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Microinjection Molding of Enhanced Thermoplastics

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1. Introduction

Injection molding is, nowadays, a well known and widely used manufacturing process to produce both thermoplastic and thermosetting polymeric material components, in a large scale, with accuracy and at low prices. Even though the electronics industry provides an economy of scale for the silicon industry, polymer devices can be produced in huge volumes maintaining the requested features and quality, with a great variety of material characteristics, a fact that has considerably opened the market to injection molding of micro-components.

A simple miniaturization/rescale of the conventional injection molding process is not valid due to problems related with the rheology of the polymer flow in the micro cavity/channel and requires that all the process layout, as well as adjacent technologies, should be reconsidered, enhanced and properly adapted. The dimensional reduction of the components requires a higher control of the overall accuracy of the devices. The molding blocks of this type of objects are bounded to an amplified wear due to the fact that the surface roughness is dimensionally very close to the dimensions being controlled. The wear of the molding surfaces and the adhesion forces involved in the part extraction stage are greatly influenced by the nature of the material being injected and are enlarged when the molded object shrinks in the core or in the pins of the molding blocks. This is even more critical due to the flow behavior of enhanced polymer materials, developed for highly demanding applications in what concerns material mechanical or chemical properties.

Tailored special polymers are of fundamental importance in the supplement of micro-components. Complex polymeric materials engineered to detain both the mechanical properties and the memory shape suitable for applications such as active control, impose enormous challenges in what concerns both the process and the molding tools.

In conventional injection molding tools, surface engineering is used to improve the molding block performance to obtain parts with superior mechanical quality. In micromolding, surface engineering has a more important role due to the above-sited requisites, in order to reduce the deterioration of the molding impressions, increase its durability and reduce the need for corrective intervention on the tool. Different thin film coatings may be used, but

diamond films seem to assume an extreme importance in these types of applications due to its superior properties. The latter are not problem free coatings and not typically used on conventional molding tools. Nevertheless, its use may constitute the premises to solve the problem posed by highly abrasive and shear intensive polymer flows on cavities with geometrical detail and poor access, due to the micro-scale developed with the solely purpose of obtaining parts with high quality requisites.

In this chapter, the challenges that involve the micro-injection of enhanced thermoplastics will be discussed. Special attention will be given to the microinjection technology and tooling, but also to the injection materials, which impose further challenges, the so called enhanced thermoplastics.

2. Microinjection molding

In this section the topic microinjection molding will be developed. The injection molding machine, molding tools and inserts, insert fabrication techniques, rapid heating/cooling process, mould evacuation, demolding, factors affecting the replication quality of micro parts and process monitoring and control will, therefore, be discussed.

2.1 Adaptation of the molding tools and equipment for the micromolding of thermoplastics

2.1.1 Injection molding machines

There are a variety of motives why the conventional injection molding machines fail to satisfy the requirements of the microinjection molding. So far, as typical macroinjection molding machines are concerned, the most important issue becomes its minimum metering size, which apparently is too big in comparison to the tiny quantity of material required to produce a microcomponent. The latter turns precise metering very complicated along with a considerable increase of the time of melt residence in the barrel and eventually may lead to material degradation. In addition, clamping force also has to be reduced in order to guaranty free damage release of the micropart (Giboz et al., 2007; Attia et al., 2009). To accomplish precise, free defect molding of the micro components, every functional system of the macro molding machine has to undergo a series of profound modifications (Giboz et al., 2007). So far, several commercially available and home-made machines are utilized for production of the micromolded components and may be divided in two main groups. In the first one, modifications are accomplished by simple rescale/miniaturization of the metering and injection units addressed to precise dosage of polymer melt in every shot (Giboz et al., 2007). Another approach consists of separation of the plasticization from injection unit, where the plasticization is being performed in the extrusion screw or hot cylinder, mounted at angle to the inject axis. Next, polymer melt enters into the injection unit, where the mini plunger pushes the prepared shot to fill the mould cavity. The above mentioned classification includes both hydraulically and electrically driven microinjection molding machines. However, for the sake of accuracy and repeatability of the process, higher precision of plastic metering and clamping may be achieved by the servo mechanisms of the electrically driven machine allowing for more accurate process control along with low noise level and energy efficiency. (Whiteside et al., 2003; Chang et al., 2007)

2.1.2 Mould insert fabrication

In the conventional injection molding process, cavity is usually machined directly in the mould plate. The procedure, however, has undergone substantial alterations for the tools tailored for the microinjection molding applications. It turns to be more practical, in terms of energy saving and versatility of the mould tool, to machine the impression in the interchangeable mould insert. This way all necessary mould tool transformations can be applied locally and the microparts of different configuration could be produced using the same injection mould. The choice of the technique for the insert fabrication generally depends on three main factors: insert material used, surface finishing (roughness) and the aspect ratio demanded by the application. A number of techniques currently in use for microfabrication include: LIGA-process; silicon etching; laser ablation, micro electrical discharge machining (μ EDM) and mechanical micro machining (diamond turning, micro milling) (Rötting et al., 2002).

The LIGA process is a technology developed in the Forschungszentrum Karlsruhe in Germany in 1980s. Since the start of the micro technology development, it has been referred as a suitable technique for fabrication of the high aspect ratio microstructures with surface roughness down to 30 nm and such a low lateral resolution as 200 nm (Despa et al., 1999; Hormes et al., 2003; Munnik et al. 2003). Being a multi stage process, LIGA may be divided in three main steps: lithography, electroforming and plastic molding (Fig. 1). At first step (Lithography), the CAD information for the micro features is stored on the mask membrane (a very thin metal foil) covered with a layer of absorber generally Cu or Au. Synchrotron radiation passes through the transparent part of a lithographic mask and penetrates several hundred microns into a layer of sensitive X ray resist polymer (PMMA). The plastic modified by radiation is removed by solvent, leaving the template of resist structure. On the second step (Electroforming), the space generated by removed plastic is filled by electro deposition with metal normally Ni or Ni based alloys and negative replication of the resist structure is obtained. On the final step of LIGA process, the obtained metal structure is used as a mould insert for micro plastic parts production (Hormes et al., 2003). Among the variety of factors affecting the quality of X-ray LIGA generated patterns, the latter to a great extent is correlated with radiation intensity, mask composition and substrate type.

Novel approaches for improvement of X-ray LIGA process for micro insert fabrication are in permanent research in academy (Kim et al., 2006; Meyer et al., 2008). Although with deep ray X LIGA it is possible to obtain very accurate patterns of micro features with high aspect ratios up to 100 and micro structures with size less than 250 nm, it is still not a widespread commercial technique for micro replication, being time consuming and costly (Despa et al., 1999; Meyer et al., 2008). UV-LIGA and IB (Ion Beam) LIGA technologies are less complex and costly comparing to the X-ray LIGA process. In the former application, the ultraviolet source instead of the X-ray is used to expose the resists, while in the latter impressions are obtained by irradiating of photoresist materials with light ions (Munnik et al., 2003; Yang et al., 2006). It, however, should be pointed out that despite the fact that size of the micro structures obtained by this technique may reach 100 nm, the electrons are very light and may cause the loss of resolution and poor surface finishing at depth (Munnik et al. 2003). In case of low volume production, silicon microstructured inserts may be a suitable alternative to the expensive LIGA process. The impressions in silicon are usually obtained by wet etching and in spite of the inherent fragility of the material low roughness surface finishing

makes this technique quite satisfactory for molding of the microparts in limited quantities (Heckele & Schomburg, 2004).

