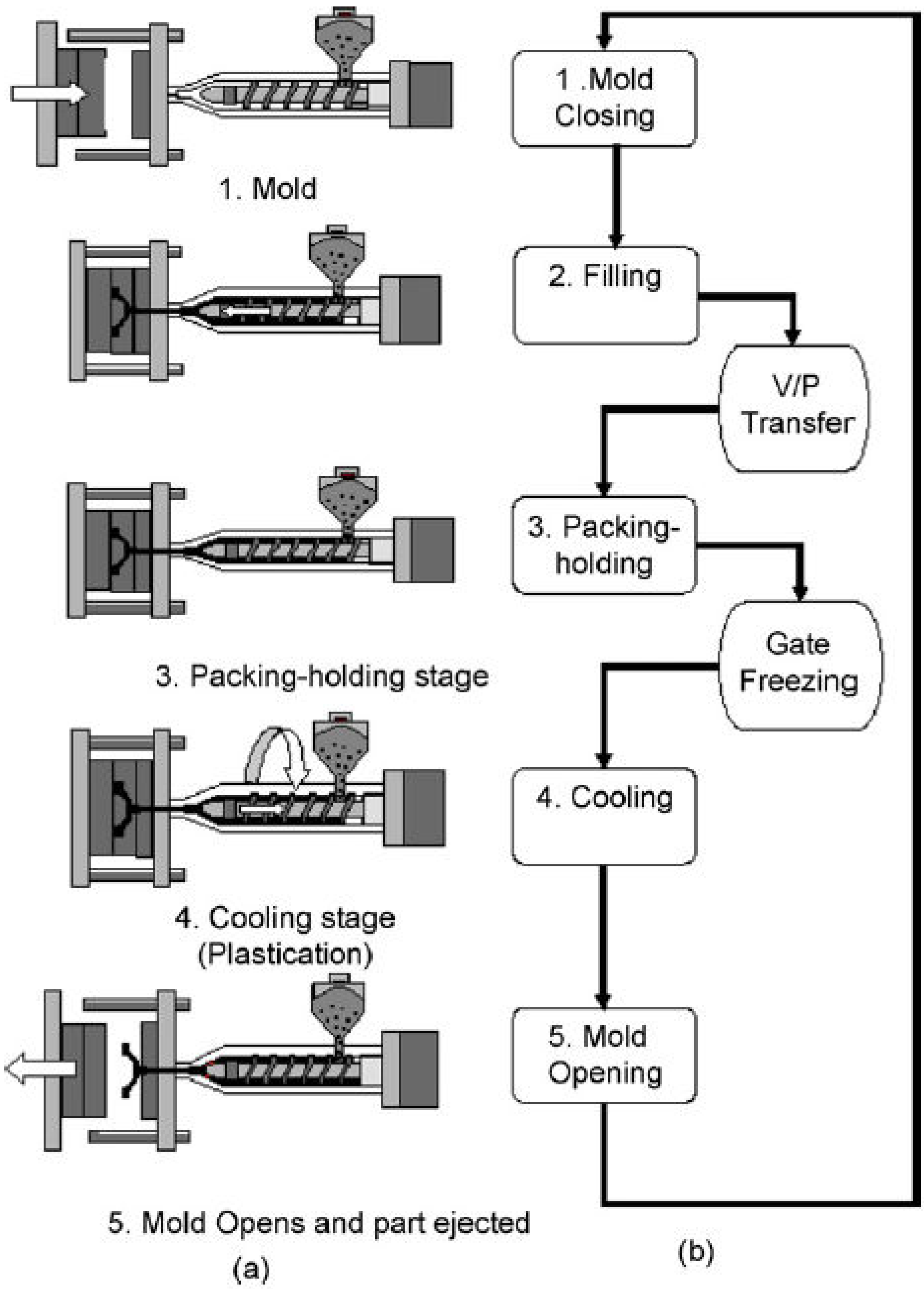

Figure 2: (a) Simplified diagram and (b) flow diagram illustrating the injection molding process [40].

In this common injection molding process a microstructure on a stamper that was placed in the cavity is replicated onto the polymer. This micro structured stamper is designed for a certain application and replication process. If available, a design from a similar glass based application is used as basis for the polymer stamper. This stamper system makes the microstructure on the polymer part independent from the mold (macro geometry). Different stampers for the same tool can be manufactured by a toolmaker out of metal, usually steel or nickel. The injection molding cavity in case of micro-fluidic applications contains the stamper that holds the structures and can be changed without any change of the mold itself. This allows the production of different applications with the same macro-geometry (micro slide format). For example different micro-fluidic applications on the micro slide format.

2.2.2 Hot embossing

Hot embossing is defined as the stamping of a pattern into a polymer (see Figure 3 “imprint”) which was softened before by raising the temperature of the polymer above its glass transition temperature. Unlike injection molding the polymer does not flow into the micro structure to replicate it, but the stamper is pressed into the polymer and thereby replicating the structured area.

The second step is the demolding (see Figure 3 “demolding”). Similar to the injection molding process the polymer cools down until the stamper can be pulled out without damaging the microstructure. This technique is commonly used for low quantity productions, prototyping and defining micro-channels and wells for fluidic devices. The cycle time needed to produce a part is a lot longer than for injection molding. But in comparison very thin structures can be reproduced more accurately. This is why industrial fabrication of plastics components is normally achieved by injection molding, but the advantages of hot embossing are low material flow, avoiding internal stress which induces e.g. scattering centers unfavorable for optical applications. So more delicate or fragile structures can be fabricated, like free standing thin columns or narrow oblong walls.

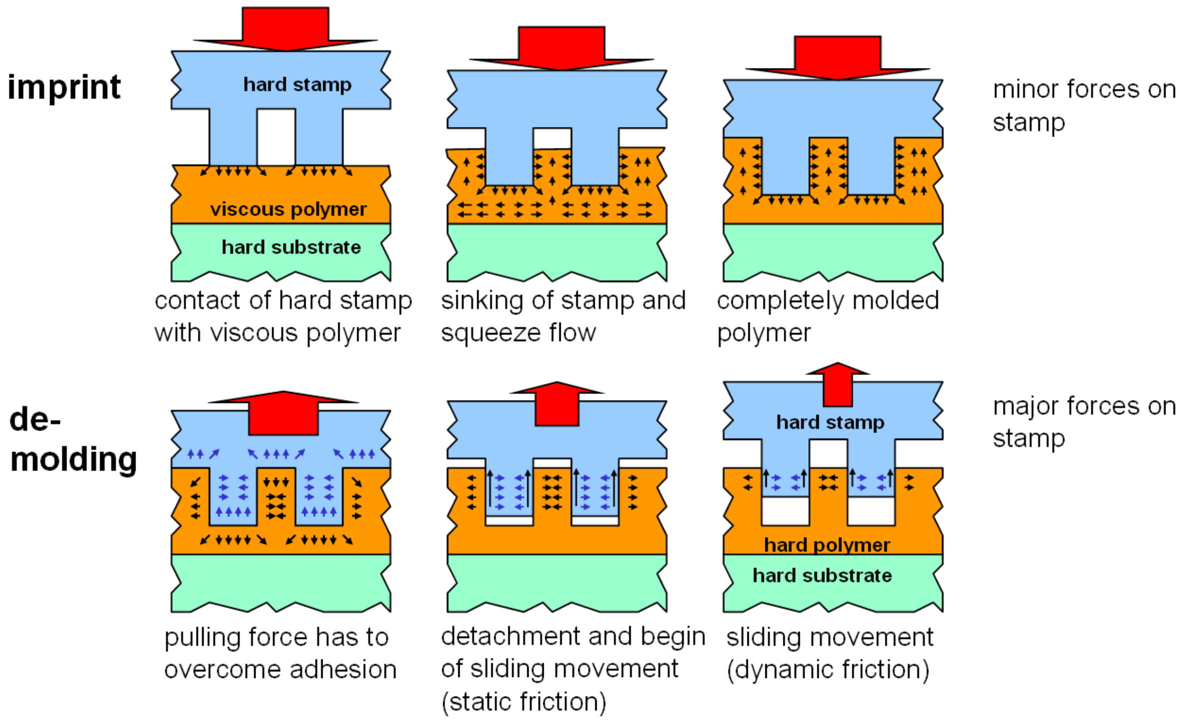

Figure 3: Hot embossing process with a patterned stamper [32].

Hot embossing has the potential of increasing production rates and therefore decreasing production costs. This can be done by the enlargement of the molding surface and automatization of the molding process coming from a molding prototype. Still hot embossing is not able to reach cycle times similar to those of the injection molding process. The average cycle time of the hot embossing process is rarely lower then a few minutes and more often above half an hour.

Still the controllability of the process makes it favorable for scientific purposes to study the demoldability in the hot embossing procedure. Also the hot embossing can be used for rapid prototyping and therefore decreasing the time to market for different applications.

Despite its differences to injection molding, the demolding problems that occur in hot embossing are similar and allow a lot of transitions of conclusions in between both replication methods.

2.2.3 Variotherm processing (dynamic mold temperature)

Variotherm processing is an extension to the common hot embossing or injection molding cycle. It means that the temperature of the mold can be regulated according to each process step. For the processing cycle this means that an additional heating and a cooling phase are introduced.

In the normal process cycle the melted polymer is injected into the much colder mold cavity that has the desired cooling temperature. The cavity heats up as it draws thermal energy out of the polymer. The surrounding cooling channels will cool the cavity down to its original temperature. In-between this cooling process the polymer part can be ejected at any given time usually when the ejection temperature (Te) is reached. The ejection temperature is defined as the temperature below which the polymer is dimensionally stable and can be demolded. In this common cycle the polymer is injected while the mold temperature is already below the ejection temperature which remains that way over the entire process cycle. Therefore, the injection and ejection temperature of the mold is theoretically the same.

Due to the cold mold surface the polymer solidifies instantly at the contact surface. This increases the local viscosity and reduces the crystallization. The inhomogeneous crystallization leads to an unpolished looking polymer surface. The increasing viscosity at the contact surface increases the flow resistance and inhibits the molding of microstructures.

In the variotherm process cycle (see Figure 4) the temperature of the mold cavity will change over time (over the process cycle). After the ejection of the last produced part the mold starts heating up to a certain injection temperature (Ti) which is at least above the glass transition temperature of the polymer. When this high temperature limit (Ti) is reached, the polymer is injected. Due to the mold temperature above the glass transition temperature, the polymer remains fluid during the entire filling-phase. After the filling is complete the cooling starts. The cooling lowers the mold temperature and finally the polymer below its ejection temperature. Once the polymer is sufficiently solidified – the low holding temperature is reached – the mold opens and the polymer part is ejected. The rest of the injection molding cycle remains the same.

This variotherm technique is used for optical applications like contact lenses which need to have a homogeneous crystallinity which leads to a homogeneous refraction index. It has also found its way into the production of polished surfaces on everyday products like modern TV-screen frames.

Additional benefits of variotherm processing are:

- The molding of the polymer - especially of microstructures - can be improved.
- The injection flow resistance and pressure can be lowered.
- Polymer part quality can be improved, e.g. surface, state of stress, no sink marks.
- Increasing of weld line strength.

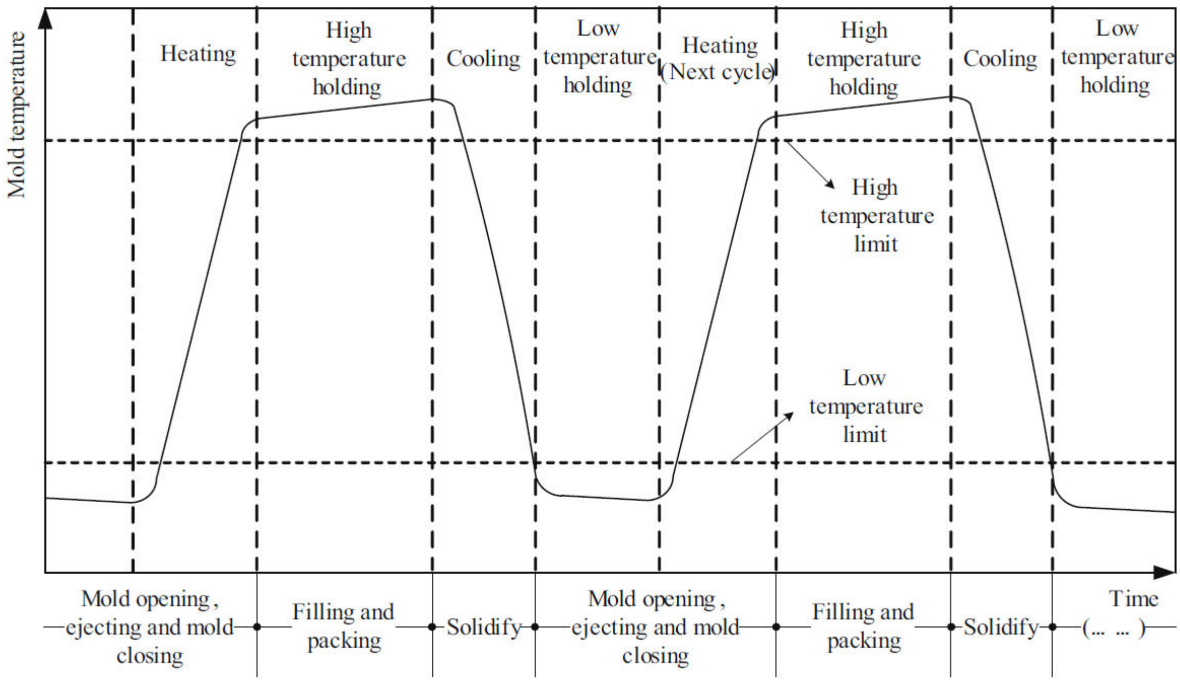

Figure 4: Diagram illustrating the variotherm process on the basis of the injection molding cycle [38].

For the production of nano and micro structured surfaces variotherm process handling is essential. Figure 5 shows that the variotherm process can be used to realize high aspect ratios. This evaluation done by Fu [*12*] tested the moldability of certain microstructures with and without the variotherm system. As in other studies he relies on a metal polymer feedstock but draws conclusions that should apply to similar injected polymers. Unfortunately, it is not described how the maximum attainable aspect ratio was defined or determined. The evaluation of several SEM (scanning electron microscope) pictures by Fu suggests that the moldability was determined by optical means.

Important to note is, that Fu found, that the smaller micro structures (micro features) get the better the moldability for high aspect ratios become. One would expect small features to exhibit a bad filling behavior. Still Fu makes no effort to explain this contra intuitive behavior in any of the papers quoted in this thesis.

The conclusion of Fu’s study is that variotherm systems will enhance the moldability of microstructures.

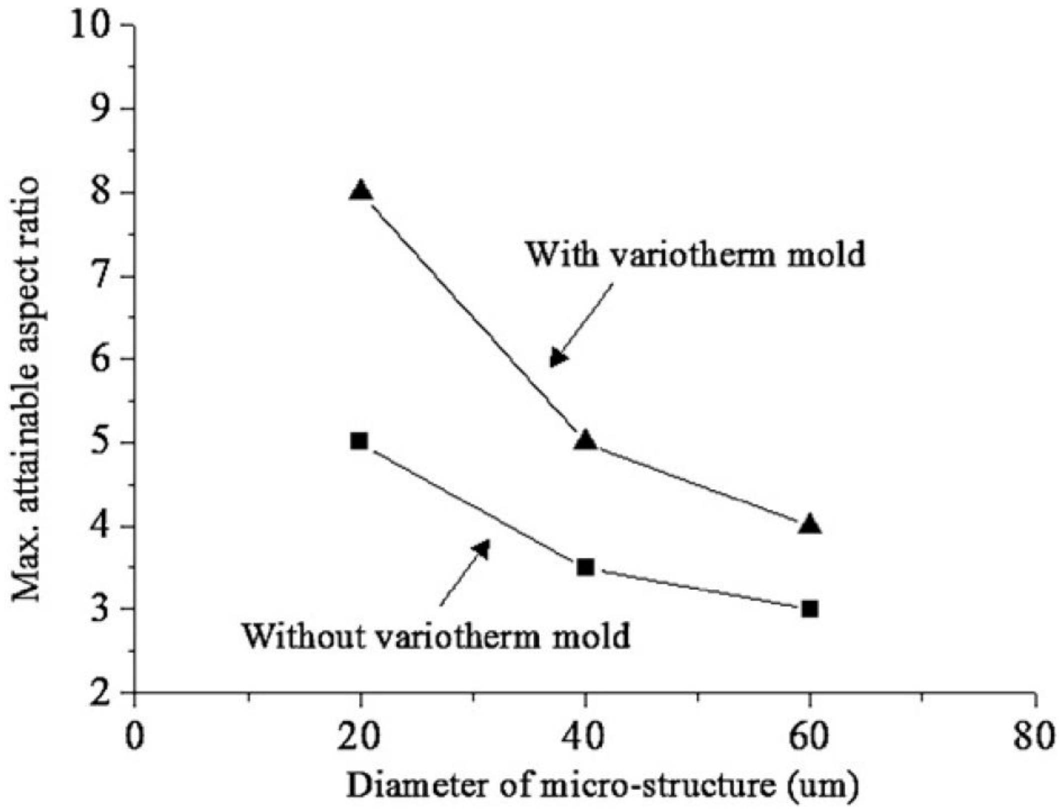

Figure 5: Maximum attainable aspect ratios with and without the variotherm mold [12].

2.3 Common problems

In the replication process for micro structures many problems can occur in the demolding step. The most critical effect is the destruction of the structured area. Figure 6 shows, that not only the polymer can rip (a), but that the demolding may also destroy the (silicon) stamp (b). In this particular case (a) shows a PMMA microstructure that ripped after a thermal imprint process, while a stamper made from silicon (b) can also be severely damaged. For many different reasons both of these effects can occur to various extents leaving the product or even the stamper unusable. Especially dense and fragile structures like pillars with high aspect ratio tend to bad demoldability. Song [34] emphasizes however, that research on demolding is still lacking despite the fact that it is the demolding step that, as the last processing step, determines the success of imprinting because most structural damages in imprinted patterns occur at this step.

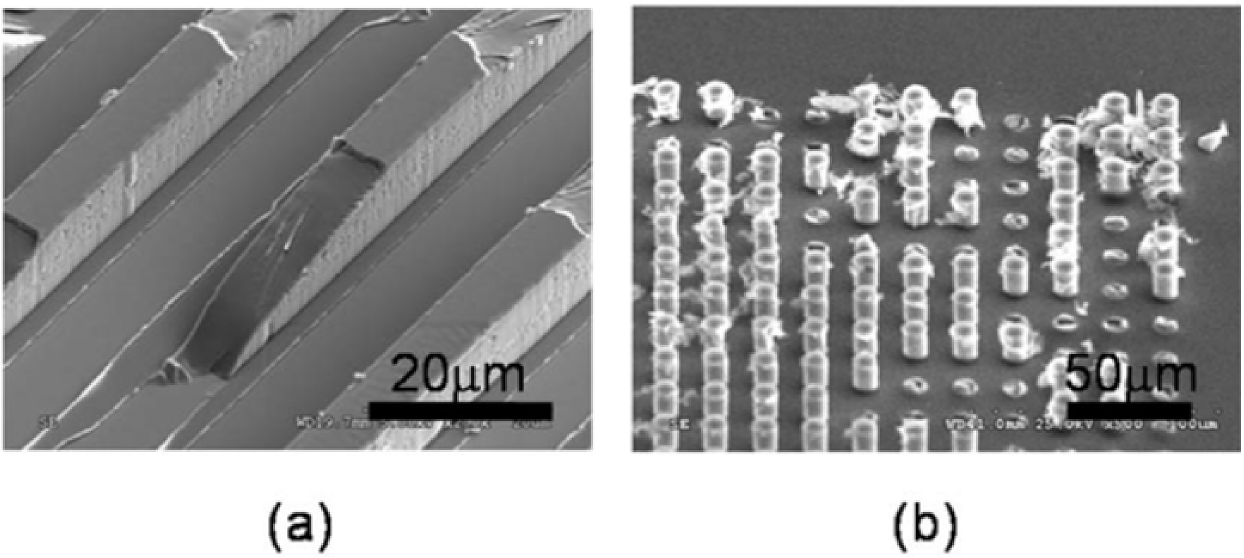

*Figure 6: Scanning electron micrographs for damaged structures in (a) imprinted PMMA and (b) silicon stamp [*34*].*

Figure 7 shows a similar example of demolding defects. On the left is an overview of the molded part with the 5 mm x 5 mm structured zone in the middle. This study [*10*] was done with metal feedstock as molding material. This can also be seen due to the large ejection marks in the first picture. It also illustrates that almost a whole area of pillars could only be partially demolded. Solving, or at least studying these problems is crucial for the improvement of future applications since miniaturization and small surface effect structures due to complex patterns are the goals (compare chapter 2). These improvements will lead to smaller and denser structures, which are even more likely to exhibit these destructive effects.