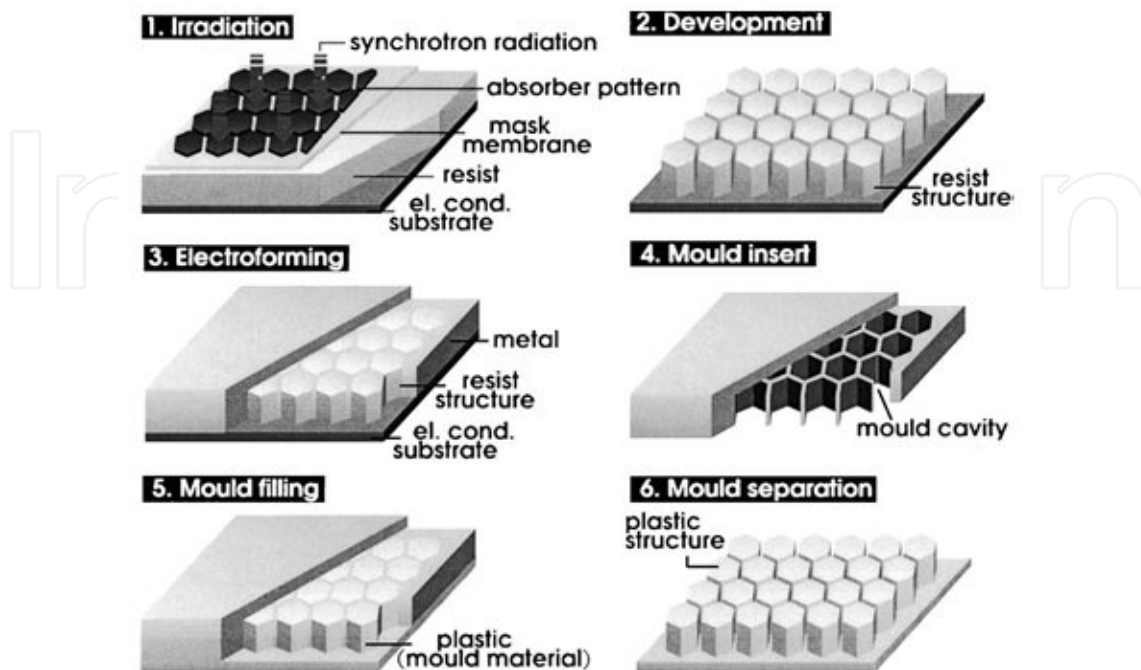


Fig. 1. Principle process steps for the fabrication of microstructures by the LiGA technique (Hormes et al., 2003).

The direct structuring techniques are far more attractive economically and can be easily applied for the micro inserts fabrication from hard metals and alloys. When the complex geometries of the micro features are concerned, a variety of micro cutting techniques are currently available and may be enumerated as follows: micro milling (for microgrooves and micro 3D shapes); micro turning (for micro pins); and micro drilling (for micro holes) (Franssila, 2004). To achieve the required cavity surface finishing, diamond and cemented carbide cutting miniaturized tools are currently in use whether their applications will eventually depend on the properties of processed material (Franssila, 2004). Although with diamond cutting tool such fine resolution as of 48 nm of roughness could be achieved, its applicability is limited to the soft non ferrous metals as brass, aluminium, copper and nickel (Davim & Jackson, 2009). More resilient materials like steel are processed with the cemented carbide tool of diameters down to 50 μm yet with less surface resolution (0.1–0.3 μm) (Fleischer et al., 2007). Despite the fact that maximum aspect ratios achieved by micro cutting are considerably smaller in comparison with the other micro fabrication techniques, high level of automation and continuous improvement in the tools precision as well their ability to work with hard metals make it an appropriate technique for the microstructured insert fabrication.

Another popular direct structuring technique for hard metals and alloys is micro electrical discharge machining (μEDM). The heat in the form of pulsed discharge is applied through the thin metal wire (usually brass), allowing to cut through metal by melting and evaporation (Franssila, 2004). Based on this general description, there are a wide range of the μEDM techniques which may be classified by the type of electrode or/and electrode-

workpiece movement (Franssila, 2004; Uhlmann et al., 2005). Size and precision of the pattern replication, to a great extent, depend on the size and shapes of the electrodes and eventually with optimum conditions aspect ratios of 100 may be realized (Franssila, 2004). For machining of the patterns of more complex shapes, electro discharge grinding (WEDG) with the electrodes of micrometric range (down to 20 μm) is reported to realize the micro structures of 5 μm and roughness of 0.1 μm . However, a maximum aspect ratio of micro structure is less than that of μEDM and only reaches 30 times of the wire diameter (Uhlmann et al., 2005). Surface resolution obtained by laser ablation is similar to that of micro cutting techniques making this method very popular for machining of the wide range of engineering materials (Gower, 2000). Ultra short pulsed lasers with optimized pulse energy and focus size are able to produce microstructures with size from 10 μm , aspect ratio of 10 and roughness of 0.16 μm (Heyl et al., 2001). It is worth mentioning, however, that in terms of surface quality and minimum achievable dimensions, the output from the micro laser ablation is inferior to the LIGA and μEDM .

2.1.3 Rapid heating/cooling process

As a rule of thumb, in conventional injection molding process mould temperature is far below the injection temperature. At such conditions, the frozen layer forms near the cavity wall while the core is significantly hotter and continues cooling down to ejection temperature at the end of the cycle. When the polymer melt is injected to the micrometric cavity, high surface-to-volume ratio and reduced dimensions of microparts promote the instantaneous melt temperature drop and as a result incomplete filling even when high pressures are applied (Su et al., 2004). To guaranty complete filling of the microcavity, the mould should be heated up to the glass transition temperature (T_g) for amorphous thermoplastics and melt temperature (T_{melt}) for the crystalline ones. This definitely requires implementation of a special rapid heating/cooling (variotherm) system. The latter (Fig. 2) allows for a rise of the mould temperature above T_g / T_{melt} during injection with subsequent cool down to the ejection temperature in order to assist successful part release (Piotter et al., 2008).

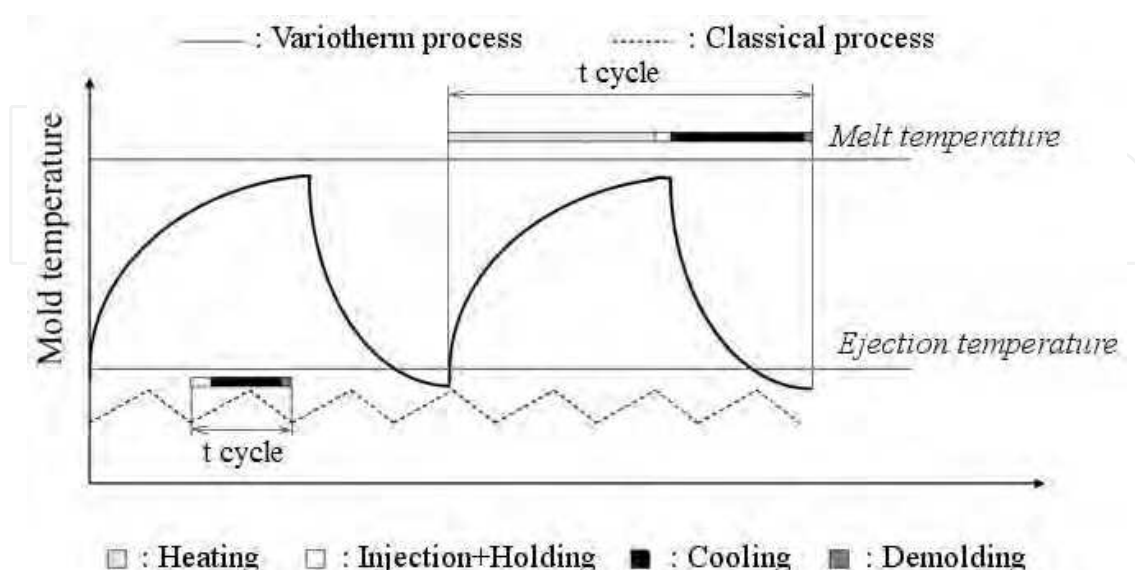


Fig. 2. Comparison of the mould temperature profile in the classical and variotherm processes (Gornik, 2004).

Nowadays, the variotherm process is widely applied for molding of the microparts. When mould temperature is close to processing temperature, even microstructures of the high aspect ratios may be eventually filled. Moreover, isothermal filling induces less residual stresses and surface defects in the micro parts (Chang & Hwang, 2006). How it can be easily noticed from Fig. 2, the temperature gradient for variotherm process is significantly higher than that for the conventional process and may lead to longer cycle times compromising the economic feasibility of the micromolding process (Gornik, 2004).

Considering the variotherm process, two main issues have to be addressed. The first is concerned with the choice of the heating technique capable of rising promptly mold temperature above T_g / T_{melt} . While the second issue is related to the efficient heat removal for the fastest possible cycle times. So far, there are two principal approaches to transport the required power to the mould: external type (infrared radiation and induction heating) and internal/built-in (joule/resistive, high-frequency proximity, water and oil heating). The main limitation to use water as a heating media is that the maximum heating temperature does not exceed 95°C, which is less than the glass transition/melt temperature of the majority of polymers. As a result, water is generally used for cooling in the variotherm process (Su et al., 2004; Chang & Hwang, 2006; Xie & Ziegmann, 2008). Heat retention properties of oil and its ability to be heated up to 140°C makes it a more adequate candidate as heating medium. However, the lower heat transfer coefficient, comparing to water, leads to longer cycle times (Gornik, 2004; Whiteside et al., 2004; Tseng et al., 2005).