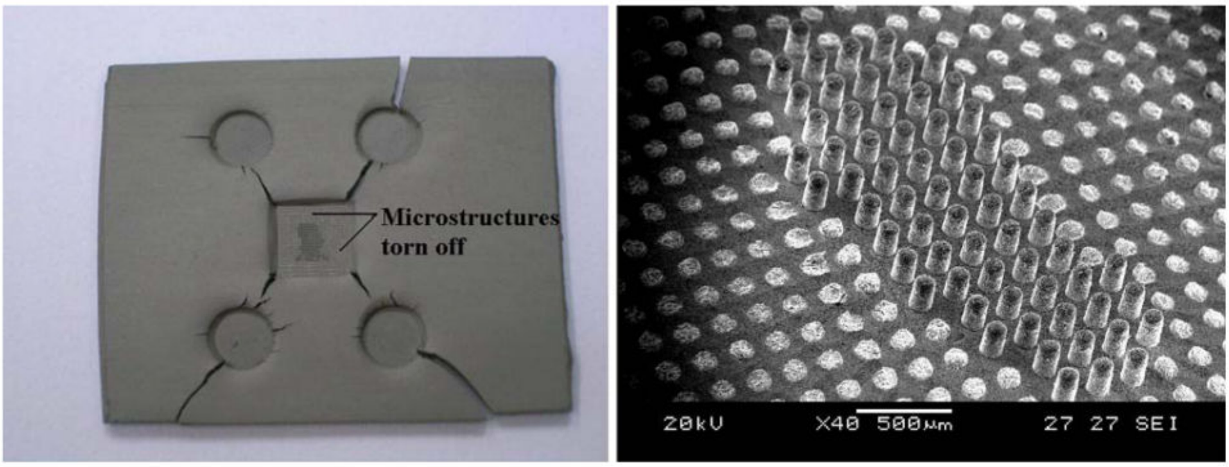

*Figure 7: Demolding failure of a hot embossed micro structure [*10*].*

3 State of the art

3.1 Friction

The most obvious quantity to influence demoldability is friction. Friction depends on the interaction between the surfaces of different specimen. While static friction is the force needed to initiate motion between two bodies, dynamic friction is the force needed to maintain motion. The friction coefficient is a dimensionless number often used to describe the interaction of two surfaces. It is defined as the relation of the normal force acting between the two surfaces and the resulting friction force that is acting on the body (Equation 1). This leads to a static and a dynamic friction coefficient depending on state of the body (moving or not moving).

$$F_f = \mu \cdot F_n \qquad (1)$$

F_f horizontally acting friction-force
F_n normal force on the contact surfaces
μ friction coefficient

To describe demolding both coefficients are of interest. The onset of demolding corresponds to initiation of the motion and therefore to the static friction. The rest of the demolding occurs while the polymer part is moving and is influenced by the dynamic friction. To accurately start describing the demolding the need to characterize this interaction becomes urgent.

Figure 8 illustrates the outcome of a friction force measurement by Worgull [*43*]. In this particular example it shows the friction coefficient between copper or brass and a corresponding polymer counterpart. The friction measurement device for this diagram is explained in chapter 3.5. The first peak to initiate the movement of the polymer describes the static friction. The remaining curve describes the body in motion. The repeating cycles in the moving phase are slip-stick effects, leading to a varying friction force over sliding distance. Furthermore, the diagram shows different materials and how the friction force varies over the displacement. The critical value for the demolding process is the static friction force because it has the highest value. Static friction only occurs at the beginning of the demolding. Ripping or great deformations of replicated micro structures will most likely occur at the onset of the demolding if the static friction is too high (compare 3.3 b). Ongoing deformation happens in the dynamic phase, especially due to slip-stick effects during the demolding (compare 3.3 e).

The inhibiting force can be reduced by two means. One way is to reduce the normal force between the surfaces by decreasing the shrinkage or the expansion of the polymer. The other way to reduce the friction is by coating the stamper that is placed in the mold, or choosing a different stamper material (e.g. copper instead of brass).

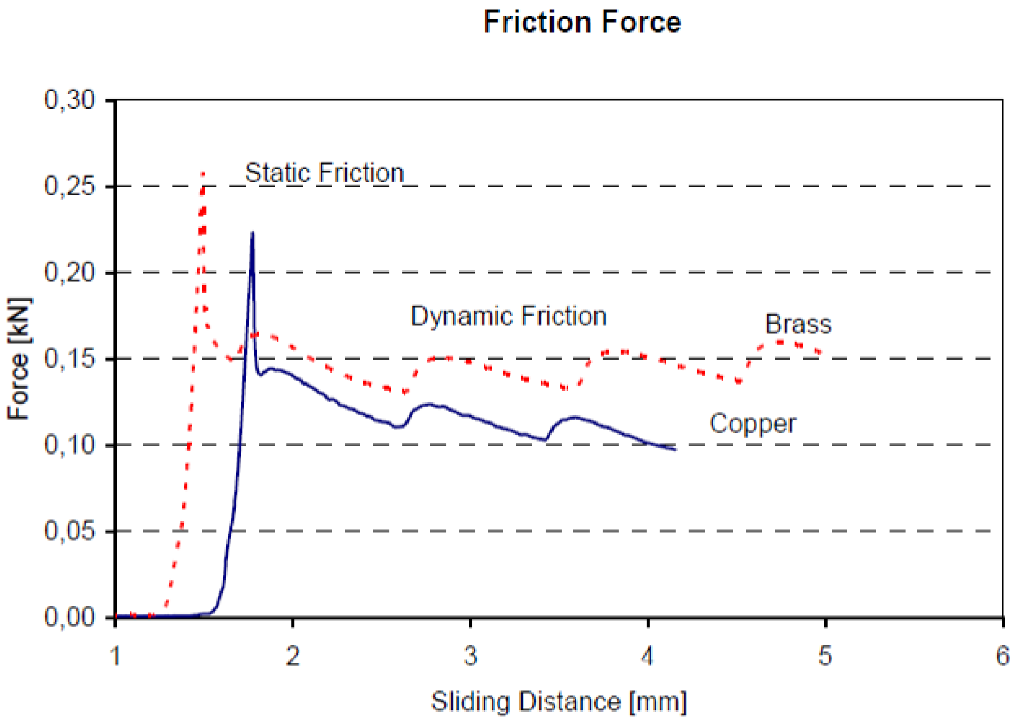

Figure 8: Friction of PMMA and the metal counterpart during the demolding process [43].

It is important to treat friction coefficients with caution. In the measurement system described there are some drawbacks when it comes to transferability and comparability of the discovered friction coefficient. As mentioned before, the calculated coefficient is strongly related to the measurement parameters. Since the ejection of the polymer in the injection molding process has completely different environmental variables the friction coefficient may not be of any use to describe the process. Similar systems like the one introduced by Worgull [42] faces the same limitations. The importance of the discovered value is still present as a basic guideline to compare different settings among themselves. This allows ordering certain coatings or metal choices among each other regarding their friction behavior. Still, this may not be fully accurate since the friction measurement is horizontal unlike the ejection process. Compare chapter 3.5 Measurement devices to detect the friction and demolding force for a different approach to measure demolding forces or friction closer to an actual production process.

To describe the friction that occurs between a micro structured surface and the mold horizontal friction measurement will not suffice. Fu [*13*] suggested a simulation of microstructures on a larger scale. He assumed that each geometric entity shrinks towards its geometrical center. Microstructures shrink away from the sidewalls which reduces the interacting force. All of the microstructures are placed on a 5 mm x 5 mm square (Figure 7). This base also shrinks towards its geometrical center pressing the microstructure against the inner sidewall (Figure 9 (a)). The resulting force equilibrium is illustrated in Figure 9 (b). The demolding force F_D, required for ejection is determined by the release force F_R and the vacuum force F_V. F_R is composed of the pressure between the surfaces p_c due to shrinking, the contact area A_c and the friction coefficient μ. F_V is an additional release force due to vacuum effects (compare Equation 2).

$$F_D = F_R + F_V = \mu \cdot A_c \cdot p_c + S \cdot p_V \qquad (2)$$

S cross sectional area

p_V negative vacuum pressure

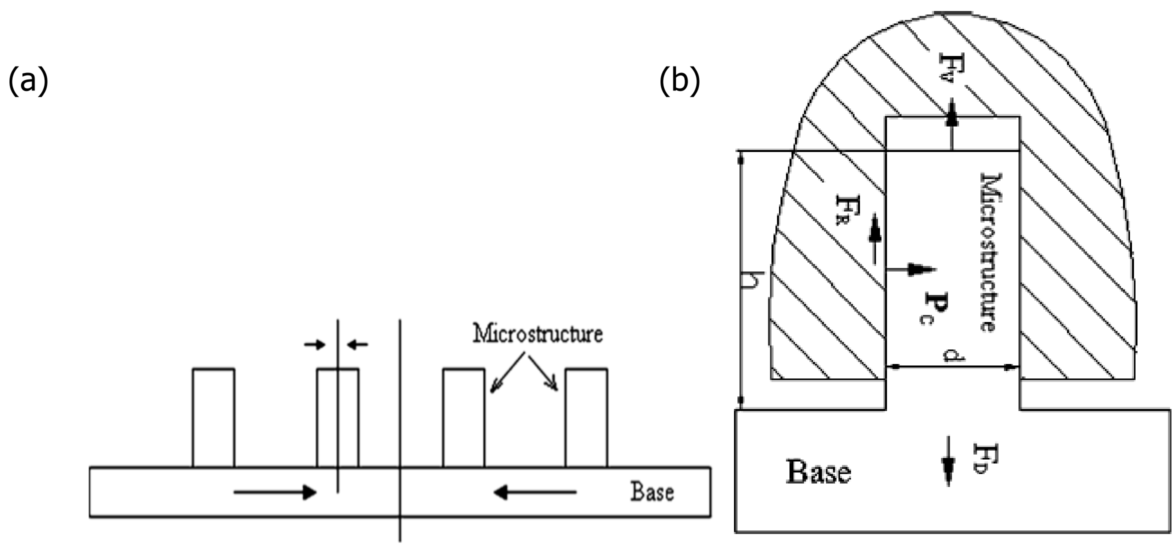

*Figure 9: Shrinking direction of the molded part and the micro structure (a), model of demolding a single microstructure (b) [*13*].*

The simulation that was done by Fu shows the stress situation that occurs in the microstructure (compare 4.1) [*13*]. Although this particular simulation provides expected results, e.g. higher stress in microstructures further from the shrinkage center, there are some limitations. The simulation has been based on metal feedstock injection molding, with the polymer acting as a binder for the injection process. This greatly changes the material properties as metals exhibit foremost elastic mechanical properties and completely different adhesion and friction properties. Despite that, the assumptions remain valid and can be used to describe polymer demolding to a certain degree.

3.2 Contact angle and roughness

The force needed for demolding results from the various interactions of the mating surfaces. A good indicator for surface interactions is the contact angle which is a representation of the surface energy. The surface energy is by definition “the potential work the surface can perform”. Thus lower energy of a surface mean less possible interaction. This interaction is often defined as the wetting of a surface (see Figure 10). As the surface energy gets lower the contact angle increases, and the wetted surface decreases. Bormashenko [6] shows that there is a interrelation between the surface energy and the contact angle for different materials. This was first described by Baxter and later refined by Cassie and is now used as the Baxter-Cassie Equation [20]. *1* This equation is derived from the variation of the free energy per surface. For simple calculations a simplified model of the thermodynamic equilibrium leads to the Young relation (see equation 3). Due to the low cost of contact angle measurement devices and comparatively easy evaluation and high availability this measurement method is suited well as practical characterization method.

$$\gamma_{lv} \cos\theta_Y = \gamma_{sv} - \gamma_{sl} \qquad (3)$$

θ_Y Contact angle

γ_{lv} Surface tension between liquid and vapor

γ_{sv} Surface tension between solid and vapor

γ_{sl} Surface tension between solid and liquid

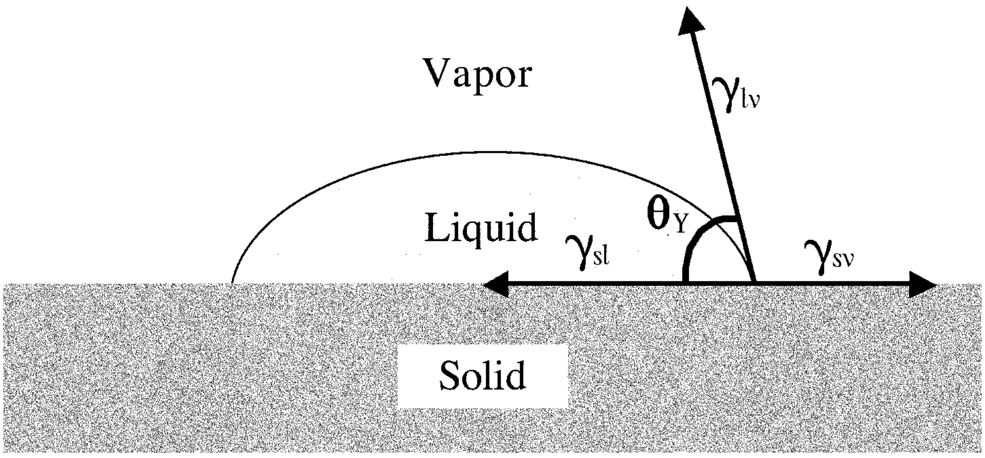

Figure 10: Schematic drop contact angle system [23].

Figure 11 shows how the contact angle varies with different surface properties (surface energies). While a normal, untreated surface (a) exhibits a low contact angle, super hydrophobic surfaces (b) that do not interact with polar water will exhibit high contact angles. Wolansky shows that for a homogeneous surface more roughness leads to a larger contact angle [*39*]. This effect may be familiar from the lotus effect, the "self-cleaning" effect of the leaf of the lotus flower. Relatively rough surfaces yield comparably low surface energies (Figure 11 c). This connection was first described by Wenzel. He proposed equation 4 to describe the apparent contact angle formed by a liquid wetting a rough surface for any given intrinsic contact angle. The apparent contact angle θ_W describes the measured surface angle that is representative for the given surface. θ_Y describes the intrinsic surface angle as property of the material without roughness (contact angle on the perfectly plain and smooth surface).

$$\cos\theta_W = \vec{r} \cdot \cos\theta_Y \qquad (4)$$

θ_Y intrinsic contact angel

θ_W apparent contact angle

r average roughness ratio

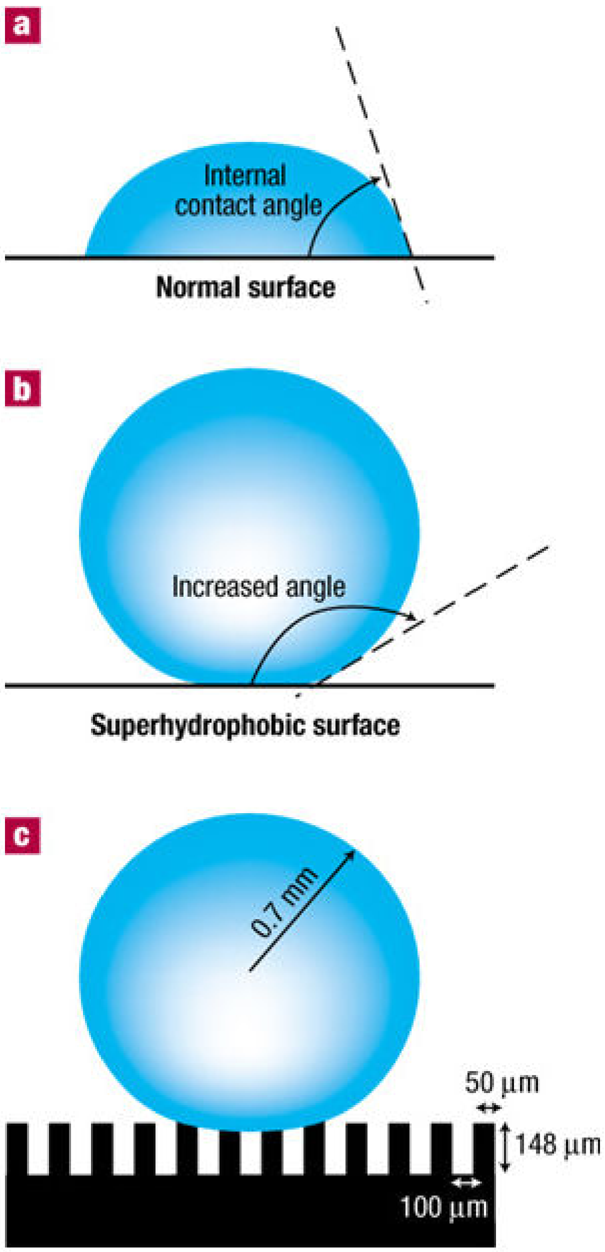

Figure 11: Contact angle of water on different surfaces (a, b and c) [30].

Demolding tests done by Kawata [*21*] show that there is indeed a great impact of the surface roughness on the demoldability of polymer parts. Figure 12 shows that different processing conditions (in this case inductively coupled plasma etching) lead to different surface roughness (top row roughness: a > b > c). The quality of the demolded polymer part can deteriorate. The bottom row of Figure 12 shows that the polymer part can be totally defective after demolding if the surface parameters are unfavorable. The upper row proves that roughness is a critical parameter. This is evident because the roughest surface (a) has the worst demolding properties. Additionally, the demolding force drops from 71 N for (a) to 16 N for case (c).

Unfortunately these tests, done by Kawata, lack some additional information about the results. It is not evident if the destruction of the demolded polymer in case (a) is only locally or all over the polymer part. An estimated percentage or statistical evaluation would be helpful, as one expects even in case (c) minor defects of the demolded polymer. It is also misleading that case (a) and (b) seem to be undercut which would be an explanation for the significantly worse demolding behavior. But a follow up study done by Kawata strengthens the assumption of the surface roughness influence (compare 4.1).

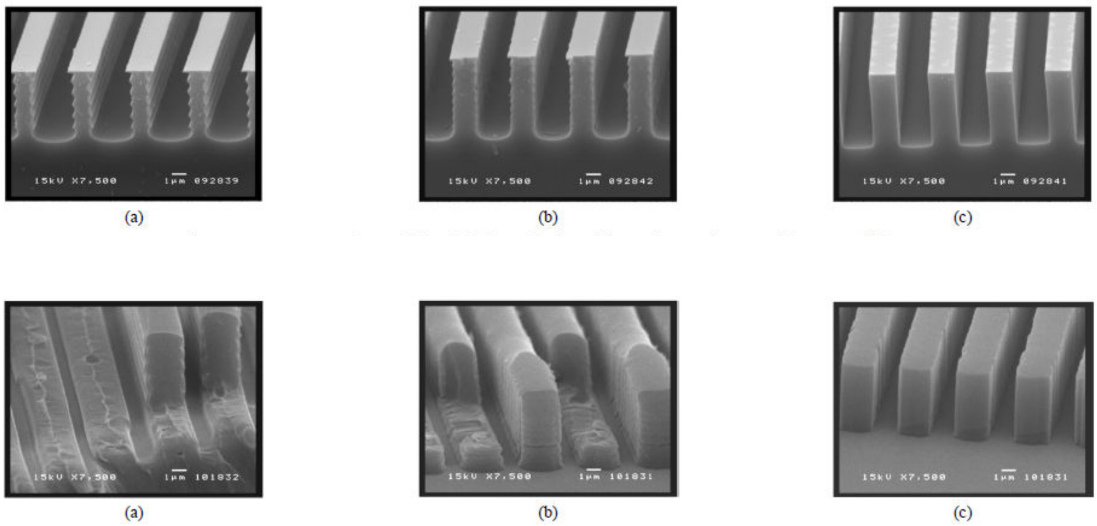

Figure 12: Cross sections of the fabricated Si molds under various etching conditions (top) and cross section of the imprinted PMMA patterns (bottom) [21].

3.3 Definition of demolding and demolding mechanisms

Many steps are necessary to ensure a certain quality of the final product. The bottle-neck of micro structured applications, due to a lack of knowledge are often the last two steps in the injection molding process [37]. These steps are the molding and the demolding of the polymer part. Most difficulties in polymer micro molding are not caused by the filling of the mold, but by demolding. While molding defines the accuracy in which the polymer can reproduce a given structure, demolding defines the separation process of the polymer and the mold. If either one of these two steps is poorly executed the desired quality can not be achieved. Worst case is, that during the demolding process microstructures are deformed or torn apart [47].

Furthermore, it is sometimes suggested that a better molding of the microstructure induces worse demoldability. This can be explained because of the different friction forces that occur in the microstructure. A perfect molding will fill out the microstructure and therefore increase the exerted pressure on the contact surface and subsequently the friction force.

The molding can be managed by adjusting process parameters; e.g. high injection speed and high or long holding pressure lead to better molding. No such simple relations are known for demolding and at some point demolding becomes impossible without major damage to the structured part.

The molding of a micro structure as well as the demolding of a micro structured polymer part has been discussed in different scientific articles. The exerted influence of the demolding on the quality of the final product is described. Figure 13 shows the different mechanisms that occur while demolding the microstructure in the hot embossing process.

The mechanisms that define the demolding are [*32*]:

a) A completely sealed channel structure will be air tight. The impossibility for air to get into the microstructure inhibits demolding due to the vacuum voids generated (shown as (v)).
   This can lead to structural defects like ripping at the micro structure ground or partial ripping. It can also lead to the deformation of the micro structure, e.g. the elongation of an element until the stress and vacuum is released.

b) A single structure is ripped apart due to the high stress level at the bottom of the micro structure.
   Additionally to the stress induced by the vacuum, the local adhesion and friction exert a strain on the micro structure. This can also lead to ripping or narrowing at the bottom of single micro structures.

c) The micro structure can withstand the stress level. Instead the polymer is ripped off the substrate.
   Due to the effects from a) or b) the micro structure is under a certain level of stress. But instead of ripping the weakest link in this case is the substrate which gets ripped off of its base.
   For injection molding this could mean, that the polymer part sticks to the nozzle side of the mold preventing the indented release.

d) Draft angles allow air to easily get into the voids.
   The stress reduction in combination with easier manufacturability of the

stamper is the main reason for the introduction of draft angles and generally improves demoldability.

e) Despite the stress reduction due to the draft angle deformation can occur. The unsymmetrical shrinking onto a draft angle can generate rims in the process of demolding. This can lead to an inhomogeneous deformation of the microstructure.

f) Relaxation of frozen-in strain due to orientation and thermal expansion mismatch can be beneficial for the demoldability. The relaxed micro structure exhibits less local stress and therefore little deformation.

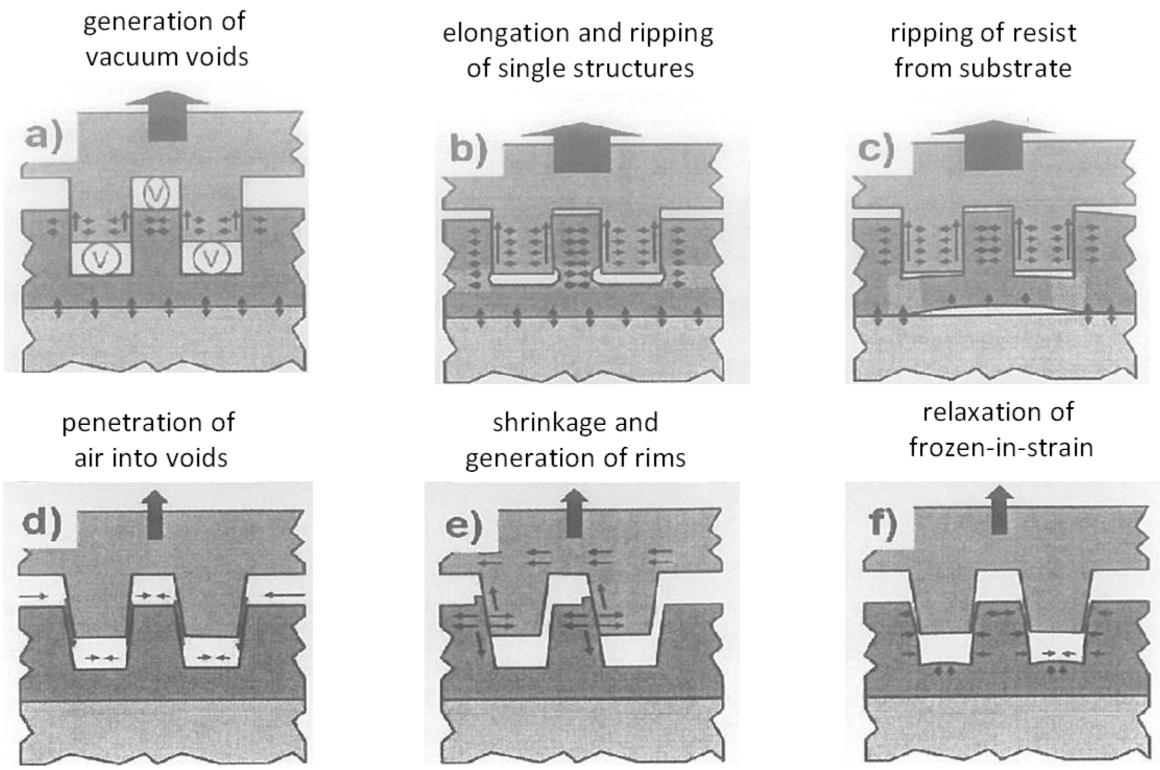

Figure 13: Demolding mechanisms in hot embossing [32].

Figure 13 shows that friction and adhesion between the surfaces and a build up vacuum in the microstructures are responsible for hindered release, inhibited release or damaging of the microstructure during the demolding process. The effects in injection molding are similar to the ones described for hot embossing. The main difference due to the filling of the polymer and the shorter cycle times are polymer orientations and increased shrinking in injection molding. This can lead to higher strain on the polymer and an additional mechanism that is a variation of Figure 13 c) as described before.

Figure 14 is a good example for a possible improvement if one considers the effects previously shown. In this case Merino suggests an implementation of a demolding assisting pneumatic system [*25*]. It illustrates an extensive improvement of the microstructure (1, 2) compared to a process without additional aid (3, 4). The pneumatic system injects air while the polymer part is demolded. The air is injected from the side and will travel alongside the parting plane of the polymer and the mold. This aid reduces the generation of vacuum voids and lowers the stress exerted on the microstructure. Additionally, the demolding force is not solely distributed among the few ejection pins. This reduces local stress and deformation of the whole stamper. This produces a uniform almost non-deformed microstructure.

For the unaided ejection process (3, 4) a combination of effect a) and b) leads to an in homogeneously deformed and elongated micro structure. These tests by Merino have been done for three different PMMA resin types and a variation of different structures. The structures are line elements of six different widths ranging from 125 nm to 800 nm with constant depth of 500 nm. All of them are placed on one silicon wafer and replicated all at once in a hot embossing process. This allows studying the effect of the aid for different polymers and different aspect ratios. While aspect ratios up to 2.5 are demolded perfectly using the pneumatic system, greater aspect ratios will still be damaged. This corresponds to the general assumption that the aspect ratio is a critical parameter for demoldability [*37*]. Still aspect ratio alone is not enough to predict demoldability as aspect ratios up to 20 have been reportedly demolded [*37*]. The pneumatic system may even have more impact when the structural size is getting bigger, e.g. 100 µm. The airflow can more easily enter the microstructures even at higher aspect ratios.

Still Merino disregards the effects among microstructures since all of them are placed adjacent to each other. This is especially true for microstructures in the injection molding process as the shrinking becomes a bigger issue. This understanding of the occurring mechanisms can help to design appropriate demolding-aids for certain applications to increase the production yield and reduce the number of defective parts.

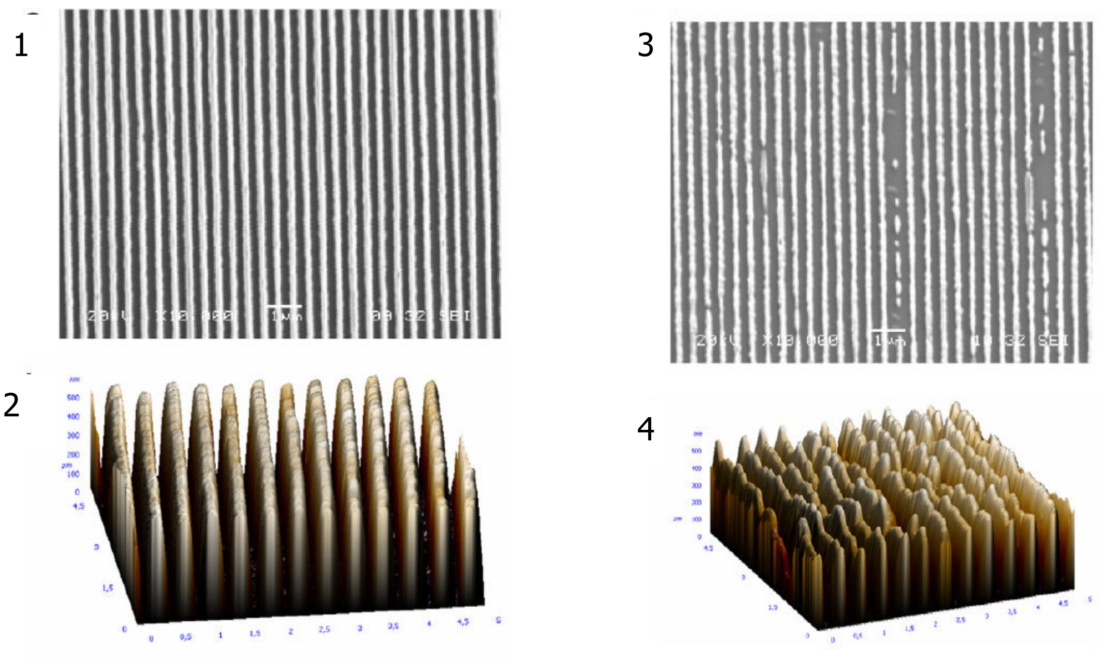

Figure 14: SEM picture of the demolded structure with a pneumatic demolding aid (1, 2) and without an additional demolding aid (3, 4) [25].

3.4 Characterization of demolding

Since many factors influence the demolding behavior, a measurable parameter needs to be defined. As literature suggests [*15*, *36*, *43*] the demolding force acts as an indicator for the demoldability of the polymer part. Increasing forces suggest a worse demolding and more likely of damaging the micro structures.

Figure 15 shows examples for the measured demolding forces in the hot embossing process [*36*]. One can see the force, needed to move the stamper, over time. A better measure would be the force over displacement, which is impossible to measure in this particular setup. As described in 3.5 (page 14) the initial force is positive, due to the embossing, and decreases afterwards. The negative force represents the pulling of the piston after the embossing of the microstructure. The piston moves at a speed of 0.4 mm/min and the force signal is recorded every 20 ms. The peak (marked by pointers) that follows a disruption in the movement, is interpreted as the necessary force to demold the microstructure. Despite the slow demolding speed, the measurement resolution is only 133 nm per measurement step, which limits the reproducibility. For the plain surface in (a), the induced force is 65 N. This is a lot less than the 111 N caused by the structured surface in (b). This is but one example to emphasize the strong relationship between the demolding force and any configuration that may increase or decrease the demoldability. In this case a change in the surface properties of the molded part induces the rise of the demolding force. The higher the demolding force, the poorer the demoldability will be.

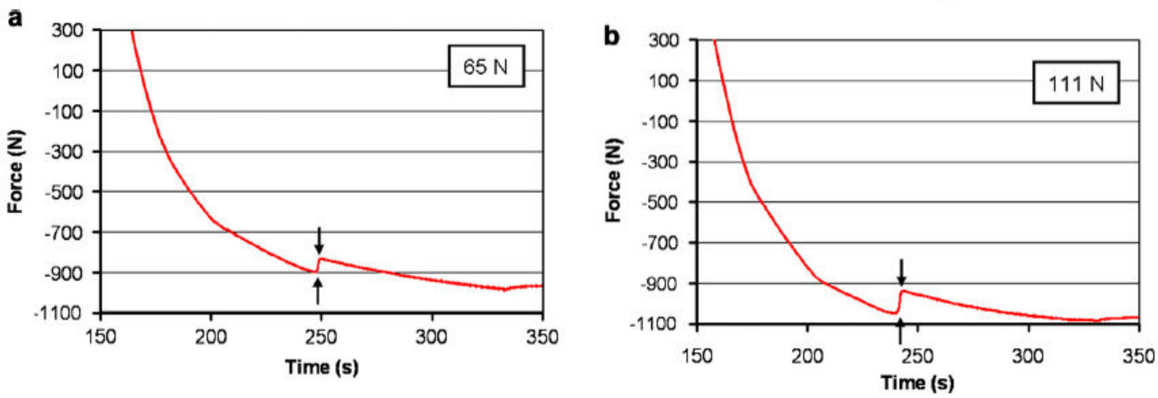

Figure 15: Comparison of the demolding force, (a) without surface structure, (b) with surface structure [36].

Figure 16 shows the important effect of the demolding temperature in hot embossing. The optimal demolding temperature is contrary to intuitive anticipation not at the lowest possible temperatures but at a certain optimal temperature. Even though the measurements consist only of four distinctive points a trend can be seen. It can be wrong to assume that the curve is polynomial and has an explicit minimum. Still the demolding forces increase for low and high temperatures. The optimal temperature must therefore lie in between the rising demolding forces. The measurements of Trabadelo [*36*] therefore point towards an optimal temperature, which is confirmed by Fu [*11*] in experiments and simulation and Song [*34*] again in simulation. The number of measurements was deliberately kept low to ensure reproducible and comparable measurements. This was necessary because the silicon wafer containing the 500 nm pillars will accumulate damage after a certain amount of imprints. At that point the damaged wafer can no longer be used for actual measurements.

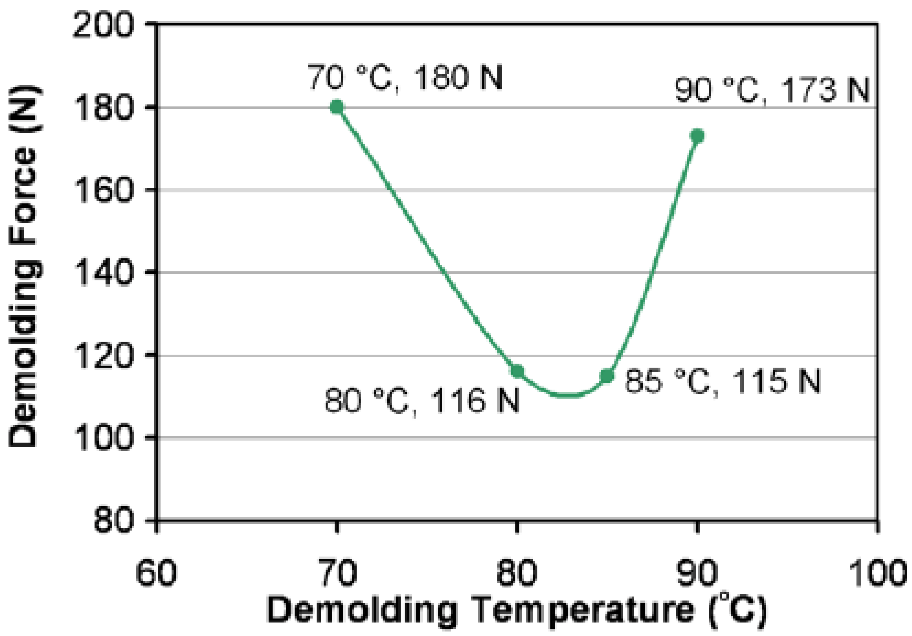

Figure 16: Influence of the demolding temperature on the demolding force in hot embossing [36].

This temperature relation is caused by the overlapping of two different phenomena. Higher temperatures lead to the expansion of the polymer and induce stress as the microstructure presses against the mold. This can be seen in Figure 17 when the diameter of the pillar structure gets bigger than its original 100 µm (positive Δd). This leads to a poor demoldability. On the contrary a long cooling time or low cooling temperatures lead to the shrinking of the polymer onto the structured mold surface. This effect with negative Δd can be seen on the volumetric contraction side of Figure 17. This contraction has a similar effect as the expansion of the polymer and produces a non-stress-free microstructure. The contraction exerts a force on the stamper sidewall which increases the friction force (compare 3.1). Both effects decrease or even inhibit demolding to a certain degree. This suggests that it is true to assume an optimal demolding temperature (Figure 17) for a similar process exists. This point is found at the expansion and contraction equilibrium with the dimensional difference Δd equal to zero [*11*].

The polymer molding- and demolding-temperature can become a critical parameter for replication processes like injection molding or hot embossing. In the molding phase of the replication (molding window) the polymer needs to have the lowest possible viscosity, thus a high mold temperature.

After the molding ends and the demolding begins, no deformation must occur. Therefore, the polymer has to have reached a certain temperature to ensure enough stiffness of the polymer part. A lower temperature in return will increase the production cycle time (cooling time). Despite that, the melt temperature should not be chosen too low as this would unnecessarily increase the polymer viscosity and in the end the will influence molding results [*24*]. Furthermore, it has to be taken into account that there can be different behaviors, e.g. shrinking, of semi-crystalline and amorphous polymers due to their different morphology.

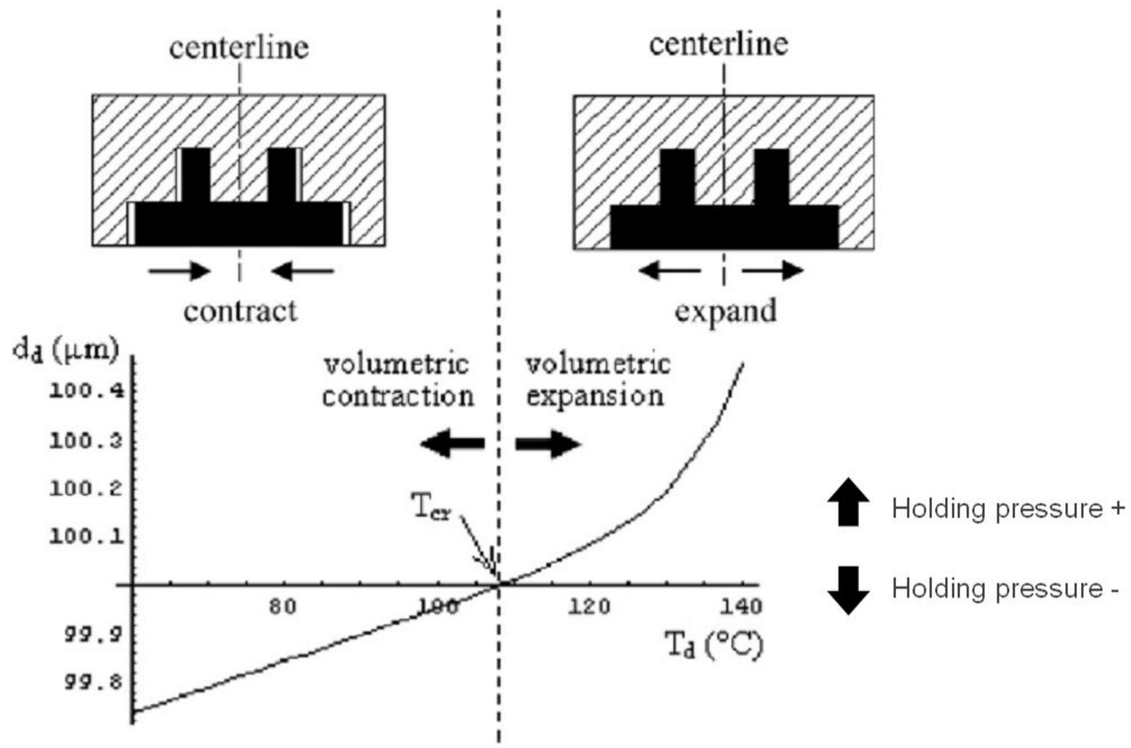

*Figure 17: Thermal expansion and shrinking of the polymer [*11*].*

3.5 Measurement devices to detect the friction and demolding force

Among many polymer testing procedures, few are appropriate for micro structured polymers. Usually two different parameters, i.e. demolding force and friction, are consulted for analytic purposes. Friction measurement has many established and standardized measurement procedures [*4*] and is as described in chapter 3.1 a relevant parameter. The more profound and not so well established measurement tries to characterize the demolding force. Both, the friction and demolding force measurement, are discussed for the injection molding and for the hot embossing process. This is done to see if there are significant differences in the measurement of the hot embossing process and the injection molding process. Especially the cycle time and the shear stress are completely different.