Application of the joule/resistive heating in variotherm process has been extensively investigated by many researchers (Su et al., 2004; Xie & Ziegmann, 2008). Eventually, nano features with aspect ratios up to 300 could be realized if molded above the glass transition/melt temperature of polymer. Unfortunately, the cycle times may increase up to several minutes due to the thermal inertia of the mould material (Xie & Ziegmann, 2008). Adequate isolation of the heating elements from the mould base will favor the cycle time reduction and increase economic efficiency of the microinjection molding process (Gornik, 2004). Yao et al. (2006) have implemented a local heating of the mould insert by high-frequency current. Unlike the conventional resistive techniques, mould surface heating rate can reach 40°C/s with an apparent heating power of 93 W/cm², while only the local electrical insulation of the mould insert is necessary.

The main advantage of the external heating over the internally built systems is an ability to heat up locally the insert surface allowing for the faster cycle times. In a number of studies infrared heating has been applied for precise localized heating of the microcavity surface. Although the local temperature rise with an aid of halogen lamps requires considerably less time in comparison to the resistive heaters, it may lead to uneven distribution of the mould surface temperature and therefore, special attention should be given to more uniform distribution of the heating sources (Gornik, 2004; Chang & Hwang, 2006). During processing, residual oil or resin particles may burn and contaminate the microcavity surface causing surface defects in the micromolded parts. This problem could be eventually solved with periodical cleaning of the mould cavity (Chang & Hwang, 2006).

Direct infrared radiation heating of polymer inside the cavity has been proposed by Saito et al. (2002). As long as CO₂ laser is directed towards the polymer melt through the transparent window in the mould wall, temperature gradient during injection is significantly reduced.

With this technique, the molecular orientation in the surface region of the micropart has been decreased along with significant improvement of the surface replication. Very quick rise of the cavity temperature may be achieved with induction heating. It was reported that heating could be accomplished in several seconds and consequent cooling is also very fast because of minimum amount of heat generated in the mould (Michaeli & Klaiber, 2007a). However, high-temperature cycling may lead to thermal fatigue and eventual shortage of the mould service time (Tseng et al., 2005).

2.1.4 Mould evacuation

Negative effect of the air presence in the mould cavity is a well known phenomenon in the conventional injection molding. The latter is responsible for burn marks on moldings and long-term formation of corrosive residue in the mould which may lead to its permanent damage. While the moulds of conventional size are supplied with special venting channels, this solution cannot be adapted for the micromolding where the part dimensions are frequently comparable in size to the venting grooves. Moreover, high injection speed and complex geometry of micro features may contribute for air entrapment and could eventually lead to incomplete filling, especially in case of the blind hole features with high aspect ratios (Heckele & Schomburg, 2004). In a number of studies, evacuation of air from the cavity prior to injection is referred as an efficient method for improvement of the microparts replication (Despa et al., 1999; Heckele & Schomburg, 2004; Sha et al., 2005; Liou & Chen, 2006; Chang et al., 2007; Sha et al., 2007b). A typical layout of the mould evacuation system is shown on Fig. 3. However, sometimes it is impossible to clearly distinguish the effect of cavity evacuation on the part filling. For example, it could be attributed to the fact that micro cavities are aligned with the parting line of the mould and therefore air can escape easily through the partition (Sha et al., 2005). To assist more efficient air evacuation, the mould platens must be properly adjusted for hermetic sealing of the cavity (Despa et al., 1999).

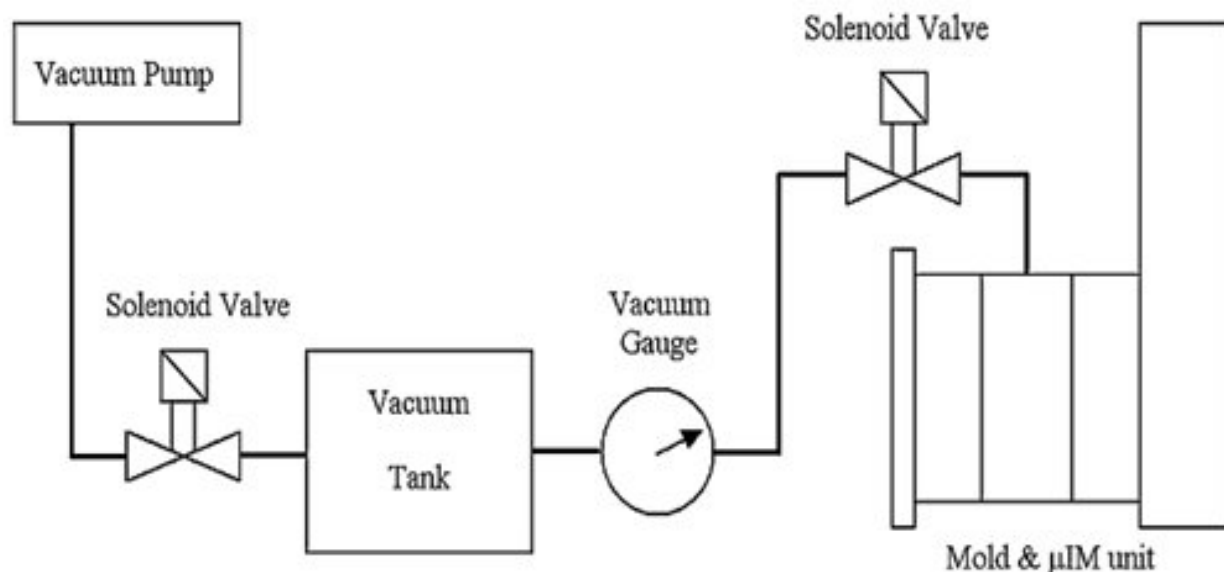


Fig. 3. Layout of the vacuum mould unit (Chang et al., 2007)

It is also worth mentioning that air suction prior to injection may decrease the cavity temperature. The latter may have a negative effect on the mould filling, being especially

critical in the case of the thermally sensitive polymers as polyoxymethylene (POM) (Sha et al., 2005; Sha et al., 2007b).

Implementation of the vacuum assisted cavity evacuation might be carefully considered in every case of the microinjection molding taking into account polymer type, geometry and surface finishing of the cavity.

2.1.5 Demolding

Demolding of microparts becomes a critical issue as failure frequently occurs at the onset of ejection. The interactions of polymer shrinkage and the coefficient of friction between the polymer and the molding tool may have detrimental effects on the component failure during ejection (Pouzada et al., 2006). Moreover, the micro features with high aspect ratios have a larger contact surface between the mould and the polymer which results in higher frictional resistance during part release. Smooth surface finishing is highly desirable for decreasing the friction on the polymer/insert interface (Attia et al., 2009). Coatings are frequently used to improve the roughness properties of the mould cavity and achieve superior surface quality of microparts. For example, if a cavity is coated with diamond-like carbon (DLC), fewer forces are required for the PC and ABS microparts ejection (Griffiths et al., 2008). In order to avoid breaking during ejection, the adhesive bond between polymer and stainless steel mould tool should not exceed the tensile strength of the polymer (Navabpour et al., 2006). In addition to the experimental techniques, the magnitude of the stress on the polymer/metal interface can be accessed via finite elements stress analysis (Grave et al., 2007).

Considering fragility of the microstructured parts, conventional ejection with pins becomes unlikely and may eventually lead to their irreversible damage. In order to overcome those weaknesses, alternative solutions have to be considered. For example, if geometry of micro parts allows for a positive draft angle, the latter could assist the proper demolding of the microparts (Grave et al., 2007; Wu & Liang, 2005). A concept of more even distribution of ejection forces has been applied when ejection with pins was substituted with the micro ejection block used as striper plate to thrust the microparts (Wu & Liang, 2005). Ejection of the high aspect ratio micro structures, molded within the insert of rough surface finishing, may be successfully accomplished with vacuum assisted demolding (Michaeli et al., 2000). Choice of demolding system at micro scale will eventually depend on the cavity geometry, surface finishing and the material to be molded. In addition, a special attention should be given to correct calculation of the ejection forces and proper design of the ejection system, so far as both of those factors could be detrimental for the micropart quality.

2.2 Process monitoring and control

Microinjection molding is inherently a black box process, where the extreme processing conditions and rapid process variations do not lead to the linear correlation of the inputs and outputs. Monitoring of the micro molding process parameters is critical to assess the rheological state of polymer throughout the molding cycle. Hitherto, the majority of sensors currently available at the market are too big to be installed into the micro cavity. To overcome those limitations, an indirect monitoring is frequently applied to gather the information about the mould temperature, heat flux, injection pressure, injection speed and

displacements (Yan et al., 2003; Zhao et al., 2006). Frequently pressure sensors are embedded into the plunger of the microinjection molding machine for monitoring of the metering size and pressure evolution. It, however, does not represent the polymer behavior inside the microcavity (Zhao et al., 2006). Cavity pressure monitoring is considered to be a better approach to verify the process variation and control the quality of the molded parts. For example, more relevant information about polymer melt behavior can be acquired by single axis force sensor, embedded into the mould-core extrusion mechanism (Yan et al., 2003). In a number of studies, an integral approach has been adapted towards the monitoring of the pressure and temperature inside the cavity. Pressure monitoring has been performed with piezoelectric force transducer embedded into the ejector pin. Whereas temperature, which has early been mentioned to affect the microcavity filling, may be measured with the aid of the J type thermocouples embedded at depths of several millimeters in the cavity wall. This way, the polymer solidification inside the cavity may be recorded (Whiteside et al., 2004).