To tackle this matter, a measurement apparatus for injection molding has been introduced by Berger [*4*]. Figure 18 shows a possible solution to measure friction forces in different set ups. A vertical piston can exert a defined normal force (F_n) on the polymer part and ultimately on the surface between the polymer and the changeable insert. This insert is a metallic specimen which can be coated to modify surface parameters. After injection the mold opens, as it would in the regular injection molding cycle. The toothed surface keeps the polymer part in place. This leads to friction between the polymer part and the metallic insert. The mounted load cell measures the resulting force (F_V). This allows calculating μ as described in equation 1. It is to note that μ is not constant and will vary with sliding distance and with sliding speed.

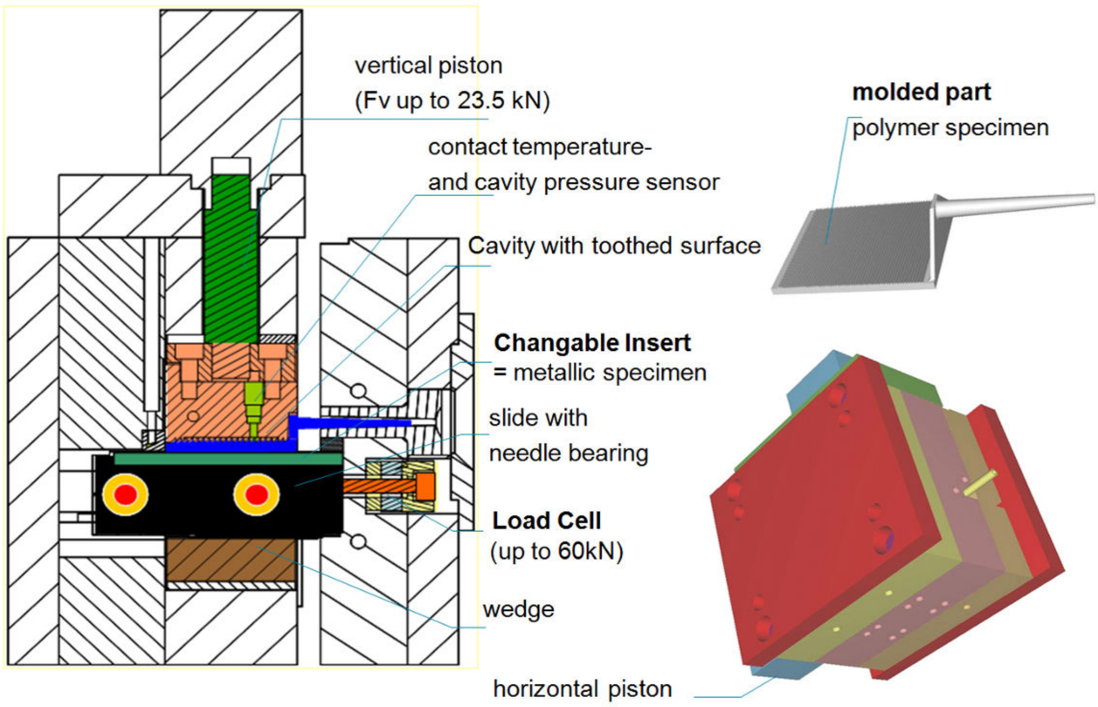

Figure 18: Measurement apparatus for friction coefficients in the injection molding process [4].

Figure 19 shows a possible solution to measure friction forces for the hot embossing process. An adapter similar to the previous piston can pull with a defined force (F_f) or defined velocity to move the metal part upwards gliding alongside the embossed polymer part. The different control is possible because an adapter on the top of the test equipment. This adapter allows a connection to a standard tensile testing machine. The thin polymer foil is fixed in the middle with undercuts and a normal force (F_n) acting on it. The normal force can simultaneously acting as the embossing force and is controlled by a spring and force transducer system. Combined with the heating element, this will allow conducting a hot embossing process before the friction measurement.

This insert is a metallic specimen which can be changed or coated to modify surface parameters.

It is to note that the friction force and ultimately μ is not constant and will vary with sliding distance and with sliding speed.

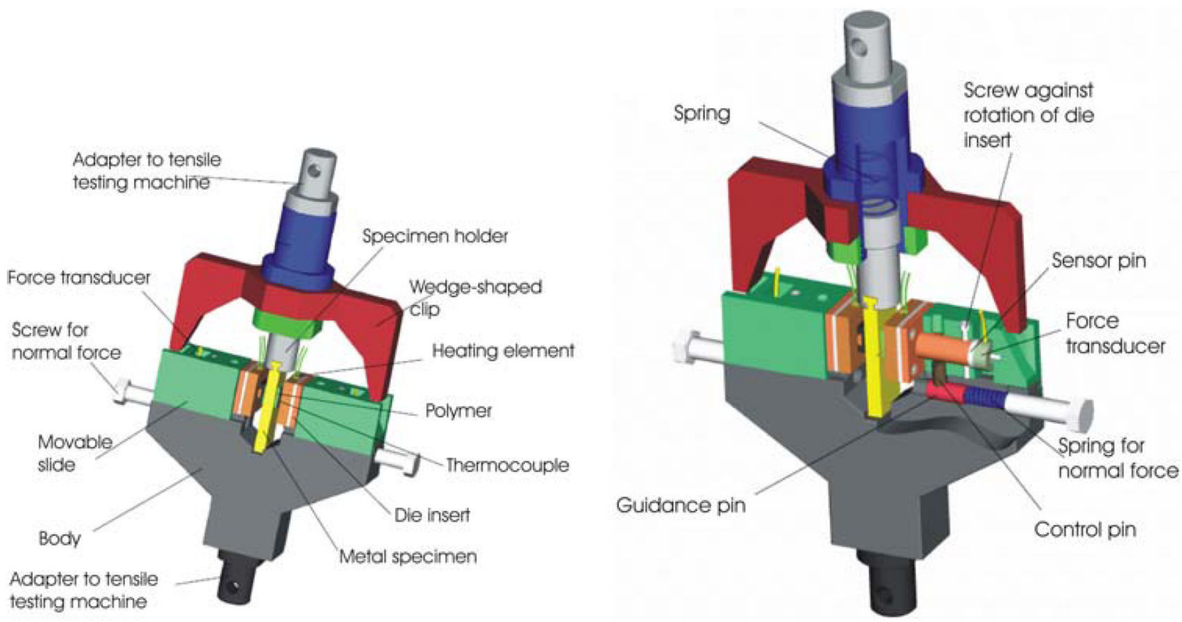

Figure 19: Test arrangement to determine adhesion and friction under typical hot embossing conditions [43].

Figure 20 shows a measurement device by Fu [*11*] for the injection molding process (compare chapter 2.2.1). A load cell is attached to the ejection pins, measuring the force needed to push the polymer part out of the mold cavity. To measure the relative demolding force that is related to the micro structure a plane surface (a) is measured in comparison to a structured surface (b). The difference between these two forces can be seen as the relative demolding force needed to demold a certain microstructure. In this case the tests were done with a 24 times 24 (total of 576) microstructure array with a width of 100 µm and a depth of 200 µm produced by deep reactive ion etching. The schematic of the structured zone is represented as grating of the golden plate Figure 20 (b). The material was a polymer feedstock with no more information given to the reader. The conclusion by Fu [*11*] was that experimental measurements and simulation support the theory of a critical demolding temperature with certain limitations. The critical temperature is pressure-dependent and material-properties-dependent, the critical temperature may not exist for some feedstock or polymers, especially when low injection/packing pressure is used. The isotropic shrinkage assumption is only applicable for variotherm mold or conventional mold with small part size. That is, the analysis is only suitable for the case of micro injection molding using high injection/packing pressure.

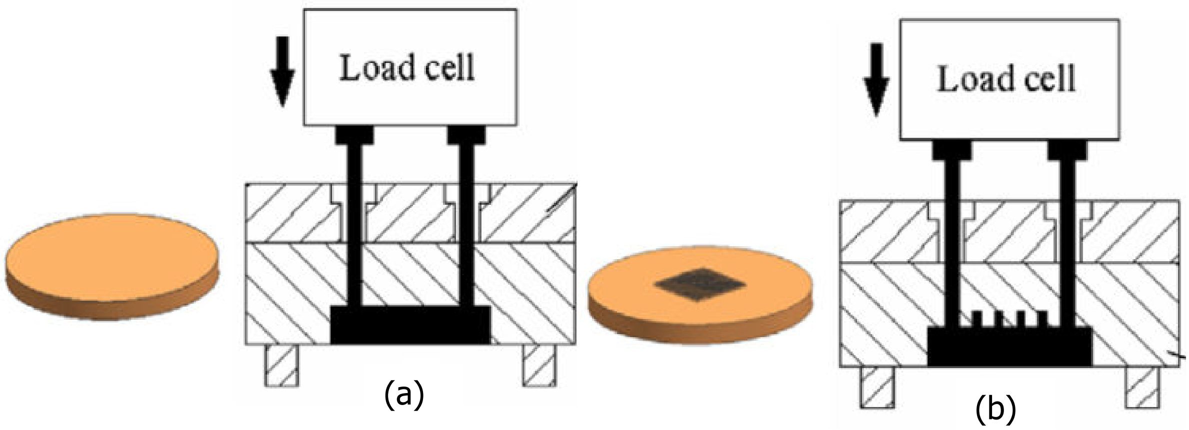

*Figure 20: Schematic of a demolding force measurement device for an injection molding process. In case (a) for a plane surface and (b) a structured surface [*11*].*

For the hot embossing the demolding measurement device is designed by Kawata [*21*] as shown in Figure 21. The mechanism for a hot embossing process right after the part is molded proceeds as described in chapter 2.2.2. The replication of the structure takes place as it usually would for any hot embossing process. Right after the replication, the support that holds the stamper, in this case the metal joint which is attached to a flexible coupling, starts moving upwards. This induces the start of the demolding of the micro structure. The pull-off force used to move the metal joint and ultimately the silicon stamp (si mold) is measured as an excitation in the positive direction acting against the negative pulling force of the micro structure on the PMMA/si Wafer. This force is what is commonly defined as the demolding force. To measure relative forces a calibration with a plane surface like described for the injection molding is possible and done as well. The coupling adds another feature to the demolding setup. The apparatus can, like the friction measurement device, be implemented in a tensile strength measurement device. This allows again for velocity controlled demolding at low movement speeds.

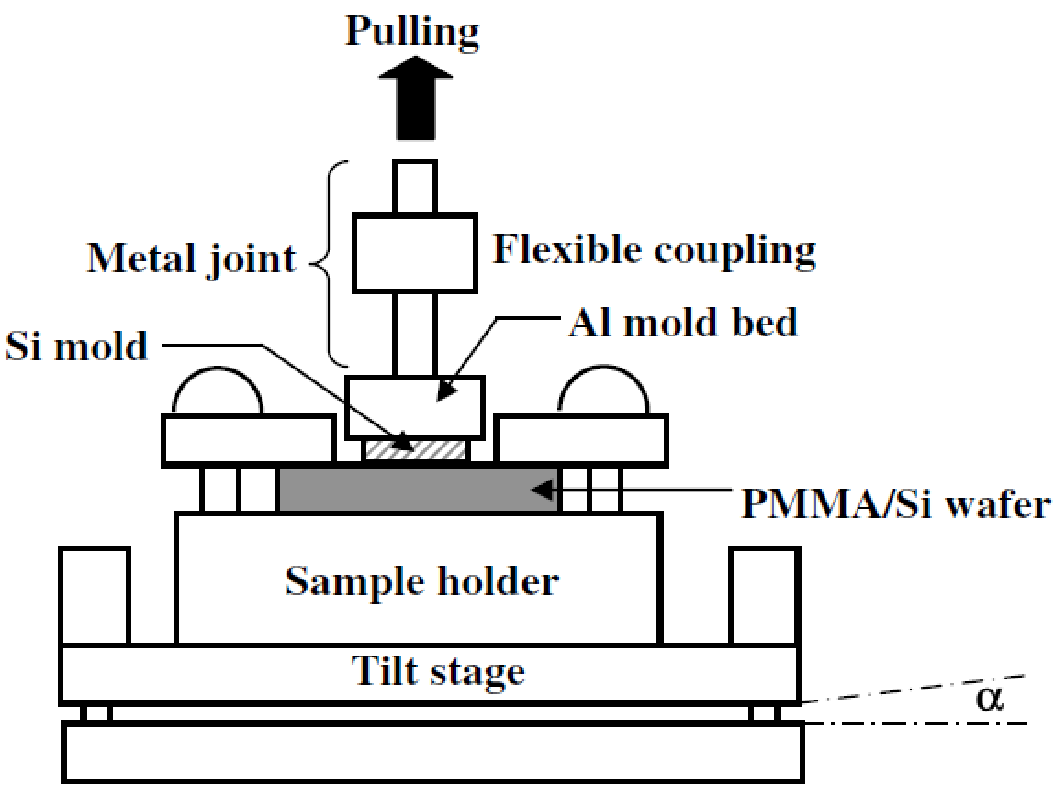

Figure 21: Schematic view of the tool for demolding force measurement in the hot embossing process [21].

3.6 Critical discussion of the evaluated literature

Because of the fact that there are different studies on different subtopics, e.g. polymers, processing or geometry, there is no unified aim. Usama [*37*] points out that due to the ongoing development of micro structured applications, specifications for these applications are hard to come by. What today cannot be manufactured, may tomorrow well be a production standard. This explains the seemingly chaotic published research of different aspects regarding what is currently needed. This leads to structural variety from pillars (Fu [*11*], Kawata [*21*]) or channels (Griffiths [*15*], Merino [*25*]) to rays (Kemmann [22]) or other uncommon structures. Furthermore, the structural size is in some cases 100 nm and in other cases 500 µm. An additional influencing factor is the structural density. While some structures are tested as one single structure, others are placed side to side leaving gaps that are not much bigger than the structure itself. A possible description that is seldom suggested but in my option can help to compare different results would be the ratio of the projected surface area to the actual surface area. This information would at least contain a lot of the information on the chosen geometry in a single dimensionless scalar and can carefully be interpreted as the “amount of interlocking area”, i.e. area that is responsible for the friction force due to demolding in the demolding step.

Sometimes little additional information on the test setup makes it hard to compare different results or compute the area ratio for comparison.

In all papers evaluated in this thesis most of the studies highlight different aspects. The same parameter is seldom investigated twice. Still, findings of influences like demolding temperature or setup changes, e.g. measurement method, of the different studies that were performed, support each other. Unfortunately in many cases even if there is a similar conclusion, a comparison is impossible. This illustrates the need of transferability of the found conclusions to other setups.

This leads to the last and probably biggest problem of evaluating the different publications. The measurement, either done for hot embossing or injection molding, uses a completely different setup. The ejection pins in the injection molding system can bend the polymer specimen and additionally distribute the demolding force unevenly and poorly. In comparison the piston for the hot embossing process bends the polymer upwards which is completely contrary to the injection molding system. Not only the secondary influences due to bending or shrinking are different, but also the evaluation is based on a definition (see 3.5 Measurement devices to detect the friction and demolding force). This allows only for relative measurement for one setup comparing one aspect at a time.

An approach for a suitable measurement device is discussed in chapter 5.6.

4 Main influencing factors

The demolding of micro structures depends on different influencing factors. They can be grouped an in general they are divided into the sections: geometry, process, polymer material and mold (*Figure 22*).

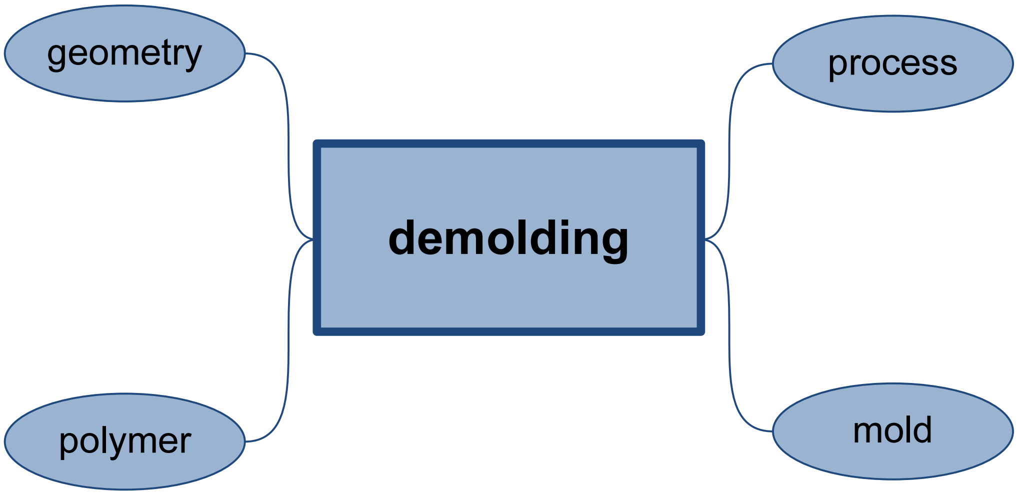

Figure 22: Main influences on the demoldability of micro structured polymer parts.

The most obvious interaction that happens in the process of demolding is the interaction of surfaces. In this case friction leads to the main problems in the demolding of the polymer part. The friction is determined by all of the main influencing factors. The friction depends on the mutual (actual) contact surface and the exerted force between them.

In case of geometry the surface of the mold and the polymer engage. The necessary demolding force is dependent on the interlocking force and area (compare projected area in chapter 3.6) and increases with higher structure density or structures which expose increased mutual surface (e.g. higher aspect ratio). At last the placement of the structure and the structural type, e.g. channels or pillars, can influence the friction due to different shrinking properties (see 4.1 Geometry).

Choosing an appropriate material for the mold influences the friction between the mold and the polymer as well. The polymer type and any used additives change the demolding-behavior, because the polymer may vary in many parameters like the flow ability or the friction coefficient between polymer and mold (see 4.2 Polymer).

In the mold, the friction can be manipulated with the help of different coatings. These are applied to the mold (mostly the insert) and can reduce the friction and therefore directly act on the demolding force (see 3.1 Friction). Any physical or chemical coating changes (ideally decreases) the static and dynamic friction depending on its morphology roughness and material properties. The contact angle is used to give a simple description of the coating properties (see 4.3 Mold and mold coating).

The last parameter to act as a main influence is the replication process itself through optimal process parameters (see 4.4 Process). Any effects of given combinations of polymer, mold material or coating are only good if the process is handled and optimized accordingly.

4.1 Geometry

The geometry, in this case refers to the geometry of the microstructure. Depending on the applications the structures may vary in size and form. While some applications make use of patterned structures, most common micro-fluidic applications utilize channel structures. While patterned surfaces like a moth-eye structure Figure 23 (a) for optical applications often range in the nanometer area, channel structures for lab-on-a-chip applications like Figure 23 (b) are significantly larger. Furthermore in applications there are only a few channels, while a pattern covers the entire surface. This means micro fluidic applications are often a lot less dense (structural density, high projected area). Figure 23 shows how different designs can define the overall surface properties.

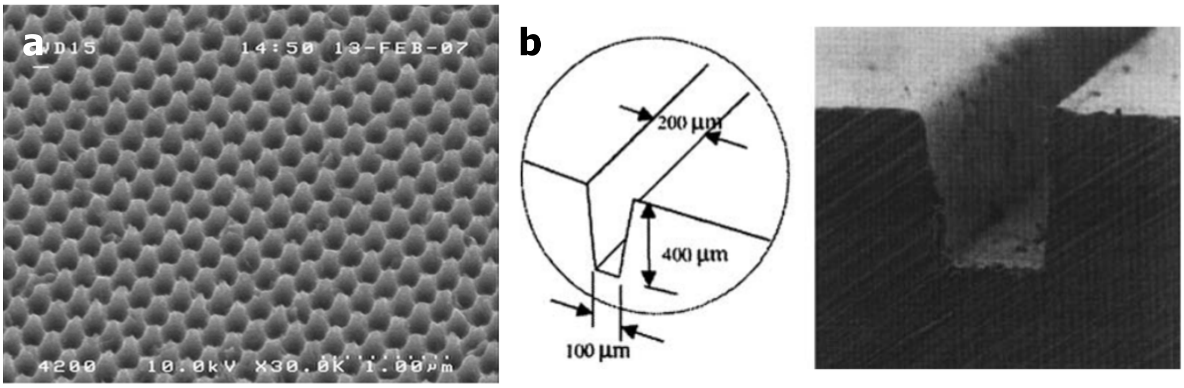

Figure 23: (a) SEM picture of a moth eye patterned structure [35].
(b) Micro channel with draft angle [45].

Figure 24 shows the main geometry parameters for a commonly used channel structure that may influence the demoldability of the polymer part. These include the size of the channel and the proportions (aspect ratio and width) as well as indirect influences of the surface structure like roughness. Depending on the processing (etching, milling, plating … see chapter 5.2) the surface roughness will change.

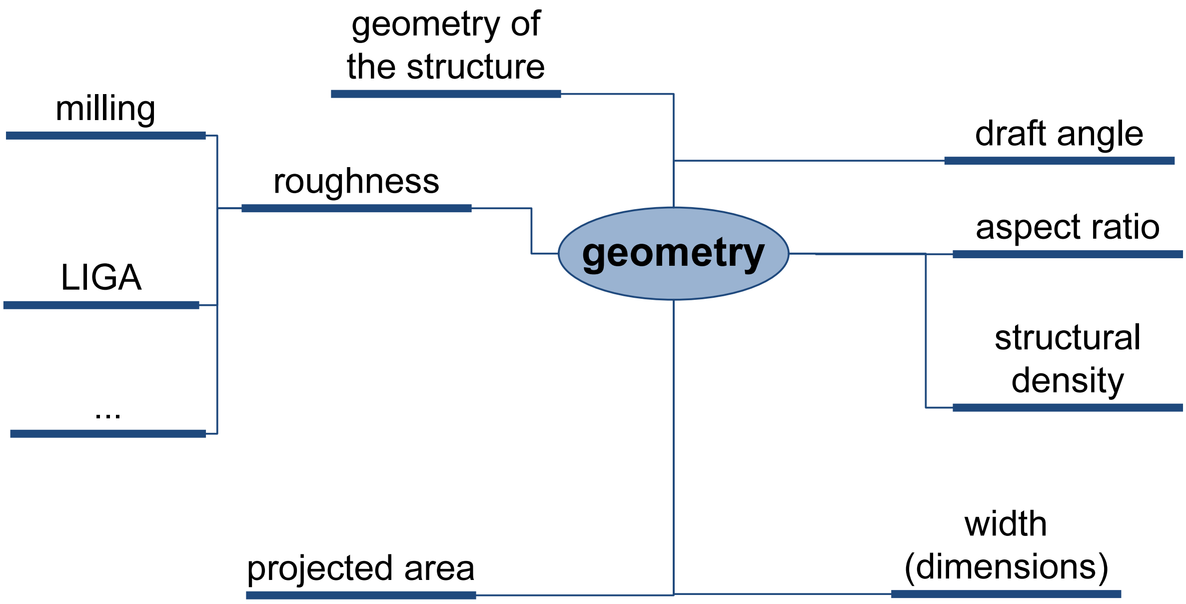

Figure 24: Main geometry influence parameters on the demoldability of micro structures.

Microstructure geometry has one of the greatest influences on the demoldability of the polymer part [*10*, *37*]. Especially the draft angle of the microstructure or its absence can induce sticking of the polymer to the stamper. Furthermore, high aspect ratios (small channel widths compared to high channel depths) will likely induce strong deformation of the structure. And the most complex effects are determined by the structure elements themselves. Hiroaki [*18*] have shown that it is reasonable to propose different channel geometries and vary several aspects. Figure 25 shows the geometries they chose to test. The measurement method is a demolding force measurement in the hot embossing process as explained in chapter 3.5 on page 31.

With this choice of structures Hiroaki [*18*] tries to compare orthogonal structures (a, c) and structures with a draft angle (b, d). Secondly, they tested the influence of a given geometrical variation. In this case the choice was a leveled channel ground (c, d). The measurements of this study show that the draft angle as expected reduces the demolding force.

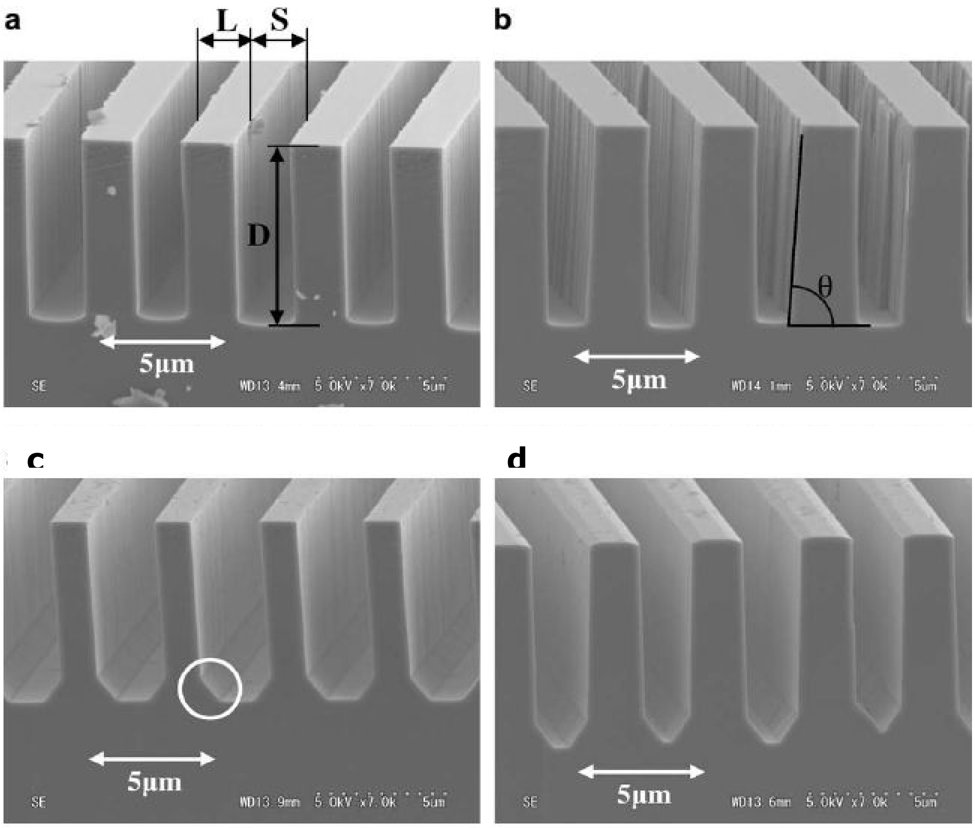

*Figure 25: Different geometries to test the feature size and draft angle influence [*18*].*

Since the draft angle reduces the stress level it is expected that other stress reducing optimizations like the mentioned leveling will have a great effect on the demoldability. Their tests show this assumption to be true, as the structure in (c) and (d) induce even lower demolding forces than the structures in (a) and (b). Hiroakis [*18*] experiments show that a reduction of over 50% indeed is possible. Figure 26 shows that the force drops with the introduction of a draft angle from approximately 0.7 MPa to 0.2 MPa. For the introduction of the leveled channel ground the force drops from approximately 0.7 MPa to 0.4 MPa. The combination of both geometrical alterations yields a force close to 0 MPa.

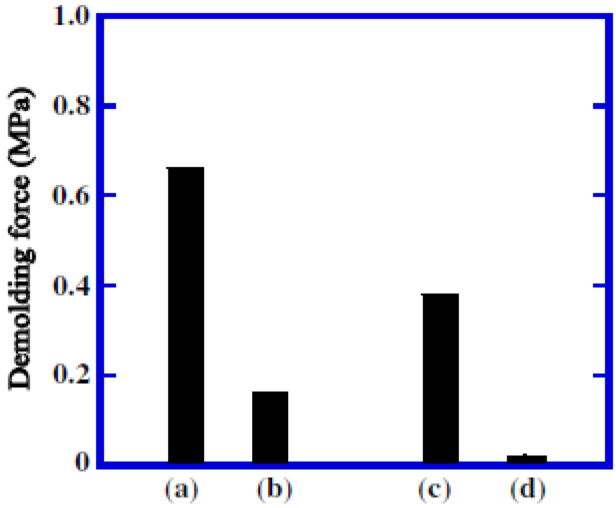

*Figure 26: Demolding forces normalized by total side wall area with a, b, c and d corresponding to the templates of Figure 25 [*18*].*

Similar effects are shown by Zhichao [*48*] in simulation of different geometries. He decoupled the influence of friction and stress induced demolding force. His simulations show that the local shear stress can be up to 20% lower for different friction coefficients (0 and 0.3) and the same polymer (PMMA) and geometry (micro channels). Changes in geometry, in particular the draft angle, can reduce the local shear stress up to 25%. Even though the influence is already bigger than that of friction alone, Zhichao suggests that the influence of the micro geometry itself can be even greater than 25% and must not be neglected.

All the forces for this comparison have been normalized with the total side wall area to ensure that influences from increased sidewall area are filtered out. Unfortunately, the area and the actual measured forces are missing. The knowledge of this area could help to locate influences that were wrongly filtered or to estimate the actual influence of geometrical change.

A similar study by Schmidt [*33*] shows the same results and makes additional effort to compare different geometry elements. Figure 27 shows the demolding force of concentric circles and square grids in comparison to a plain alignement structure. The draftangle is either 0° or 4° and the square grid is tested twice with a different aspect ratio. The lower aspect ratio grid is 400 µm deep while the other one has a depth of 800 µm. Additionally, the experiment with 400 µm depth and 0° draft angle has been done twice to ensure reproducibility. The first thing the diagram shows is, that closed structures like concentric circles can produce an immense leap in the measured demolding force. This occurs due to the shrinking-offset of the structure. This means that a closed structure either shrinks symmetrically towards the shrinking center of the polymer part or asymmetrically due to an offset of the micro structure. In both cases the microstructure acts as a clamp and drastically increases the demolding force. Contrary to the common belief, higher aspect ratio structures will not have a larger clamping force. This is explained because the demolding force is defined as the "peak" (maximum force) of the measured force over time. Higher aspect ratios need more energy - total amount of force over the entire demolding distance - to be demolded and are more likely to be deformed, but this in turn reduces the stress level at the bottom of the structure - due to relaxation - which leads to a lower maximal force (see chapter 3.3).

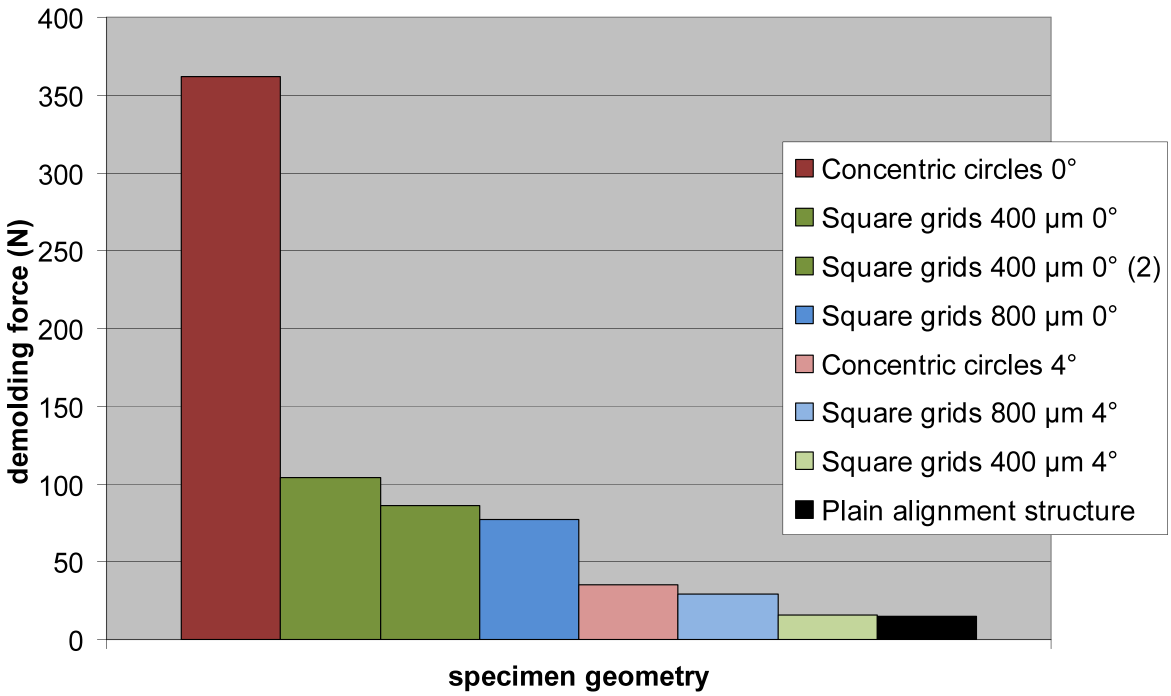

Figure 27: Demoldability of different structures [33].

The same effect of relaxation explains why the situation changes as soon as a draft angle is introduced. Among the structures with a draft angle the ones with lower aspect ratios (400 µm) are easier to demold since the contact surface is smaller. The surface area effect is larger than the stress reduction of the structure with the higher aspect ratio (relaxation). Additionally, as main effect of the draft angle the stress induced by local geometry is improved. This also leads to the conclusion that the relative effect of the draft angles increases with higher stress levels at the bottom of the structure. A good example for this is the reduction of the demolding force in case of the concentric circle from approximately 350 N to 50 N after the implementation of a draft angle.

The explanation of the clamping force upon shrinking of a micro structure on the mold, explains why a structure in form of a ray was early introduced and Micheali and Gärtner even claimed as ideal structure for demolding [26].

To illustrate, Figure 28 shows the vector field of a simplified polymer plate shrinking towards its own center. The length of each arrow represents the displacement of the particular point. Concentric circles as explained will shrink towards the center and exert a clamping force. Any structure that lies on a line intercepting the shrinkage center will produce the best demolding results, as the contact surface pressing against the mold is very small. An example would be the black outline of a structure placed on the “rays” of the vector field which would be ideally placed in according to the shrinkage. The entire outline will remain inside the microstructure after shrinking, unlike the placement of orthogonal channel structures, which will be shown in Figure 29.

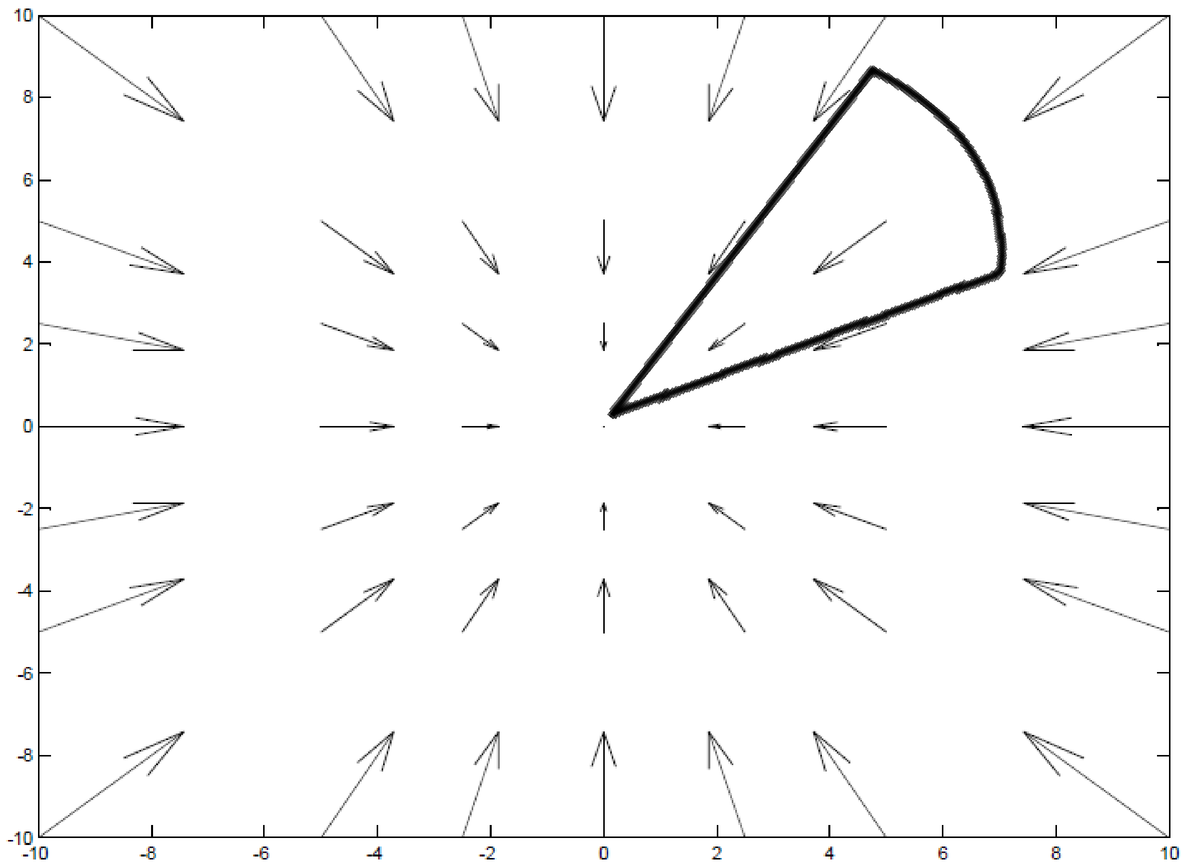

Figure 28: Exemplary shrinkage vector field of a 10 times 10 mm² polymer plate.

The following is a tough experiment based on this shrinkage theory and has yet to be proven.

In the injection molding process the shrinking is not always homogeneous. This leads to an additional effect if the shrinking of the polymer part is mainly in flow direction. A micro fluidic setup of orthogonal channels connecting the same two points can have a completely different demoldability. This happens for example if the setup is rotated for 90 degrees. Figure 29 shows these two setups (microstructures), the shrinkage vector field, the grey original microstructure and the black outline of the same microstructure after shrinking. The black outline indicates that the setup (a) is superior to setup (b). In case (a) the vertical channel is not shrinking and therefore not affected by friction. The horizontal channel is shrinking towards the middle line. The critical friction only acts on the width of the channel. In case (b) the horizontal channel is shrinking towards the middle line which results in the channel width to be the acting surface for the demolding friction. But the vertical channel will shrink also towards the middle line which in this case affects the whole channel length. This will produce a molded structure far worse to demolde than case (a).