When the direct monitoring of the micromolding is concerned, only a few sensors have been referred to be appropriate for the micro applications. The majority of the above-mentioned sensors hardly satisfy the micro criteria with the contact area diameter varying from 1 to 4 millimeters (Luo & Pan, 2007; Ono et al., 2007). However, those sensors were reported to provide reliable data about the temperature and pressure evolution in the cavity and if properly located, could be used to control the micromolding process. Further miniaturization of the sensors is one of the key factors to provide an insight to rheology of the polymer flow in the microcavity. The obtained data could be applied for the better process control as well for the improvement of the rheology models used for numerical simulation of the micro molding process. So far, by the author's knowledge, the market offer of the micro pressure and temperature sensors is very limited. For example, a combined sensor for measuring of the mould cavity pressure and contact temperature in the cavity with the front diameter of 1 mm, was recently launched by KISTLER (Kistler, 2011). Further miniaturization has been accomplished by PRIAMOS, for measurement of the melt temperature at contact with the cavity wall, with the sensor of 0.6 mm of diameter (PRIAMOS®, 2011).

The real time monitoring and control of the micromolding process are highly dependent on the sensors capable of reliably monitor the instant process variations. With further sensors miniaturization and an increase in precision, it will eventually be possible to achieve the higher level of automation and superior economic viability of the micromolding process.

2.3 Effect of the process/tool/polymer interaction on the quality of micromolded components

Quality of the micromolded parts is, to a great extent, determined by complex interaction of the process parameters, polymer and mould tool properties. Considering variability of the microparts design and purpose, their quality criteria are much diversified as well, including filling length, dimensional stability, surface finishing and a range of the mechanical properties of interest (Attia et al., 2009). Currently, two main approaches exist for correlation of the process/polymer/tool factors with the quality output: one factor at time experiment (OFAT) and design of experiment approach (DOE). While the former method highlights the leading trends, the latter addresses the optimization of the process by identifying the

interactions among factors. Both methods are extensively explored in recent research work (Zhao et al., 2003; Liou & Chen, 2006; Michaeli et al., 2007b; Sha et al., 2007b; Theilade & Hansen, 2007; Tofteberg & Andreassen, 2008).

Variotherm mould cycling along with the high injection temperature could significantly improve the weld line strength of the micro tensile test samples (Theilade & Hansen, 2007). Moreover, at higher mould temperature viscosity of the polymer melt significantly decreases and therefore requires less injection pressure and speed (Despa et al., 1999). Even in the absence of the variotherm cycling, higher mould temperature was reported to promote better cavity filling for a wide range of the tested polymers (Zhao et al., 2003; Sha et al., 2005; Michaeli et al., 2007b; Sha et al., 2007a; Sha et al., 2007b; Tofteberg & Andreassen, 2008). In the case of over-molded micro needles, an increase of bonding strength has been accomplished by the combination of the high holding pressure, high mould and low melt temperature (Michaeli et al., 2007b). An attempt of the empirical correlation of the part quality with process parameters has been proposed by Tofteberg & Andreassen (2008). In their study, replication of the micro features of Cyclic Olefin Copolymer (COC) and Poly(methyl methacrylate) (PMMA) has been significantly improved with an increase of the mould and melt temperature. It is also worth mentioning that with an increase of the micropart complexity the mould temperature factor was found out to prevail over the other process parameters (Attia et al., 2009).

Premature solidification of polymer may be reduced, to some extent, by injection at high injection speed. The latter is reported to assist in filling of the micro pins, having on the other hand, an adverse effect on the surface finishing (Sha et al., 2007a). The positive effect of the injection speed has also been confirmed by the other researchers. High injection speed was decisive for high-quality replication of the micro walls as well as its interaction with the injection temperature (Theilade & Hansen, 2007). When moulded with cold runners, it is not rare to encounter that volume of the feeding system may contain several times the volume of the micropart. Such discrepancies make precise metering unlikely, increasing the probability of incomplete filling and invalidating the holding pressure effect (Zhao et al., 2003). Nonetheless, some difficulties related to the metering precision and process fluctuations can be attenuated by applying higher holding pressure (Liou & Chen, 2006). Although with the holding pressure increases improvement of filling the micro and sub-micron structures has been reported, it seems uneasy to differentiate single holding pressure influence from its interaction with the mould temperature effect (Liou & Chen, 2006).

In the recent research, discrepancies in rheological behavior of the different grades of plastics have been widely reported. In order to guarantee the proper filling and acceptable surface quality, the easy flow grades should be preferred (Despa et al., 1999; Zhao et al., 2003; Michaeli et al., 2007b; Tofteberg & Andreassen, 2008). Adhesion forces between polymer and mould tool may vary significantly for different polymer grades and should be accounted for successful demolding of the microparts. The latter may be achieved by fine surface finishing of the mould cavity, positive draft angles and by using release agents (Wu & Liang, 2005; Grave et al., 2007). The variety of factors involved into the transformation of the polymer melt within the microcavity makes the interpretation of the cause-effect relationship uneasy task even for neat (unfilled) thermoplastics. Furthermore this relationship may become substantially more complicated for enhanced thermoplastics as their new properties will eventually influence rheological behavior at micro scale.

3. Enhanced thermoplastics

A brief introduction to the current meaning of enhanced thermoplastics will be provided. It will be given some emphasis to enhanced thermoplastics through nanoparticles loading. Then it will be presented research work done on this issue, giving special evidence to the effect of mixing carbon nanotubes (CNT) to a thermoplastic material. The consequences on the rheology and interaction with the molding tools of these materials will also be discussed.

3.1 Definition

Thermoplastics are long chain polymers that can be structurally amorphous or semi-crystalline. These polymers possess long chains, where macromolecules are bonded through the weak van der Waals forces. Their general properties are toughness, resistance to chemical attack and recyclability, i.e. they can be re-processed as many times as needed, till their degradation, due to processing. Despite that the continuum search for better and cheaper materials has been guiding the scientists to the development of new thermoplastics with enhanced properties, such as better resistance to water and UV; better mechanical properties (toughness, stiffness); and enhanced electrical conductivity. These new class of thermoplastics are known as “enhanced thermoplastics”.

There are different techniques to manipulate polymeric materials in order to obtain enhanced properties, such as: (a) by modifying their molecular structure, the hard and soft segments. Through this technique, the molecular structure of the polymer is changed by different combinations of: chain flexibility and hard segments, chain entanglement, the orientation of different segments, the hydrogen bonds and their intermolecular interactions. Through the modifications of the hard/soft segments ratios of the polymer, it is possible to obtain different physical, thermal and mechanical properties (Chattopadhyay & Raju 2007); (b) the incorporation of plasticizers, which are substances, usually plastics or elastomers, that are incorporated in a material in order to increase its flexibility, workability or extensibility, and modify the thermal and mechanical properties (Wang et al. 1997; Rahman & Brazel 2006); (c) throughout the incorporation of particles into a polymeric matrix (Tjong 2006). Some of the most commonly used reinforced particles are: CaCO_3 , glass, carbon fibres, and in the last years, carbon nanotubes have been frequently used due to their extraordinary thermal, electrical and mechanical properties (Wang et al., 1998; Coleman et al., 2004).

3.2 The effect of incorporating carbon nanotubes (CNTs) into thermoplastic materials

The incorporation of carbon nanotubes (CNTs) in thermoplastic materials has been one of the hottest topics in materials science in the last years, since their discovery by Iijima (1991), essentially due to the extraordinary properties of CNTs

CNTs can be classified as single-walled carbon nanotubes (SWCNT), which consist on a single grapheme sheet wrapped into a cylindrical shape and are characterized by a small diameter (0.4 - 3 nm) and lengths up to centimeters; and multi-walled carbon nanotubes (MWCNT) that detain a number of grapheme layers coaxially rolled together to form a cylindrical tube, and their outer diameter ranges from 1.3 - 100 nm and their length can be as long as tens of micrometers (Baughman et al., 2002). It has been reported that CNTs possess an elastic modulus in a range of TPa (Yu et al., 2000) and detain high aspect ratios (>100),

due to its small diameter (in the range of nanometers) and long length (as long as 100 micrometers). However, the incorporation of CNTs into a polymeric material is quite difficult due to the Van der Waals forces that tend to clump nanotubes together, leading to a poor dispersion of them into polymeric matrix. For an effective reinforcement there are essentially four important requirements: 1) the CNTs must have high aspect ratio; 2) they must be uniformly dispersed; 3) the alignment of CNTs through a preferable direction, and 4) should be verified interfacial stress transference. The distribution of CNTs into polymeric matrix could be the most important parameter to obtain an enhanced thermoplastic reinforced with CNTs. The CNTs must be individually dispersed and should be coated by polymeric matrix, in order to achieve efficient load transfer to the nanotube network, which is of utmost importance. The aggregation of CNTs is generally accompanied by a decrease in strength and modulus.