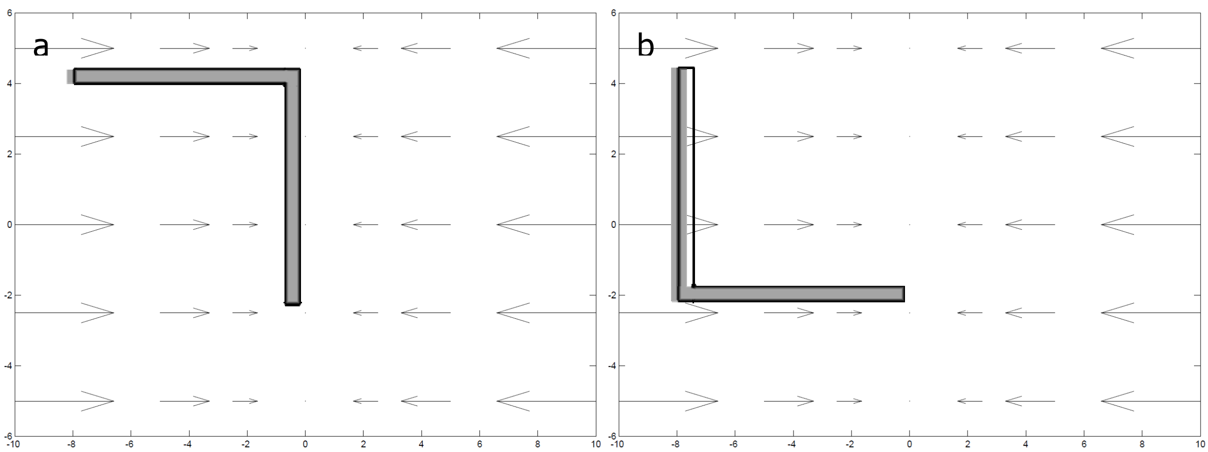

Figure 29: Micro fluidic channels with the same purpose but different placement (a, b) resulting in different shrinking and demoldability.

The previous conclusion and assumptions lead to the simulation done by Guo et al. [*46*]. As mentioned, closed structures will produce a unique state of stress. It is erroneous to assume that this is always a disadvantage. In special cases this effect can be put to good use. As shown in Figure 30 the placement in the hot embossing simulation of the so called stress barrier can affect the local stress distribution. In this case it emphasizes the stress distribution in the PMMA polymer part micro structure at the beginning of the demolding. Remembering the shrinkage vector field the occurrences can be envisioned. The stress barrier, which is placed as far on the outside as possible is strongly exposed to the shrinkage. It shows that the clever placement of an, otherwise unneeded, stress barrier, "absorbs" stress that occurs due to shrinkage. This prevents a stress build up in the enclosed microstructure. The maximum stress of the adjacent microstructure will be reduced from 165.5 MPa to 67.4 MPa [*47*]. Thus, the stress barrier protects the microstructure against high contact stress. The "protected" microstructure has therefore a reduced possibility for any damage. It also agrees with previous studies by Song [*48*] and Worgull [*41*] that suggests that the critical stress is at the bottom of the microstructure.

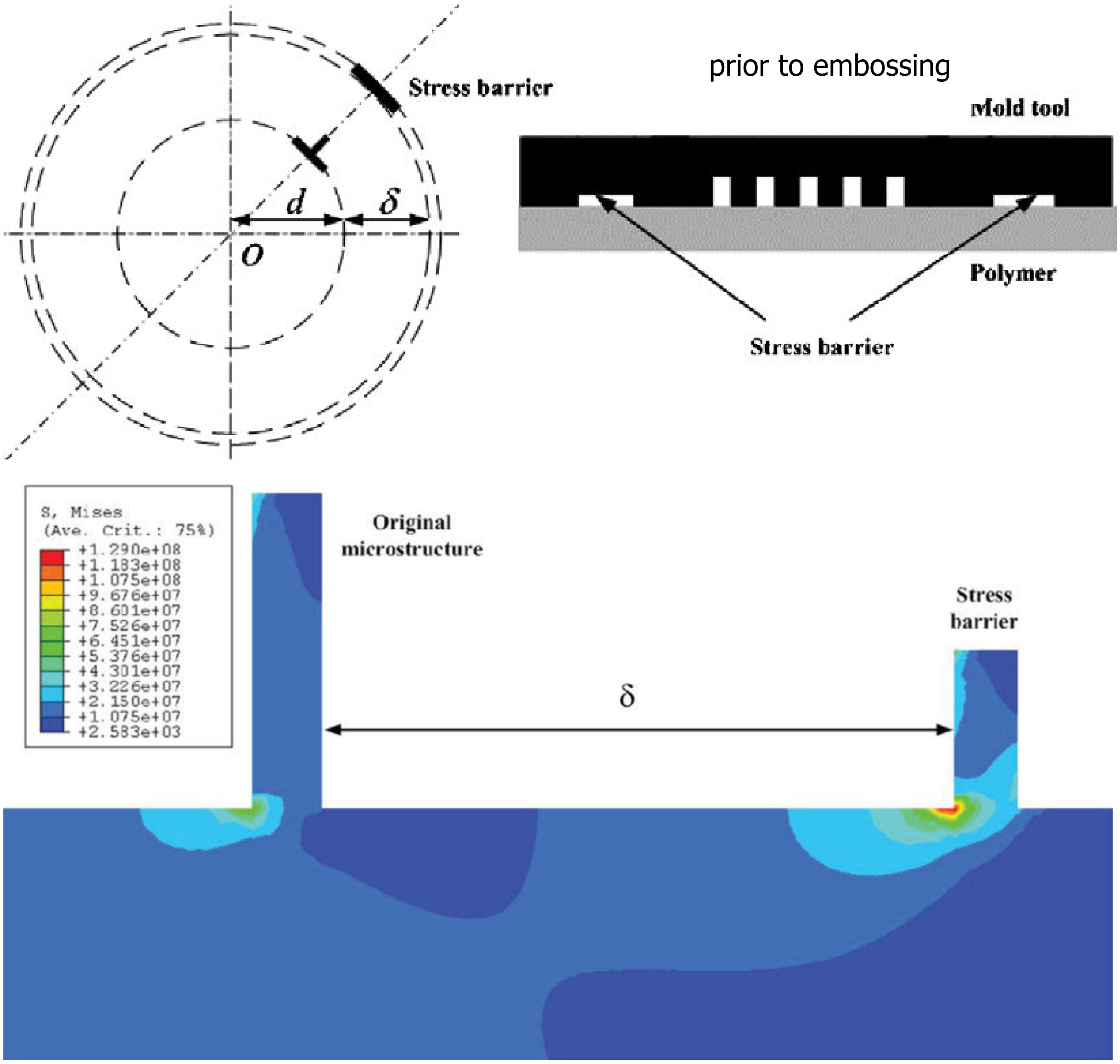

Figure 30: Stress distribution of the microstructure with an auxiliary structure acting as stress barrier [47].

Figure 31 shows the influence of the aspect ratio (channel depth over channel width). The indicated depth ratio represents the aspect ratio, as the PMMA layer thickness and the width of the structure remains the same. It has been discussed before and is in literature always regarded as critical parameter for moldability and demoldability. Simulations by Zhichao [48] show that the influence of the aspect ratio is critical, especially in the area of small ratios (from 0.1 to 0.2). But the stress in the microstructure rises continuously with in this case higher micro structure depth (h).

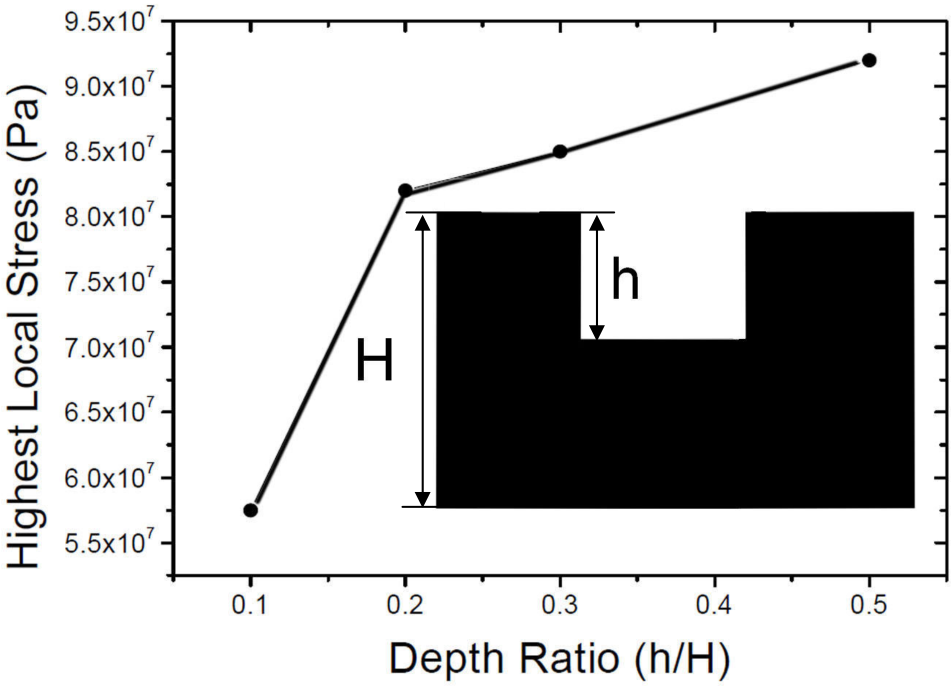

Figure 31: The highest local stress as a function of the depth ratio at the first maximum in the highest local stress versus demolding time curve for different depth ratios [48].

4.2 Polymer

The polymer material choice is crucial. While some materials may induce sticking, others can prove to be almost resistant to demolding problems. This means the material choice is important as it defines the material properties. Many additives can enhance the flow ability and therefore guarantee a better molding; lubricants can reduce friction and improve demolding (Figure 32).

Polymers have a wide variety of properties. It is important to distinguish between processing and application parameters. The challenge is to find or create a material that has all necessary properties for molding and demolding while maintaining the properties needed for the application. Ideally, a polymer for demolding would posses almost no shrinkage and thermal expansion/contraction at all, low surface energies and low friction with various metal surfaces.

Classical processing properties are:

- Glass transition temperature.
- A low viscosity for the injection molding process.
- Thermal expansion/contraction.
- Tendency to shrink.

These properties are important for any injection molding process. A good molding behaviour is even more critical for micro structured zones on the polymer part. Additionally, the particle size of fillers is important. Commonly used glass fibres to enhance mechanical capabilities can inhibit the molding of microstructures. Especially particles that are larger than the micro features of the polymer part, e.g. a channel with a width of 50 µm is in the same size category as a glass fibre.

Material requirements for the application are completely different to the processing requirements. Depending on the field of application optical properties like transparency, transmittance or florescence are important. Even more, chemical stability or in life science biocompatibility are of great importance. Other applications like Figure 1 use electrical potential to enhance separation processes. This requires electrical insulation to suppress unwanted currents or electro osmotic flow. These medical applications unfortunately restrict the choice even further, as the use of most additives is forbidden and allow only a certain approved materials.

Additional to the above mentioned requirements the demands exceed regular injection molding applications requirements. Despite that most micro injection molders use common injection molding grades. This happens because the amounts of polymer needed for these special applications are so low, that almost no material design is feasible so far.

Despite the possible improvements of the demoldability through the material choice, the general idea is to demold any material under given circumstances. This leads to the conclusion that different materials must be tested because their different demolding behaviour for different circumstances needs to be investigated. Still the material choice cannot be disregarded as demolding improvement.

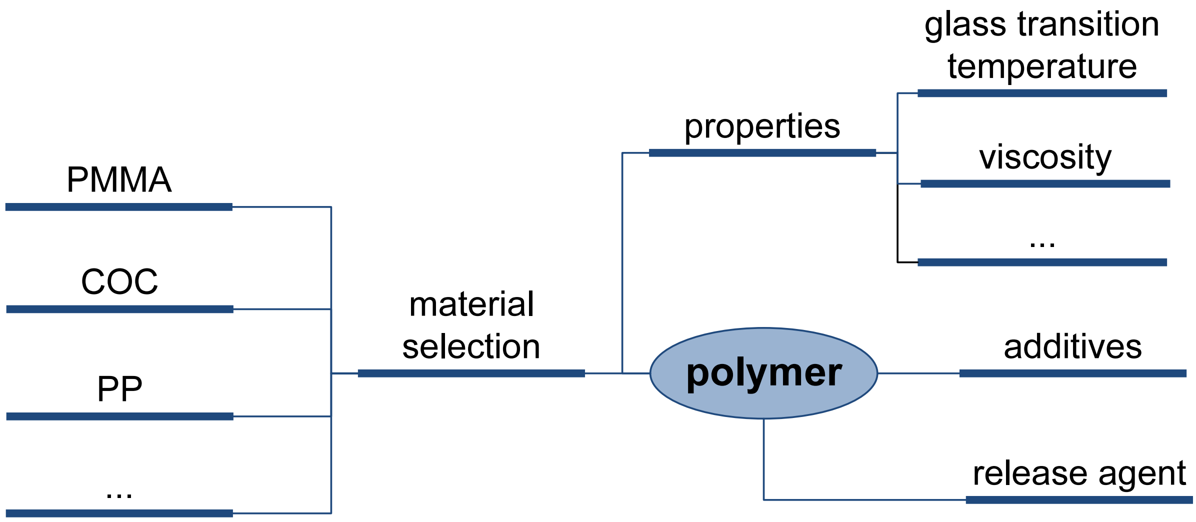

Figure 32: Main material influence parameters on the demoldability of micro structures.

4.3 Mold and mold coating

The mold or the stamper that is placed in the mold is the part that interacts with the polymer. The fact that the final polymer part can be manufactured with different setups leading to (almost) the same outcome allows many possible improvements. Furthermore, unlike the polymer choice these improvements can be done without constraints. A good start to investigate the demolding behaviour is the mold material, in particular the material of the micro structured mold or stamper, which is often steel or nickel (see Figure 33). The stiffness of the chosen material will influence the part dimensions as steel will be more resistant against warpage. On the other hand, surface properties will vary with different morphologies. This effect becomes even more apparent if the stamper is coated. Since it is known that the surface energy and therefore friction and adhesion can vary greatly among different coating materials, a great influence of coatings regarding the demoldability is expected.

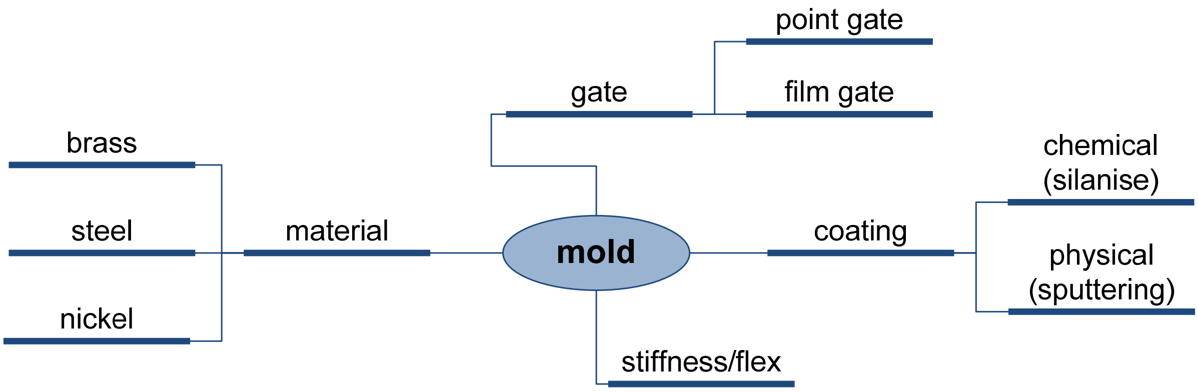

Figure 33: Mold properties that can influence the demoldability of micro structures.

Coating in this case is defined as the deposition of a material on the stamper. Table 4 shows how the demolding force varies with coatings of the interacting area in the mold [*44*]. In this example the demolding force was 340 N for an uncoated pin with PMMA. The mold was then coated with a flour carbon based coating. The coating was checked if it had properly formed, was then washed and prepared for the injection process. After an unstable starting phase - approximately 10 injection shots - the coated mold yielded a force of only 140 -170 N. However, there was a loss of effectiveness after a certain number of molding cycles. This can be seen in the rise of the demolding force after 13,000 shots to 280 N. After rewashing the force dropped again to the initial 140 – 170 N. Finally after 20,000 shots the demolding resistance went back to the starting value of 340 N. This leads to three conclusions:

- The demolding force depends on the coating of the mold and can thereby be improved.
- The coating may not be stable and can lose effectiveness.
- There is a certain amount of interaction and mixing of the polymer and the coating (contamination).

An unstable coating can occur as the detachment of the coating after a certain process time or due to contamination of the coating. In the study performed by Yamamoto [*44*] no degradation of the coating was observed, since the washing of the die restored the positive coating effects almost to the initial level. The first 10 injection shots are necessary to form a stable process. In these steps the coating becomes contaminated until there is a stable contamination. The polymer contamination of the coating lasts for several thousand shots and furthermore explains, why similar contact angles yield different demolding forces (80°-340N, 85°-270N, 90°-340N).

The delamination that can happen to the coating can leave unwanted remains on the polymer. In some cases these remains may be fatal for the medical application and make the coating inapplicable. This has to be checked as coatings may behave completely different.

Important additional information of the study performed by Yamamoto can be gained through the observation of the contact angle. The wetting of the surface (contact angle) only describes the interaction of the coated surface and water or a solvent. It is not evident that it should give any information about the interaction of the polymer with the given surface. Still this is true as the study shows, that the increasing of the contact angle is accompanied by a dropping demolding resistance.

Table 4: The relationship between the demolding resistance and the contact angle of water on a core pin at crucial times during the molding run [44].

Experimental state/number of molding shots	Demolding resistance	Contact angle
Ejector operation load	4–7 N	–
Untreated pin after initial washing	340 N	80°
After corona discharge treatment	–	15°
Chemically adsorbed film treatment	–	115°
After final die washing	140–170 N	120°
After 13,000 shots	280 N	85°
After rewashing the die	140–170 N	105°
After 20,000 shots	340 N	90°

Although many coatings have already been tested for different applications which may allow conclusions for the use in micro structured applications, most knowledge is in the area of friction and wear resistance.

Heinze [*19*] shows the application of different coatings in injection units. Titanium and Chromium based coatings are in these cases very promising regarding their wear resistance. Chuna [*8*] also suggests the use of Chrome based coatings and points out that it can lower the friction coefficient as well.

Miikkulainen [*27*] shows that nitride coatings, tungsten and molybdenum provide a good protection of the stamper against abrasion or destruction. Furthermore, the adhesion to a nickel stamper was strong enough to endure over 10,000 shots with PC (Poylcarbonate) and PMP (Poylmethylpentene). He also points out that in his case all coatings were monolayers with a thickness less than 20 nm. The same properties are true for perfluorinated silane. They also reveal good protective properties while maintaining an extremely small layer thickness. Tribological tests show that the silane based coating is less stable than metal based ones, but still sufficient for the injection molding process.

Griffiths [*15*] tested the influence of two coatings (amorphous DLC and SiOC) on two polymers (PC and ABS) and concluded that a great improvement through coating is possible. His parameter study shows, that process parameters need to be optimized for each material combination and do not relate among different polymers.

Figure 34 shows the surface energy of different materials considering the polar and disperse component. The surface energy is measured through the contact angle (compare 3.2) using a polar and non-polar solvent. These contact angle values allow, using the not explicitly described Owens and Wendt method, to calculate the respective surface energy. Surface energy is a good indicator for the expected adhesion [*1*]. Adhesion plays a lead role for the demoldability of a micro structured polymer part (compare 3.3) and can help to predict of the influence of different coatings on the demolding force by considering their surface energy. This leads to the first assumption that titanium nitride, compared to a graphite based coating, will yield a lower demolding force. Further investigations need to consider the polar and dispersive part of the surface energy. This can lead to different view of this matter, as CrN will be ranged lower if only the polar or dispersive part is singled out. In fact the interaction will depend on the polymer – polar versus non-polar, e.g. polypropylene has no polar parts. The applicability will therefore not only depend on the surface energy as a sole “number” but on the resulting interaction (polar-polar, dispersive-dispersive).

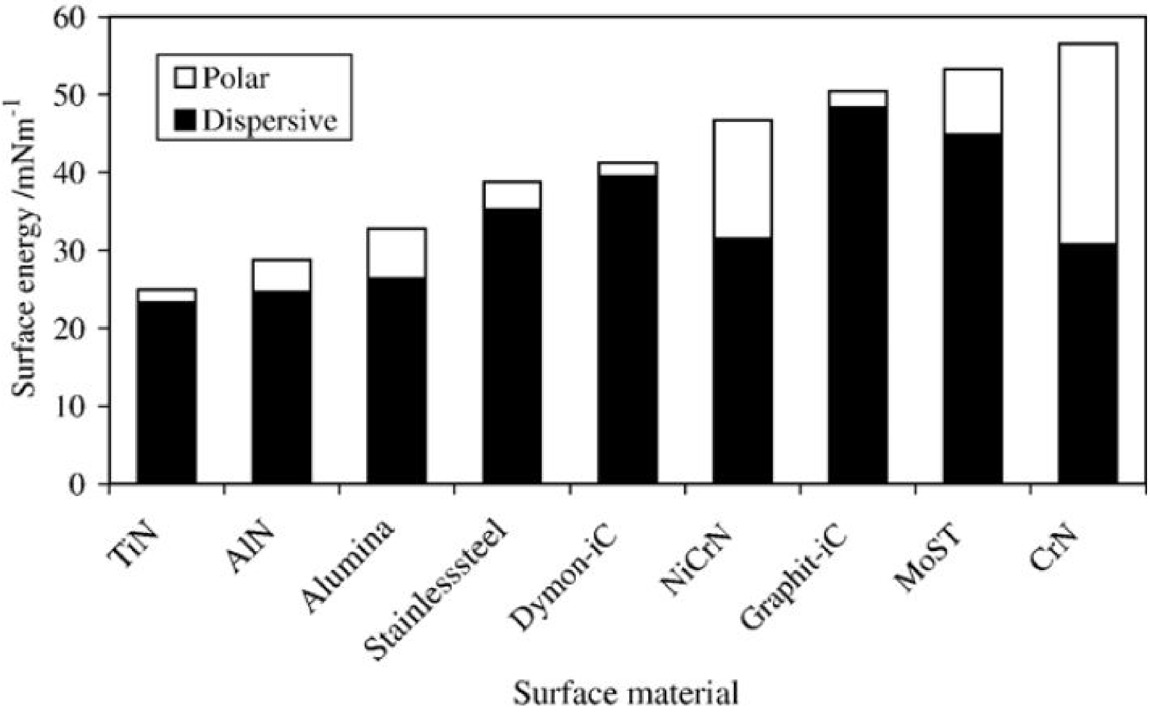

Figure 34: Surface energies of different materials calculated using the Owens and Wendt method [28].

4.4 Process

Several process parameters define the replication process (see 2.2 Replication). Good processing parameters are needed to ensure the quality of the final part and a short cycle time. For economic efficiency the cycle time is lowered to the least possible value with the help of an expensive and complex heating and cooling systems (compare 2.2.3). The mainly altered parameters are temperatures and pressures (see Figure 35). Temperature history will effectively change the filling behavior, the polymer shrinkage and the demolding. The pressure will counteract the shrinking and ensure the maintaining of the desired part dimensions. While the parameters like injection speed and vacuum are responsible for a good molding, demolding strongly depends on the demolding temperature and holding pressure (shrinking).

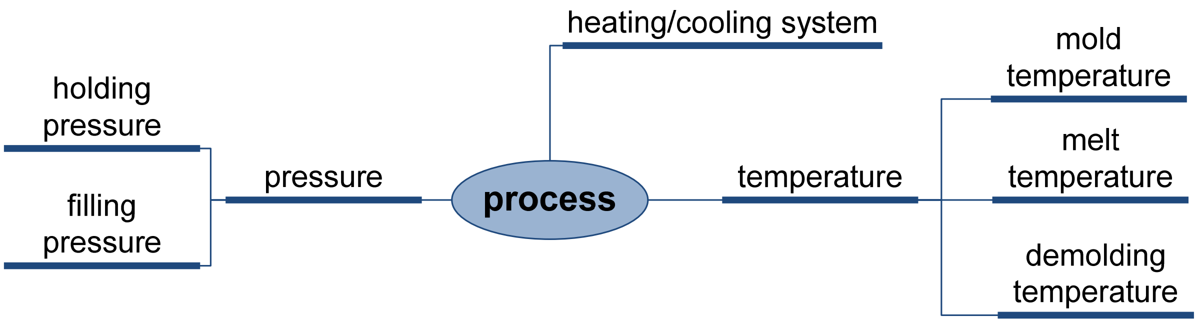

Figure 35: Main process influence parameters on the demoldability of micro structures.

Figure 36 shows the outcome of the same line grating structure in PMMA at different demolding temperatures. These experiments done by Zhichao [*48*] provide the same conclusions as the one done by Trabadelo [*36*] (compare 3.4). Low temperatures in this case 25°C will increase the stiffness of the polymer and wide areas will rip in the demolding process. In contrast at 100°C the polymer will be rather ductile. This will lead to local warpage and deformation of the microstructure in the demolding process. 70°C not only produces the most accurate reproduction of the grating but also the lowest demolding force of approximately 10 N compared to 80 N at 25°C and 50 N at 100°C.

The measurements by Zhichao [*48*] were done on an adapted mechanical tester from MTS functioning like a hot embossing machine.

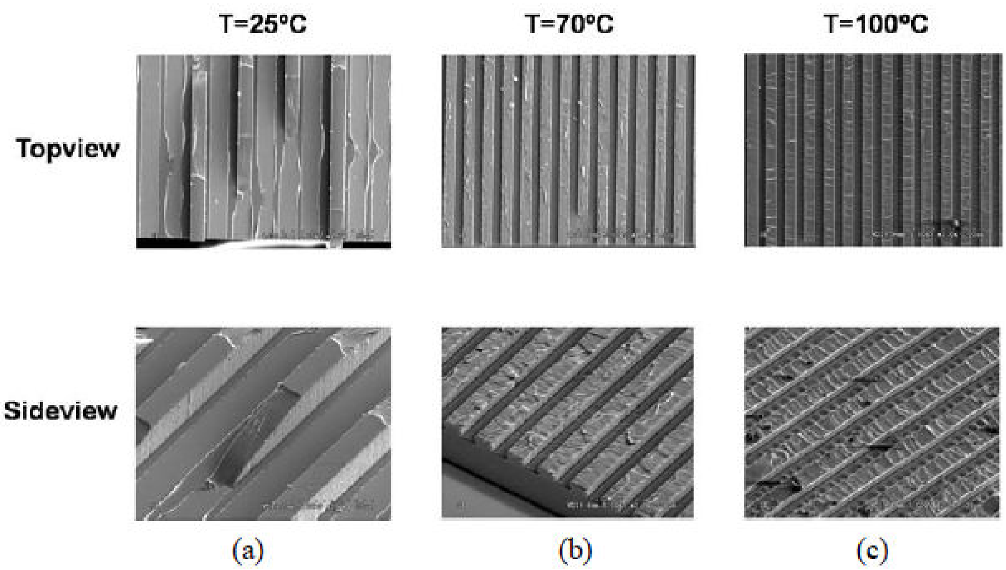

Figure 36: Imprinted PMMA patterns (line gratings) at different demolding temperatures of (a) 25°C, (b) 70°C and (c) 100°C [48].

4.5 Summary of the main influences

Figure 37 shows a schematic overview of important influencing parameters on the demolding force. The diagrams represent the relation as expected by the author. The y-axis in all cases represents the demolding force. The x-axis represents the respective parameter. The following parameters are illustrated:

- The demolding temperature, which is measured at the onset of the demolding, shows the suggested optimal temperature at the minimum of the demolding force.
- The flow distance implies the distance of the microstructure from the injection gate. Further distances lead to higher demolding forces.
- The holding pressure reduces shrinkage and at the same time the demolding force.
- The draft angle of the microstructure reduces the demolding force drastically until its effect on the demolding force diminishes.
- Higher aspect ratios (depth to width) starting at zero (no structures) will systematically increase the demolding force until demolding and structural deformations get out of hand.
- Structural density starting at “not structures” as well will have the same tendency as the aspect ratio with less inclination to demolding failure.
- The roughness, especially the sidewall roughness, will increase the interaction of the polymer and the mold and finally the demolding force as well.
- Surface energy and friction coefficient are hard to separate and will both directly act upon the demolding force.

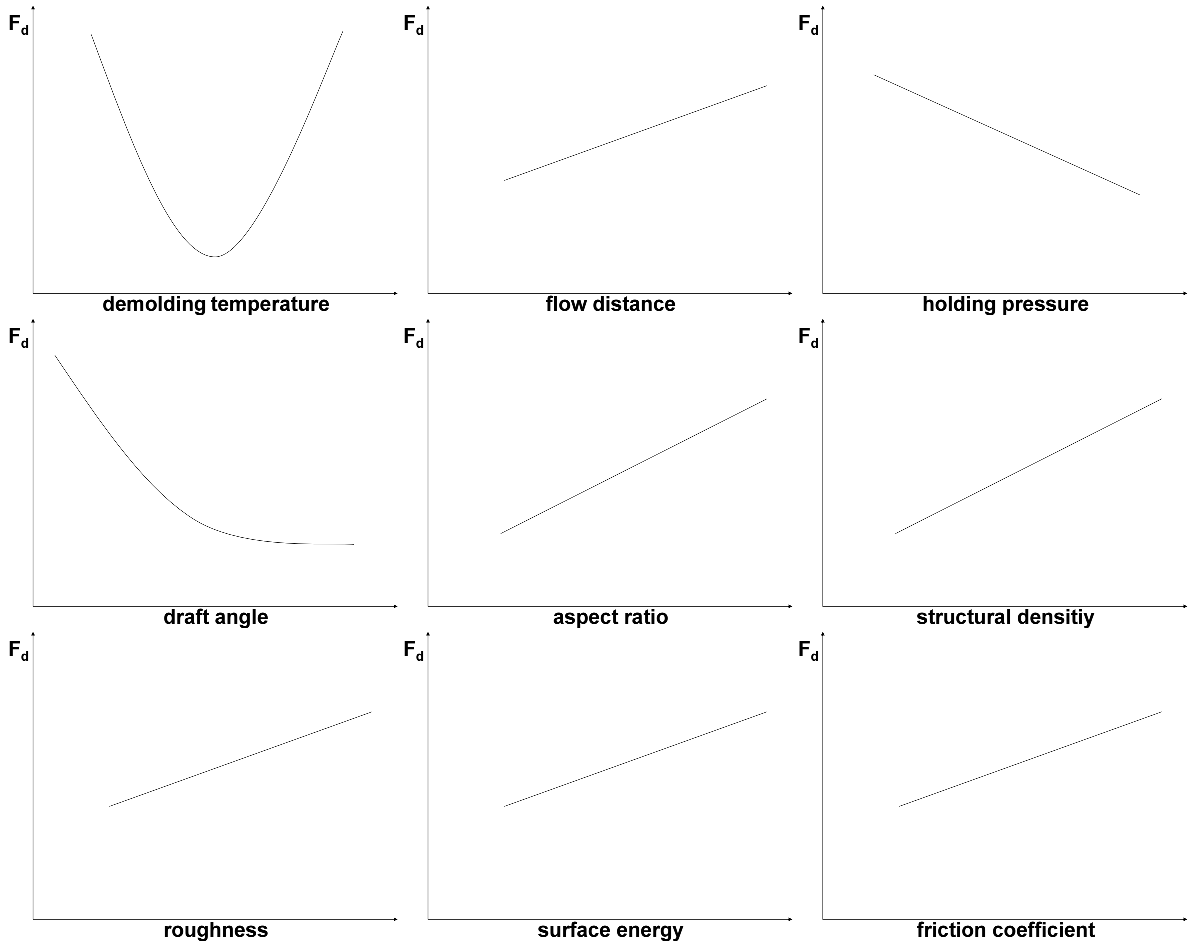

Figure 37: Schematic diagrams to illustrate the effects of different parameters on the demolding force F_d.

The geometry of the micro structure contains several parameters like width, depth, aspect ratio or draft angle, which makes it complex to study although the effects are most likely to be the strongest. The test will be expensive and time consuming because many variations need to be studied. Furthermore, improvements that can be achieved through geometry related knowledge can prove not to be applicable for many applications, e.g. if the customer defines the micro structure or the functionality limits the necessary changes.

Coating is generally a “yes it improves the demolding” or “no it doesn’t” decision. So it is feasible to test different pairings of coating and polymer to assess their compatibility. Since a mold coating can be picked independently from any application, neither the functionality, nor the application design can present a limitation. The only limitation can be a non wear resistant coating that can leave remains on the polymer application.

Polymers will be varied in any case since many products use different materials and at least some of them should be tested. It is important that only certain materials are tested because lots of state of the art processes use lubricants or different additives to improve the demoldability. These enhancements reduce the friction coefficient or the surface energy along with general improvements of other polymer properties. Unfortunately any additive will need to be approved for medical use. This limitation makes it almost impossible to use any polymer fillers that as an enhancement.

The measurement of the demoldability remains complicated in all these test scenarios. The molding can be easily characterized by measuring the deflection of the molded part to the original structure. But demoldability is no parameter itself. It can only be quantified by an artificial definition as the force that is needed to separate the polymer and the mold. Even with this definition the measurement remains tricky and is the subject of future work.
Only coating retains a way of estimating probable differences in the demoldability, without demolding force measurements. This is possible by measuring the contact angle as a reference instead of the friction or demolding force, which will at least provide some general knowledge about the expected interaction of the mating partners.

The screening of the four main influences, geometry, coating, polymer and process, helps to estimate the feasibility of a parameter study for upcoming tests.

Table 5 arranges three of these parameters estimating its economic repercussion. The process parameter is not regarded in this estimation as it can and should be tested for any other parameter chosen to investigate. This helps to evaluate the situation and support the choice which parameter to prioritize and analyze first.

The feasibility screening shows that the focus of the second part of this work is solely on the design of experiment focusing on reasonable coating and polymer combinations.

Table 5: Economic overview of the different approaches to improve the demoldability.

change of / effect on	**geometry**	**coating**	**polymer**
production	expensive, time-consuming, extern manufacturing,	cheap, less time-consuming, intern/extern manufacturing	cheap, less time-consuming, extern
influence	strong effect	Surface energy: Influence defined in literature	known dependence (lubricants)
measurement of the effect	Complicated, expensive	easy (contact angle), cheap	complicated, cheap
limitations	defined by the customer	no restrictions	strongly defined by the customer/application

bad	average	good

5 Test chip and planned experiments

5.1 Definition of test structure

For the purpose of testing the different defined parameters that affect demoldability, i.e. geometry, coatings, polymer and process, a suitable test structure needs to be defined. This includes the overall part geometry and the implemented surface structure. This design suggestion for the structure and the chip geometry will be referred to as “test chip” in the following. Figure 38 shows the commonly used 1 – 3 mm thick micro slide format (ms-format). The ms-format is a standardized formate for many applications and is therefore used as a reference for the macro geometry. Then a placement of the 3 structured zones is suggested. The idea was to place the surface structure three times on a micro slide to distinguish between near-, middle- and far-gate-influences. More structured zones will increase the demolding force but will also lead to conclusions about the molding of the micro structures depending on its position on the insert. This could help to point out differences in moldability and demoldability caused by the covered flow distance.

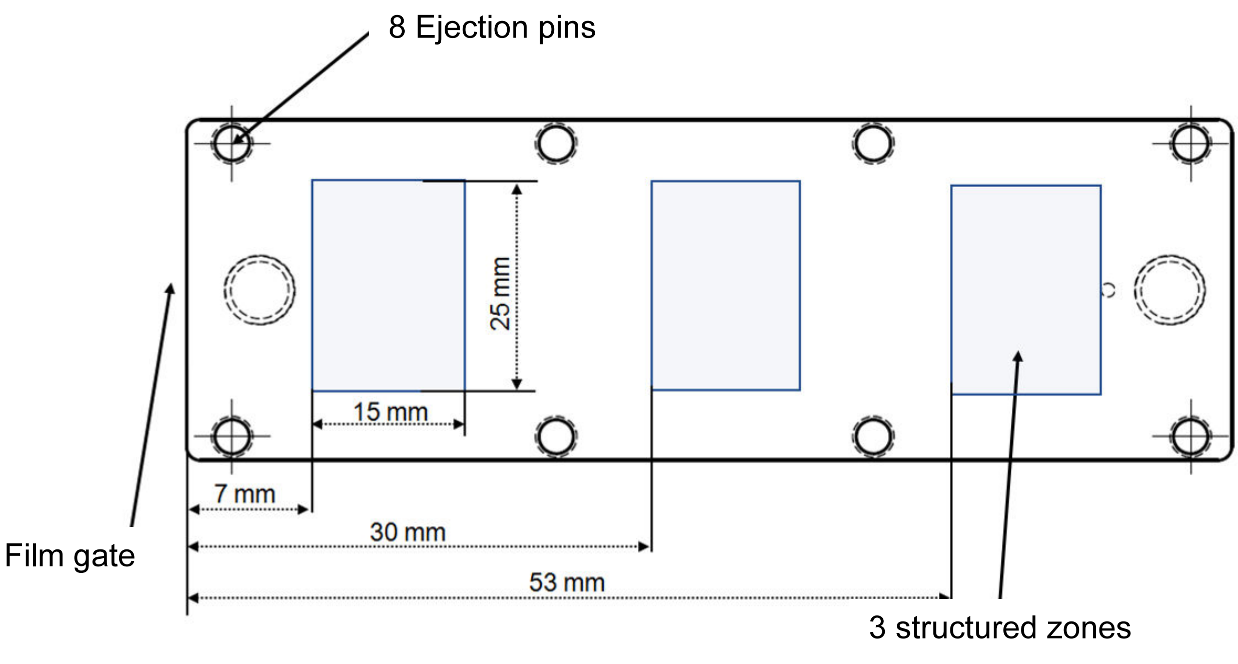

Figure 38: Layout proposal for the test chip.

The most important necessity for the structure is to represent the different most common applications used for medical applications. This ensures comparability of the measurements to the presently used structures. All the gained knowledge can be easily transferred immediately to improve currently running industrial developments and processes. Moreover, the knowledge that can be accumulated through testing is strongly related to the experimental setup. This means, that if possible the test chip should allow direct conclusions to the origin of any given influence. Ideally, only one influence will be tested at the same time. This limits the complexity of the design, since a simpler structure allows reducing the number of unknown influences. An appropriate choice between similarity to application and a solely scientific setup is necessary. Table 6 shows the possible range for structure geometries that harmonizes with many different life science applications. Furthermore, these are all element sizes that can be easily produced in a light exposure - and a consecutive electroplating - process.

Table 6: Common range for micro structured element sizes for medical applications.

	channel	bar	pillar	bore	effect structures
height or depth (µm)	10-100	10-100	10-100	10-100	1-100
aspect ratio (height/width)	0.5-5	0.5-5	0.5-5	0.5-5	0.5-3
length (µm)	>100	>100	-	-	pattern

The next steps were to choose types of structures and, more specifically, a combination of different types. Since an interaction between different structures is expected, the setup has to be chosen carefully. To reduce the complexity of the test chip as many restrictions as possible were postulated:

- The structure should be symmetric at least in direction of the polymer flow.
- All chosen structure elements should have the same dimension (depth, width and aspect ratio).
- Structural density should be low.
- The draft angle is constant.
- Channels and bars, or pillars and bores are not mixed in one layout. The structures are either uniformly elevated or immersed.
- No effect structures will be used.
- Inner structural interaction will be minimized, enough “safety” distance between elements (e.g. distance between two channels to minimize the

interaction between those two, ranging from two times the channel width to six times the channel width).