In order to improve the dispersion of the CNTs, and to prevent the agglomeration, many techniques have been developed, such as, ultrasonic activation, the addition of surfactants and chemical treatment with sulfuric and nitric acids (Esumi et al., 1996; Gong et al., 2000; Deng et al., 2002; Safadi et al., 2002). The present authors applied a chemical treatment, with sulphuric and nitric acids in a proportion of (3:1) to modify the surface of CNTs and the results have shown that CNTs maintain their physical integrity (diameter, length) and that they are no longer entangled as previously to chemical treatment (Fig.4).

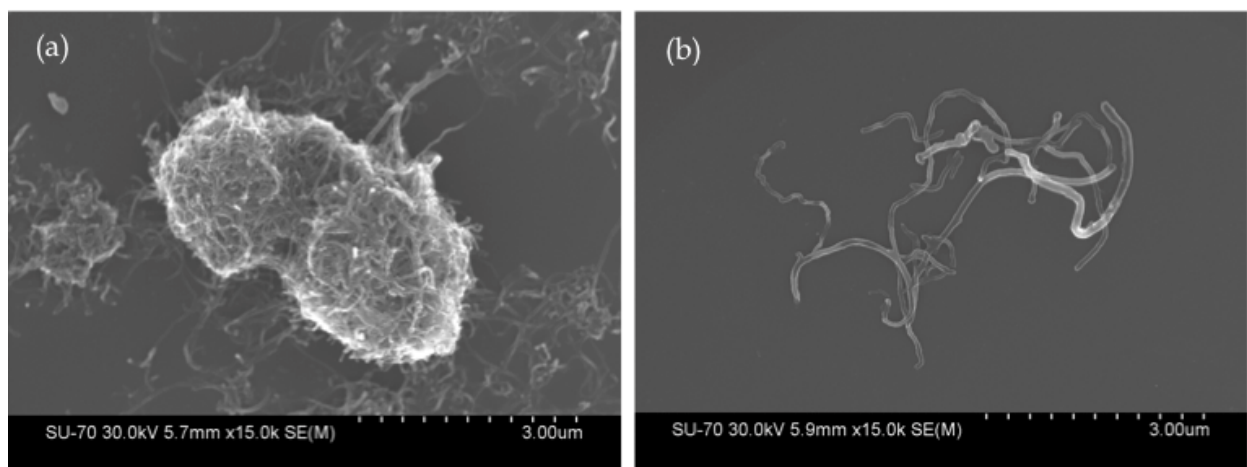


Fig. 4. Scanning electron microscopy of the (a) non-treated CNTs and (b) chemically treated CNTs.

There are essentially three methods to incorporate CNTs into polymeric matrices: 1) solution mixing or film casting of suspensions of CNTs in dissolved polymers; 2) in situ polymerization of CNTs-polymer monomer mixture; and 3) melt mechanical mixing of CNTs with polymer (Jia et al., 1999; Haggenueller et al., 2000; Jin et al., 2002). Recently, Fonseca et al. (2011) proposed a simpler technique based upon the general methodology described by method 3, where the CNTs and polymeric matrix are prepared by mechanical ball-milling.

The solution mixing is probably the most applied method to produce polymer nanotube composites. The basis of this method is the mixing of the CNTs and the polymer in a suitable solvent before its evaporation occurs and, thus, forming a composite film. This

method has the advantage of the agitation of the CNTs powder in a solvent that could facilitate the de-aggregation and dispersion. The in-situ polymerization has been used because the obtained composite presents a good dispersion of CNTs into polymeric matrixes. This method is particularly important for the preparation of insoluble and thermally instable polymers that cannot be processed by solution or melt processing. The main disadvantages of this method are the time consumed and the complexity involved in the process to obtain the composite material. The melt processing method is commonly used for thermoplastic polymers. The advantages of this technique are the speed and simplicity, and essentially, its compatibility with standard industrial techniques (Andrews et al., 2002; Potschke et al., 2003).

The melt mechanical technique is characterized for the melting of the thermoplastic and then the addition of CNTs by shear mixing. However, the processing conditions should be optimized for each thermoplastic and desired composite, because CNTs can affect melt properties, of the pure thermoplastic, such as viscosity (Potschke et al., 2003). As it was mentioned earlier, Fonseca et al. (2011) has prepared ultra-high molecular weight polyethylene (UHMWPE) reinforced with CNTs through a variation of the melt mechanical processing technique. Previously to melt processing, they used the mechanical ball-milling to mix the raw UHMWPE with the chemically treated CNTs. After mixing the powder composite was processed by compression molding technique. The results have shown a homogenous distribution of the CNTs into the polymeric matrix (before and after melt processing), and an enhancement of the main mechanical properties, such as the elastic modulus and toughness.

The incorporation of CNTs in polymeric matrices has been extensively studied in last years. Different polymeric matrices have been considered, such as PMMA (Jia et al., 1999; Gorga & Cohen, 2004), polystyrene (PS) (Qian et al., 2000; Yang et al., 2005), polypropylene (PP) (Dondero & Gorga, 2006; Bao & Tjong, 2008), polyurethanes (PU) (Koerner et al., 2005; Xiong et al., 2006; Zhang et al., 2011) and polyethylene (PE; high density polyethylene - HDPE, ultrahigh molecular weight polyethylene - UHMWPE) (Ruan et al., 2003; McNally et al., 2005; Kanagaraj et al., 2007; Fonseca et al., 2011).

In 1998, Schadler et al. (1998) studied the effects of the dispersion of 5 wt% of MWCNT in an epoxy resin, and the results have shown an increment of the modulus in tension and in compression of about 20% and 24%, respectively. Jia et al. (1999) prepared PMMA/CNT composites with different weight fractions of CNTs. The composites were prepared by an improved in-situ process and the results reveal an enhancement of the mechanical properties as well as an increase of the heat deflection temperature, as the CNT loading increases. However, for weight percentages higher than 7% the mechanical properties of the PMMA/CNT composite starts to decrease and for 10 wt% the composite becomes brittle. Later, Gorga & Cohen (2004) presented results consistent with the previous one. They studied the mechanical properties of MWCNT/PMMA as a function of nanotube orientation, length, concentration and type. The results reveal a good dispersion of the MWCNT into PMMA matrix for weight percentages ranging from 0.1 – 10 wt%, although, for loadings higher than 5 wt% there was evidence of aggregation. The orientation of MWCNT in PMMA seems to be the better way to improve the toughness of the material. Qian et al. (2000) mixed 1 wt% MWCNT to polystyrene (PS) and the results have shown an increase of about 36 - 42% in elastic modulus and about 25 % in the tensile strength, for the

PS/MWCNT composite as compared with pure PS. Yang et al. (2005) obtained an enhancement in microhardness, of about 40%, for the composites of PS/CNT with CNT loading lower than 1.5 wt%. They also observed a considerably decreasing in wear rate and friction coefficient as CNT loading increases. Dondero & Gorga (2006) studied the mechanical properties and the morphology of the MWCNT/PP composites, prepared by melt mixing, as a function of nanotube orientation and concentration. The results reveal an enhancement in toughness and in modulus of about 32% and 138%, respectively, for 0.25 wt% CNT loading, as compared with pure PP. The effects of loading rate of CNT on thermal and mechanical properties was studied by Bao & Tjong (2008), for PP/CNT composites. The x-ray diffraction (XRD) reveals that the presence of CNT did not influence the crystal structure of PP/CNT composites and differential scanning calorimetry (DSC) shows that the glass transition (T_g) and the activation energy (ΔE) increases with the increase of the amount of CNTs, demonstrating that the mobility of the polymer chains is reduced with the presence of CNTs. The tensile tests reveal an enhancement on Young's modulus from 1570 MPa for pure PP to 2107 MPa for 0.3 wt% of CNTs loading.