The restrictions gained through the simplification, drastically reduced the available choices and make it easier to pick structures for a certain combination of structural elements.

50 µm elements were chosen for the micro structures as a representative mean value of different values from medical applications. The aspect ratio was chosen to be 1 out of commonness and for being a good mean value.

After defining the boundary conditions, three variables remained undecided:

- The position of the microstructure on the chip.
- The orientation of the structure (if not invariant under rotation).
- The draft angle.

The position on the chip was decided in cooperation with the scientific advisors to be in the center of a micro slide chip. Figure 39 shows the proposal from Figure 38 on the left and on the right a subsequent modification. The stamper in form of a circle rather than a micro slide is a mold design requirement. The demolded part remains in micro slide format. One structure on the test chip is sufficient to measure the demolding force. Here green indicates the nickel or steel insert, blue the structured zone and red a symmetric fraction of the structure which is defined later in greater detail.

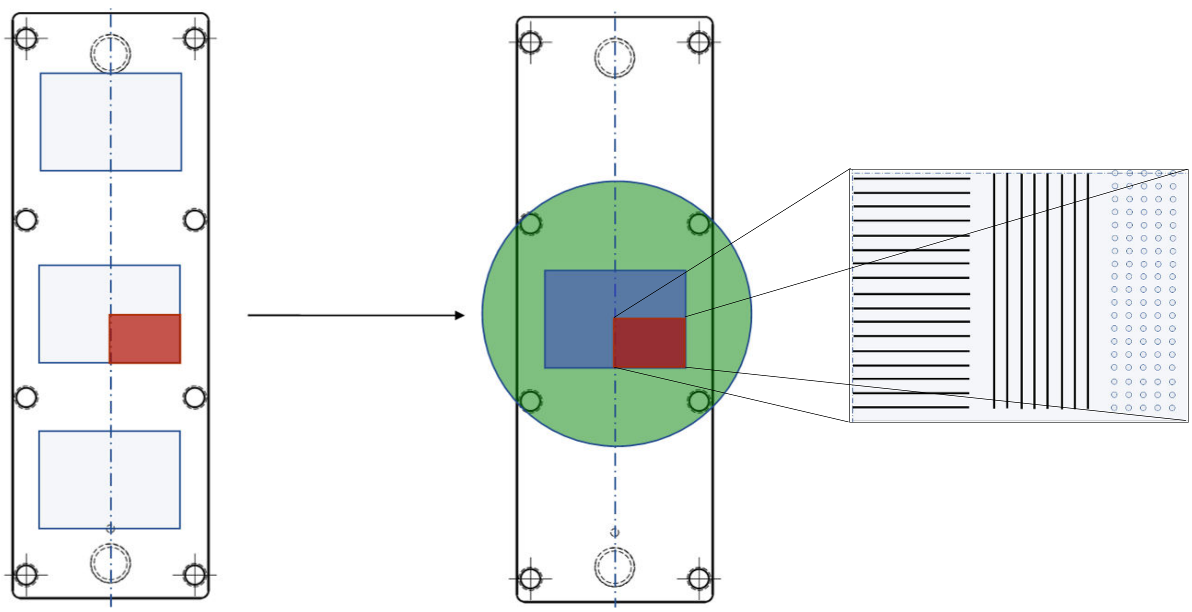

Figure 39: Simplification from the previous suggestion, to the final design proposal for the stamper geometry.

Figure 40 shows three proposals for test structures. All of the structural elements are oriented either in polymer flow direction or orthogonal to it. The polymer flow direction in Figure 40 is upwards or downwards. The structural density (number of channels per mm²) and length of the channels varies in these proposals and thus the number of microstructures changes. Proposal 1 has the highest density (300 µm distance between each channel) and most complex layout, while proposal 3 has the simplest layout (600 µm between each channel).

The choice even among these simple structure-configurations tends towards the simplest one. First step is to prefer the low structural density, to ensure that the part can be demolded. Second step is to use only “stand alone” elements. This means no interaction or combination in-between the structure. This leaves proposal 3 as the design choice.

The draft angle is chosen based on experience coming from different micro structured applications and will be in between 5° and 10°. The exact value is determined by the manufacturing process.

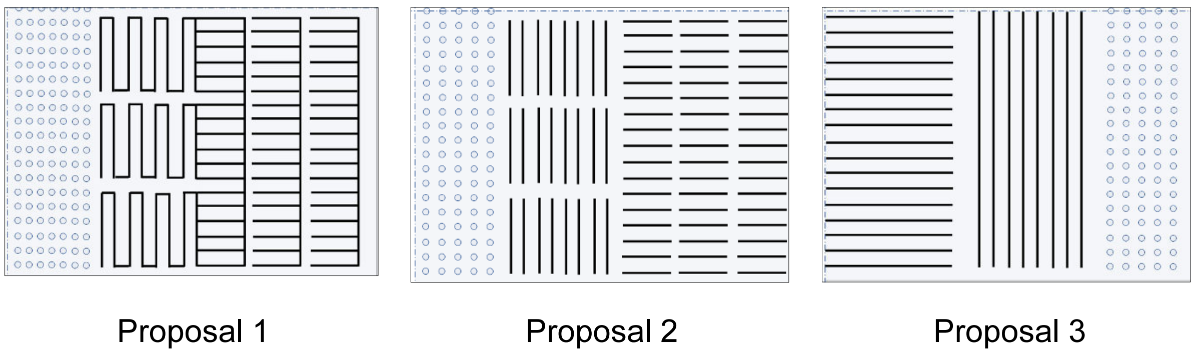

Figure 40: Three proposals for the test structure that meet the compiled restrictions (flow direction is upwards).

5.2 Test chip material

After the appropriate structure was chosen, the next step was to decide the material of the shim. Two possible choices were interesting for later use: Nickel and steel. Since nickel is a currently used material for many purposes, it is a good choice. As alternative, steel is a reasonable competitor. The comparison of both is dependent on the manufacturing cost and time as well as on the properties in the replication process. Steel provides some material advantages. For example the coating properties are better studied than for nickel. Also the higher stiffness of steel provides a lower warpage of the stamper while demolding and thus reducing the number of external influences.

Nickel supersedes steel when it comes to processing. Yearlong experience with nickel – coming from the CD, DVD disc and Blue Ray production – provides not only a reliable manufacturing method but also strongly affects the final cost of the stamper.

The difference in cost between steel and nickel is large and disparity mainly results from the used production process. In case of steel, micro milling was chosen as a suitable processing method as for nickel it is a light exposure (optical lithography) and galvanic processing. The result is that the nickel-part production costs only a fraction of any comparable production in steel. Micro milling has an additional disadvantage when processing small and dense structures. The structure is limited by the size of the used mill and smaller mills wear out a lot faster. Light exposure is not restricted in any way regarding structural variety or structural density. The only drawback is the limited aspect ratio (compare Table 3) due to photo resist layer thickness. Since high aspect ratios are not an issue for these test runs optical lithography remains the best solution.

5.3 Overview of potential materials

In the first step of testing the relation between polymers and different coating materials is to be studied. For this purpose a list of polymer and coating materials was devised. This should give a general overview of potential as well as suitable coating candidates for the subsequent tests.

5.3.1 Polymers

The polymer choice shall establish a list of commonly used polymers regarding the list provided by literature (see Table 1 and Table 2 in the chapter 2.1) a list provided by Sony DADC and in cooperation with the Institut für nanotechnische Kunststoff-Anwendungen (INKA). The final list contains various thermoplastic polymers (amorphous and semi-crystalline) that are all used in different life science applications. From this list of medically relevant polymers that can be found in literature, Table 7 shows some that are commonly used and easily attainable. This ensures that only available and suitable polymers are in consideration for the experiments.

Table 7: List of polymers used for medical applications [29].

Morphology	Types	Grades
amorphous	**PMMA**	POQ 62
	PMMA	CMG 302
	PC	Makrolon 2854
	PC	APEC 1745
	MABS	Terlux 2802 HD
	MABS	Terlux 2812 HD
	COC	Zeonor 1060R
semi-crystalline	**PA**	Trogamid A 4000 nf
	PA	Grilamid TR 90
	PA	Grilamid TR 55
	PP	Purel HM 671T

5.3.2 Coatings

The big number of possible coatings makes it even more important to compile a reasonable list. Literature shows that one of the main issues is to improve the interaction of the stamper surface and the polymer. The goal is for the stamper coating to reduce the surface energy (interaction) between the surfaces (compare chapter 4.3). But the challenge is that the coating needs to be stable for a certain number of modling cycles to be feasible. This also means that the surface morphology can be reproduced and is not dependent on surrounding conditions like humidity or temperature. Additionally, the coating needs to be durable as well and withstand the injection forces that occur in the replication process. Furthermore, a difference of the coating depending on the coated material like steel or nickel is expected.

The enumeration below shows a choice of possible coating materials. This list is compiled from coating materials that are used for similar purposes, which are known to reduce the friction and all metal based coatings are also known to increase the durability of the given surface:

- Titanium Nitride (TiN)
- Chromium Oxide (CrO, Cr_2O_3)
- Tungsten Sulfide (WS)
- Molybdenum Sulfide (MoS)
- Diamond like carbon (DLC)
- Silanes
- Phosphonates
- Titanium Carbonitride (TiCN)
- Chromium Nitride (CrN)

The coatings need to be compact and consistent, which may become a problem, as soon as the coating thickness is very low. Due to the micro structured surface the coating thickness must not exceed 1 micrometer (monolayer coatings). A few nanometers is the best possible case. A minimal thickness is required so that the surface of the nickel-insert is covered entirely (no defects). To ensure durable adherence of the coating on the nickel-insert, intermediate layers may be required (to prevent disbanding or delamination). Inconsistencies among the same coating material are also critical. The same coating may differ as the production process changes, because the structural morphologies depend on processing of the coating (for example sputtering, PVD) and different process parameters like the coating temperature. This effect is not to be neglected as it might change the roughness of the coating or other surface properties significantly (see 3.2).

5.4 Material selection

Polymers reduction should eliminate the least favorable of the suggested materials. Since little is known about the interaction and demoldability of the different polymers and almost any polymer class is equally interesting, the selection primarily focuses on availability and use of the polymer for different applications.

Thus the first step was to eliminate grades from the same polymer type. This ensures that many different polymers are tested. The most used and therefore most favorable grades for Sony DADC were chosen.

The feedback from different coating manufacturers (Oerlikon Balzers and Laser Center Leoben (Joanneum Research)) was the following:

- Any coating that contains the same metal element but is made with a different gas often has similar properties (for example: TiN and TiCN or CrO and CrN).
- Diamond like carbon coatings (DLC) exhibited bad friction values in previous experiments (PCCL) [*5*].

Only one metal coating per element is chosen. All other coatings, especially chemical coatings like phosphonates, remain of great interest.

5.5 Final test matrix

The resulting test matrix after elimination of as many potential polymer and coating candidates as possible yields the test matrix shown in Table 8.

Six polymers and six different coatings in a fully developed design of experiment lead to 36 combinations that need to be tested, which is still a lot of effort. All of these experiments are to be performed in the injection molding process while some of the experiments will be carried out in the hot embossing process as well to support the reasonable assumption that injection molding and hot embossing can be compared to a certain degree.

Table 8: Final test matrix for future hot embossing or injection molding tests.

Polymer		**Coatings**					
Type	**Grade**	TiN	CrO	WS	MoS	Silane	Phosphonate
PMMA	POQ 62	X	X	X	X	X	X
PC	Makrolon 2854	X	X	X	X	X	X
COC	Zeonor 1060R	X	X	X	X	X	X
PA	Trogamid A 4000 nf	X	X	X	X	X	X
MABS	Terlux 2802 HD	X	X	X	X	X	X
PP	Purel HM 671T	X	X	X	X	X	X

5.6 New test device to measure the demolding force

Chapter 3.4 defines the demolding force to be a quantity that relates to the demolding behavior. Chapter 3.5 discusses how the demolding force is measured in different processes so far. Unfortunately, these systems so far are impractical to measure the demolding force of micro structures, because either the measurement is far from the injection molding process (compare concept shown in Figure 19 and Figure 21) or lacks the needed accuracy (compare concept shown in Figure 18, Figure 20). Especially inline measurements in the commonly used injection molding processes are not possible to this date. Figure 41 shows a concept for a tool that is currently being developed, at the chair of polymer processing, for exactly this purpose. The challenge is to eliminate all possible external influences and only measure the demolding force caused by the micro structure. This has to be done while the normal injection molding cycle is not disturbed. Therefore, most important difference to a common injection mold is the decoupled movement of the micro structured stamper, in the cavity, and the mold opening movement right before ejection. This allows for the system to avoid most external influences that occur due to the high movement speeds of the mold. This is ensured since the microstructure is demolded while the mold is still closed.

After the polymer is injected and sufficiently cooled down, the stamper (shim) moves down. In this concept the stamper (shim) is marked blue. The stamper starts moving as soon as the carrier, which is fixed on the lower element, engages the upper element. The movement is controlled by a hydraulic aggregate. Two sensors are placed inside this element to measure the force and the traveled path. This allows mapping the force acting on the stamper over time (displacement). Any significant changes in the acting force, while the microstructure is removed from the polymer, are interpreted as the demolding force. After the measurement is completed the tool sides eparate at the parting plane and the “red” polymer part can be ejected regularly. This ensures very slow demolding speeds before the part is ejected, which is necessary to measure the demolding force accurately.

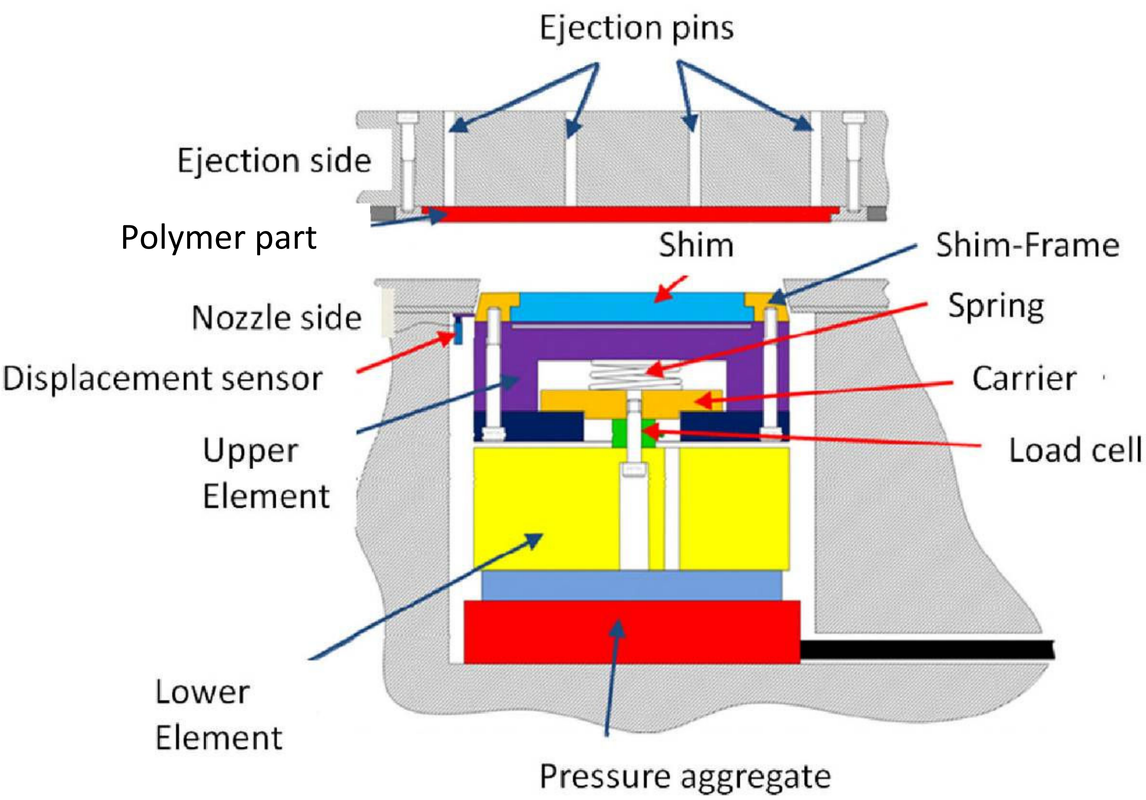

Figure 41: Injection mold concept for the measurement of the demolding forces for micro structured polymer parts. Micro structures are placed on an interchangeable shim [7].

6 Summary, conclusions and outlook

Glass-based medical applications are common tools in modern health care. With the recent years and improvements in polymer processing, especially the processing of microstructures, polymers started to supersede glass in many aspects. For example, cheap and disposable devices that provide the same functionality became possible. Despite this trend, the demolding of a micro structured polymer surface remains a major challenge. Both, the novelty and the complexity of this topic explain why the research has yet only been done on specific subjects, often singling out one parameter and disregarding others. This resulted in a rather fragmented state of studies on this topic, leading to large gaps in knowledge that still need to be covered. Especially cumulative effects, e.g. coating and geometry change, or coupled effects, e.g. coating and surface roughness, were often neglected and seldom understood.

This work tries to gather these different studies to generate a comprehensive overview on the demolding process of micro structured polymer parts. Therefore, the objectives of this thesis are to determine the factors that can influence the demolding and to give a good outline over the topic, by performing an intensive literature study. Furthermore, it tries to point out the importance of the different parameters, range the effects of these parameters according to their influence and applicability and provide steps for future experimental work.

The main influences, as defined in this thesis, are those which directly change the demoldability of a polymer part. These are the (micro and macro) geometry of the polymer part, the polymer type and grade, the mold material and mold coating and the processing parameters for injection molding or hot embossing.

Changes in geometry have the biggest influence on the demoldability. Regarding geometry, the introduction of a draft angle can reduce the demolding force up to 50%. Even greater improvements are suggested, depending on further modification of the geometry. For example, auxiliary structures like a stress barrier can be used to lower the stress on the application structures and to protect them from any demolding damage. Additionally, the polymer tendency to shrink influences the stress level in micro structures.

Coatings that provide a lower surface energy and a lower friction improve the demolding. Literature suggests that coatings, by influencing the adhesion, the friction and the surface morphology (roughness) can lower the demolding force up to 25%. Coatings can be used with little restrictions and are ideal enhancements for all applications.

Regarding the replication process the demolding temperature seems to be the most important process parameter to influence demoldability.

Based on the literature study, a systematic approach to analyze the influence factors - geometry, coatings, materials, and their interactions - was defined. This was done by drawing up a full design of experiments. For the resulting enormous number of tests, reasonable reductions and a rational order of experiments needed to be found.

This experimental study will focus on the interactions of polymers and different coating materials and should instantly provide a "quick fix" for industrial applications to improve the demolding behavior. The result of this study will be a correlation between the improvement in demoldability and the contact angles (surface energies) for each coating - polymer pairing. This should enable anyone to pick suitable coatings for the chosen polymer. Furthermore, if a good correlation between demoldability and surface energy is found, the resulting predictions can be used to filter the established list of coatings accordingly. Future experiments can then be designed relying on the reduced coating list.

Within the scope of the experimental work, it is planned to complete the general overview on the topic demolding of micro structured polymer surfaces for medical applications:

- Coatings:
  The experimental study on coatings, which was suggested in this thesis, shall be executed. For comparability, this should be done in both the hot embossing and the injection molding process.
    - Measurement of the demolding force in hot embossing:
      Preliminary tests at INKA (Institut für nanotechnische Kunststoff-Anwendungen, Villigen, Switzerland), will be performed.
    - Measurement of the demolding force in injection molding:
      Designing, manufacturing and implementation of an injection mold-based demolding force measurement device for micro structured polymer surfaces will be done.
- Simulation:
  Subsidiary parameter studies for the optimization of the geometry, coatings and materials are to be performed. Those shall test the feasibility of simulation methods for the prediction of the demolding behavior.
- Subsequent experimental studies will focus on the geometry of microstructures, especially on draft angles and aspect ratios. Furthermore, complex geometries and geometry placements will be analyzed. This will give a large potential for improvements in the future.

7 Literature

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8 Appendix

8.1 List of figures

8.2 List of tables