The incorporation of CNTs into polyurethanes (PU) has been studied by many groups. Koerner et al. (2005) incorporate different volume fractions of CNTs (from 0.5 to 10 vol.%) into thermoplastic PU. The results reveal an enhancement in electrical conductivity, and in mechanical properties including the modulus and yield stress. Chen et al. (2006) reported an enhancement in elastic modulus, from 4.96 MPa for pure PU to 135.1 MPa for the composite with higher weight fraction of CNTs (17.7 wt%). On the other hand, the maximum for tensile strength was occurred for the composite with 9.3 wt% of CNT, decreasing for higher concentrations, which can be ascribed to the increased frequency of localized clusters or aggregations. A study on the thermal properties of the PU/CNT composites was performed by Xiong et al. (2006) and the results reveal an increase on the glass transition temperature of the composite of about 12°C, as compared with pure PU. Results of the tensile tests also reveal an improvement of the mechanical properties of the composites as compared with pure polymer.

The reinforcement of polyethylene (PE, HDPE, UHMWPE) with CNTs is probably the most studied issue in what concerns to the enhancement of thermoplastics, due to its enormous range of applications. McNally et al. (2005) reinforced PE with CNTs with weight fractions ranging from 0.1 to 10 wt% by melt blending. The results have shown that the addition of CNTs did not affect the temperature of melting (T_m) of the PE, however, the temperature of crystallization (T_c) increases for the composite with 10 wt% of CNTs. This indicates that the CNT have a nucleation effect on PE. These composites have shown a decreasing in toughness with increased CNT addition, which can be associated with the nucleation of CNTs into polymeric matrix. On the other hand, Kanagaraj et al. (2007) has shown a good load transfer effect and interface link between CNTs and high density polyethylene (HDPE). The results of tensile tests have shown a linear increase of Young's modulus (with maximum of about 22% for a volume fraction of 0.44 % CNT). This linearity is suggested to be due to a good load transfer effect and interface link between CNT and HDPE. The thermal analysis reveals that the melting point and oxidation temperatures of CNT/HDPE composites are not affected by the addition of CNTs, although the results reveals an increasing on crystallinity of the composites. Ruan et al. (2003) reported an enhancement of toughness in UHMWPE films with the addition of 1 wt% MWCNT. Their results reveal an

increase in strain energy density of about 150% for the composites as compared with pure UHMWPE. They also reported an increase of about 140% in ductility and up to 25% in tensile strength. An analysis by nanoindentation and atomic force microscopy (AFM) of UHMWPE/MWCNT composites has been reported by Wei et al. (2006). They have observed a decrease of the friction coefficient with MWCNT content increase. Recently, Fonseca et al. (2011) prepared UHMWPE/CNT composites, with different volume fractions of CNTs, through mechanical ball-milling and processed by compression molding. In this work, for this specific materials and mould geometry, it was optimized the time of mixture, in order to obtain an homogeneous distribution of CNT into polymeric matrix, as well as the processing conditions. The results reveal that mechanical ball-milling is well suited for mix the CNTs with UHMWPE. CNTs were well dispersed and did no loose their physical integrity (as can be shown in Fig. 5). These scanning electron microscopy (SEM) pictures shown different CNT/HDPE powder composites mixed for different time (15, 45 and 60 min). Though the SEM pictures and the tensile tests, it was observed that the optimized time of mixture was for 45 min. To process the mixed composites, it was used the compression molding technique, and the cycle was optimized (Fig. 6 (a)). The SEM analysis of the processed composites has shown that CNTs were well dispersed into the polymeric matrix (Fig. 6(b)). The tensile tests of these composites have shown an enhancement on the mechanical properties of about 20% on the elastic modulus, for 0.2 % vol. of CNTs, and about 80% for higher concentrations (0.4 to 1% vol.). Similar results were reported by other groups (Wang et al., 2005; Mierczynska et al., 2007).

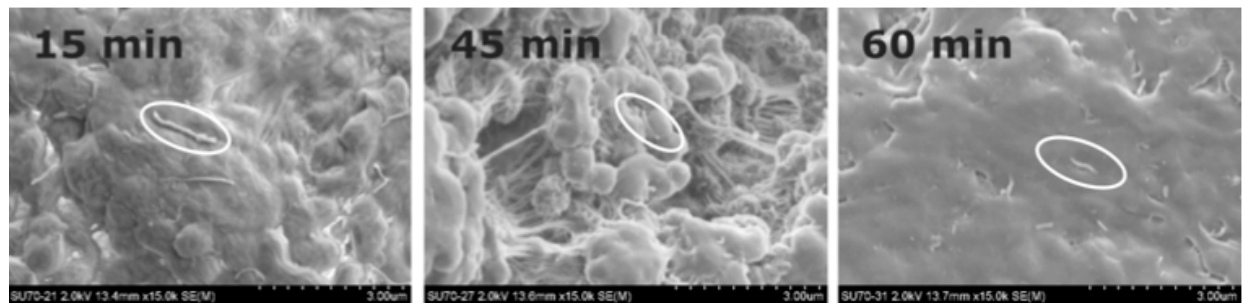


Fig. 5. SEM pictures of the 0.2% vol. MWCNT composite mixed for 15, 45 and 60 min.

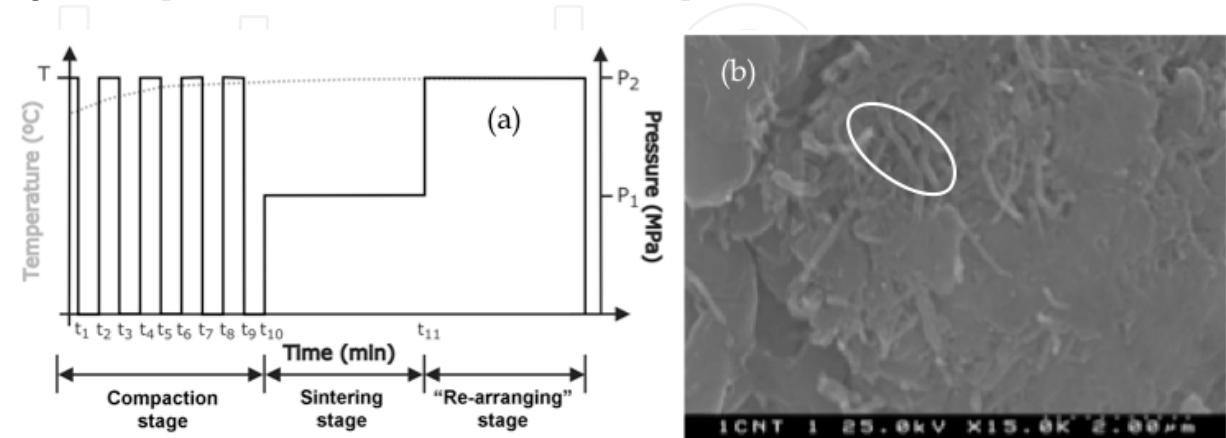


Fig. 6. (a) Optimized compression molding cycle applied for processing the composites; (b) SEM picture of the processed CNT/UHMWPE composite with 1% vol. fraction of CNTs. The round circle gives evidence for the presence of the CNTs.

The enhancement of UHMWPE properties is of utmost importance, essentially for medical applications, as UHMWPE is largely used for that purpose. However, the incorporation of CNTs into UHMWPE, for medical applications, requires special attention in what concerns to toxicity and biocompatibility of these composites. Reis et al. (2010) describe the response of human osteoblasts-like MG63 cells in contact with particles generated from UHMWPE/CNT composites. The results show the absence of significant elevation of the osteolysis inductor IL-6 values, pointed out for possible use of this superior wear-resistant composite for future orthopaedic applications.

3.3 The rheology properties and molding tools

As it was discussed earlier, with the addition of particles to thermoplastics it is possible to modify the physical, thermal and mainly the mechanical properties of the raw thermoplastic. With these enhanced thermoplastics it is of utmost importance to evaluate the relationship of the new materials with the processing parameters, and optimize them, especially when new processing techniques are arising, like microinjection molding. In the bibliography it is possible to read some studies on microinjection molding of neat polymers (Chien, 2006; Sha et al., 2007). Few studies did consider polymer compounds containing fillers, such as glass fibers, glass particles, nanoceramic materials and carbon nanotubes (Huang et al., 2005; Huang, 2006; Hanemann et al., 2009; Abbasi et al., 2011). Huang et al. (2005) study the moldability and wear particles of composites of polymeric matrices reinforced with nanoceramic particles. Their rheology analysis reveals that with increasing nanoparticle loading the shear viscosity increases, meaning that, in microinjection moulding, high pressure is needed to produce high quality parts with micro-features.

Abbasi et al., (2011) prepared PP/CNT and PC/CNT composites and studied the effects of processing conditions on its structure, mechanical properties and electrical conductivity. They concluded that the high deformation values of the microinjection molding only slightly changed the overall crystallinity due to the short cycle time of process. They also observed that the crystals were all oriented in the flow direction. Other interesting result is that the type of processing strongly affects the electrical conductivity of the composites.

4. High performance molding tools

In this section, it will be presented the results of surface modification of the molding blocks. The performance of diamond coated molding tools will be compared with the performance of other typically used coatings and non-coated tools. Different morphologies of the diamond coating will also be presented in order to evaluate their influence on the molding process.

4.1 Surface engineering in molding tools

Although the advances acquired in the past couple of years in the microinjection molding technology process, there are still some problems on the downstream that must be overcome. The micro parts may become statically charged and tend to adhere to surfaces around the molding area, making free fall extraction difficult or even impossible. In the conventional thermoplastic injection molding, the wear of molding tools is known to be one of the main sources of breakdown failures, resulting in production losses. In microinjection of thermoplastic parts, the moulds for components that are miniature complex and require

high precision tolerances are not wear free. On the contrary, the molding surface wear can be even much more critical than in conventional molding. The wear out of the molding tools creates demolding problems, compromising the molding finish quality, speeding up the corrosion of the tools and resulting in costly maintenance stops. Polymer abrasion, adhesion and corrosion are the catalysers of these mechanisms. Furthermore, the increasing usage of polymers reinforced with glass fibers, minerals, or even carbon nanotubes, enhance the abrasive power of polymers.

Coatings technologies have been strongly developed in the last decades, as did their application on mould and die tools. Ion implantation and unbalanced magnetron sputtering PVD (Bienk & Mikkelsen, 1997), High Velocity Oxy Fuel (HVOF) and Atmospheric Plasma Spraying (APS) (Gibbons & Hansell, 2008), diamond-like carbon and silicon carbide (Griffiths et al., 2010), nanostructured TiB₂ (Martinho et al., 2011), Oxide coating (Alumina) and Nitride coatings (AlN, CrN, NiCr(N), TiN) (Navabpour et al., 2006), among other surface engineering coating have been tested in order to evaluate their performance to avoid molding surface wear and assist the demolding process.

Chemical vapor deposition (CVD) of polycrystalline diamond, in microcrystalline and nanocrystalline morphology, detain a number of extreme properties that point it as a technology suitable for exploitation in numerous industrial applications. It possesses a high mechanical hardness and wear resistance, high thermal conductivity and is very resistant to chemical corrosion. Its properties and their optimization by means of the deposition process, in order to fulfill the application requisite have been investigated by several research teams (Ahmed et al., 2006; Das & Singh, 2007; Gracio et al., 2010). Some successful work has already been performed on the evaluation of diamond coating on molding tools in special for micro-featured tools (Neto, 2008b, 2008c, 2009). As refereed above, in this sub-chapter, the application and evaluation of CVD diamond thin films as a surface engineering technique to improve operation and durability of microinjection mould tools will be highlighted.

4.2 Diamond coatings

Polycrystalline diamond, in microcrystalline or nanocrystalline morphology, detains a number of extreme properties that point it as a technology suitable for exploitation in numerous industrial applications. It detains an extreme mechanical hardness (ca. 90 GPa) and wear resistance, one of the highest bulk modulus ($1.2 \times 10^{12} \text{ N.m}^{-2}$), the lowest compressibility ($8.3 \times 10^{-13} \text{ m}^2 \text{ N}^{-1}$), the highest room temperature thermal conductivity ($2 \times 10^3 \text{ W m}^{-1} \text{ K}^{-1}$), a very low thermal expansion coefficient at room temperature ($1 \times 10^{-6} \text{ K}$) and is very resistant to chemical corrosion (Das & Singh, 2007; Grácio et al., 2010).

Most of these properties are attractive for the application on cavities and mould tools; nevertheless coating an entire cavity with polycrystalline diamond is presently an utopia. CVD systems are considerably size limited due to the means of activating (thermal, electric discharge, or combustion flame) the gas phase carbon-containing precursor molecules.

A second problem related to the usage of CVD on mould tools is concerned with the fact that diamond cannot be directly coated onto ferrous substrates, the widest used row material to produce mould tools. Carbon, the precursor element of diamond, easily diffuses into the ferrous matrix, leaving behind no matter to start the diamond nucleation process.

To bypass the latter, appropriate interlayers can be used. A suitable interlayer is the one that promotes a diffusion block from and to the substrate material, enhances the adhesion between the diamond coating and the mould, and does not affect the properties of the diamond film or those of the mould tool, as pointed by Neto et al. (2008a).

A third constraint is the typical diamond deposition temperatures. The process temperature could be a limitation, since high temperatures may change the heat treatment induced in the steel material and alter its properties. Nevertheless, in the past years, deposition has been achieved at lower temperatures than the typical 800 to 900 °C (Dong et al., 2002; Petherbridge et al., 2001).

Not all molding tools are made out of steel material. Hybrid moulds or multi-material moulds are currently used for injection molding prototyping or to enhance mould heat extraction effectiveness. Aluminium, copper, silicon, silicon carbide, among others, are also used. The uses of different tool material place new constraints but also open new possibilities. The use of a silicon insert as the molding block, for example, may benefit from the microfabrication technology attained in the electronic industry. As the demand for smaller devices continues to increase, current manufacturing processes will find it more challenging to meet cost, quantity, and dimensional requirements. By merging silicon microfabrication techniques with appropriated surface engineering techniques, nano-scale features may be produced to replicate nano-features devices (Gourgon et al., 2005; Guo, 2007). Additionally, the deposition of diamond coating on silicon material is vastly reported by the scientific community, making it an excellent candidate material to be surface engineered with tuned diamond films.

CVD diamond deposition is possible by means of activating hydrogen and hydrocarbon. The growth of a diamond film starts from distinct nucleation sites. As individual randomly oriented nuclei grow larger, its diameters equal the average distance between the nucleation sites and start to form a continuous film. The subsequent film growth is dominated by competitive growth between differently oriented grains. With increasing film thickness, more and more grains are overgrown and buried by adjacent grains. Only those crystals with the direction of fastest growth perpendicular to the surface will survive. Thermal or plasma energy is the key factor to promote the fluctuations of the density to achieve small aggregates and to promote the thermodynamic environment to lead to the crystal growth. Nevertheless, it has been gradually recognized that the superequilibrium concentration of atomic hydrogen has also an important role on diamond growth. Various activating methods are used, such as DC-plasma, RF-plasma, microwave plasma, electron cyclotron resonance-microwave plasma CVD, and their modifications. More recently, nanocrystalline (NCD) and ultrananocrystalline diamond (UNCD) deposition have been researched. Many synthesis processes are described in the literature. Most of these processes require an extra gas source such as Ar, N₂ or He. The basic idea behind the deposition process is to enhance the diamond secondary nucleation rate during the deposition, thus leading to the formation of the films. (Sharda & Bhattacharyya, 2004; Spears & Dismukes, 1994)

In the following subsections, the conditions for the different diamond films deposited on steel and silicon will be presented, characterized and evaluated as polymer moulding surfaces.

4.3 Performance of diamond coatings on steel substrates

A set of AISI P20 modified steel molding inserts was prepared and pre-coated with a 2 μm thick PVD chromium nitride (CrN) film, in order to block the mutual diffusion between the ferrous substrate and the diamond growth atmosphere. All the steel plates had the molding surface polished with silicon carbide paper till grit #2000. The samples to be diamond coated were ultrasonic abraded with a diamond solution and then cleaned with isopropyl alcohol. Diamond growth was performed in a hot-filament CVD reactor, using time-modulated CVD process.

In a first experiment, four different samples were prepared to evaluate their performance has molding surfaces. Sample AC1 was submitted to 4h30 of diamond deposition and sample AC2 to 9h00. The full deposition conditions used in steel substrates can be seen in Neto et al. (2008b). Sample AC3 had only the CrN film an AC4 was a bare steel substrate. The two last samples were used in order to compare their performance with the diamond coated inserts.

Figure 7 shows the SEM images of inserts AC1, AC2, AC3 and AC4 before injection molding. Both diamond coated samples exhibited diamond crystallites mainly displaying (111) crystal orientation, although (100) oriented crystals were also observed. These growth directions are typical for the processing temperatures employed in this investigation. The average crystal size of these films is 1.74 and 1.25 μm , and the measured average roughness is 0.18 and 0.16 μm , for samples AC1 and AC2, respectively. Inserts AC3 and AC4 displayed an average roughness of 0.10 and 0.11 μm , respectively. Raman spectroscopy was used to assess the diamond Raman quality, on the diamond coated samples, as proposed by Kulisch et al. (1996) and to estimate the residual stresses of the diamond film according to Ralchenko et al. (1995). Calculated quality factor values for the diamond coatings were 56.0 and 58.3%, for samples AC1 and AC2, respectively. Samples AC1 and AC2 presented diamond peak shifts ($\Delta\phi$) of 11 and 13 cm^{-1} , respectively. Calculated residual stress (σ) values for the diamond coatings were 6.2 and 7.4 GPa, for samples AC1 and AC2, respectively.

After this preliminary analysis using the molding inserts, they were placed in a mould tool specially designed to accommodate the 10 x 10 x 3 mm inserts and mounted in an injection molding machine to perform a cycle of 500 high-density polyethylene (HDPE) sample plates.

The molded samples were analyzed using optical microscopy. Figure 8 displays 150 times magnified images of HDPE objects from the run number 1, 100, 300 and 500. Whatever the type of insert surface, the first injected object presents more heterogeneous surface than the objects injected in cycles 100, 300 or 500. After the first set of injections, the polymeric objects molded with both diamond coating are very alike. The molded pieces by AC3 and AC4, present some surface scratches, but maintain the optical brightness (observed by the naked eye). The samples molded with the diamond coated inserts presented a slightly more tarnished surface than the samples molded with bare steel or with the CrN coating.

This may be due to the slight increased roughness that the diamond coated inserts presented, compared to the non-diamond coated samples, and also due to the crystalline nature of the diamond coatings. It is also worth mentioning that the injected samples 100 by the bare steel insert was very clean, but as the number of injections are increased, the surface of the plastic sample became heterogeneous.

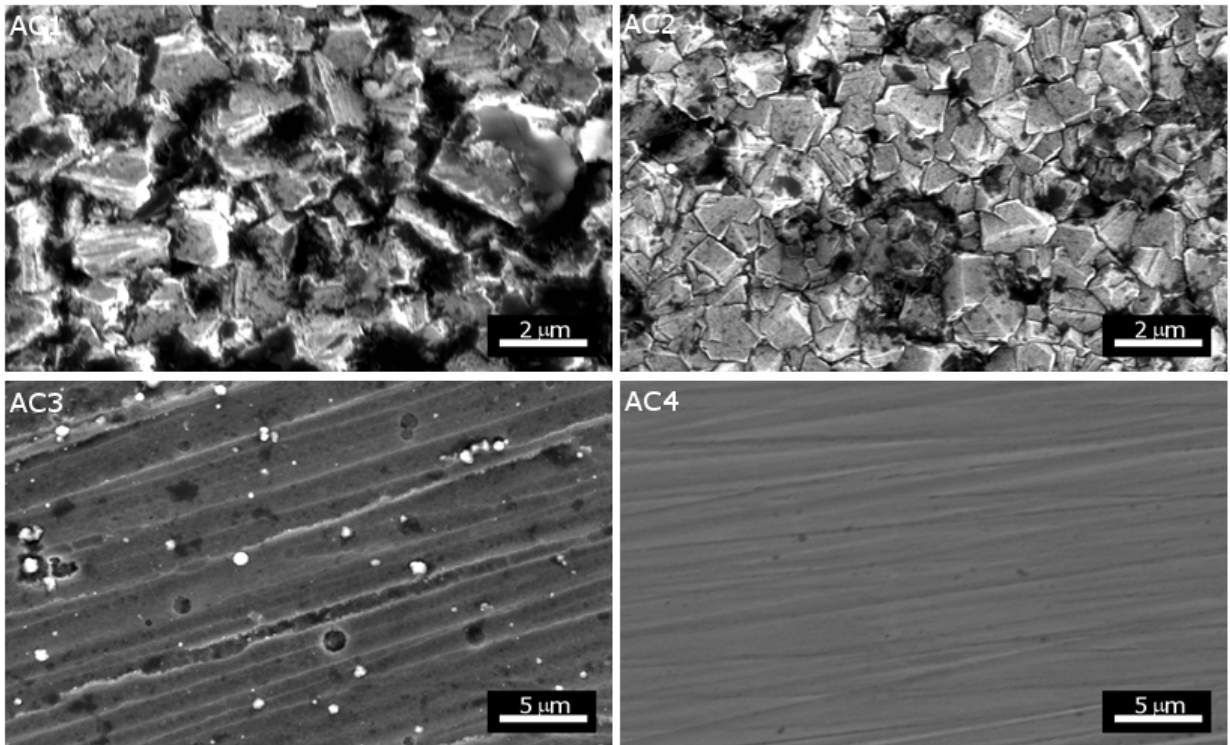


Fig. 7. SEM images of inserts AC1, AC2, AC3 and AC4 before injection molding

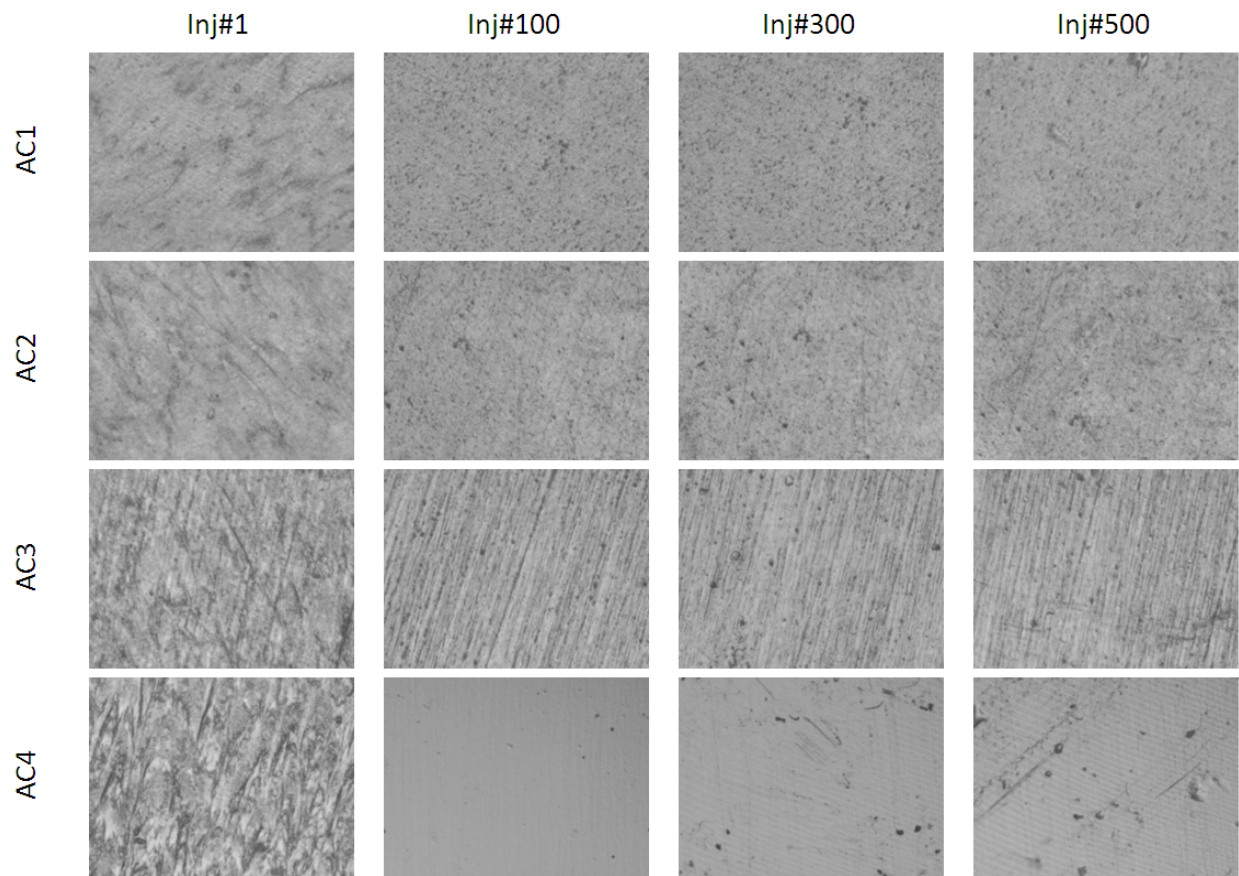


Fig. 8. Optical microscopy images of the HDPE molded surfaces

Since it was found out that the samples molded with the diamond coated inserts presented a slightly more tarnished surface than the samples molded with bare steel or with CrN coating and it is expected that if the average roughness and crystal size of the diamond film is reduced, this problem may be overcome, a new group of samples were prepared. Diamond average roughness and crystal size reduction may be accomplished by the deposition of sub-microcrystalline or nanocrystalline diamond. In order to obtain homogeneous coatings with an average crystal size of about 1 μm or less, different deposition condition were used. The deposition conditions can be seen in Neto et al. (2008c). Three different films were produced. All the as-grown films exhibited sub-micron diamond crystallite size, mainly displaying (111) crystal orientation. The average diamond crystallite sizes of the deposited films were 0.61, 0.71 and 0.83 μm , for sample FD1, FD2 and FD3, respectively. The three coated samples and a bare steel plate (sample F1) was also used in the adapted mould, to serve as a reference sample.

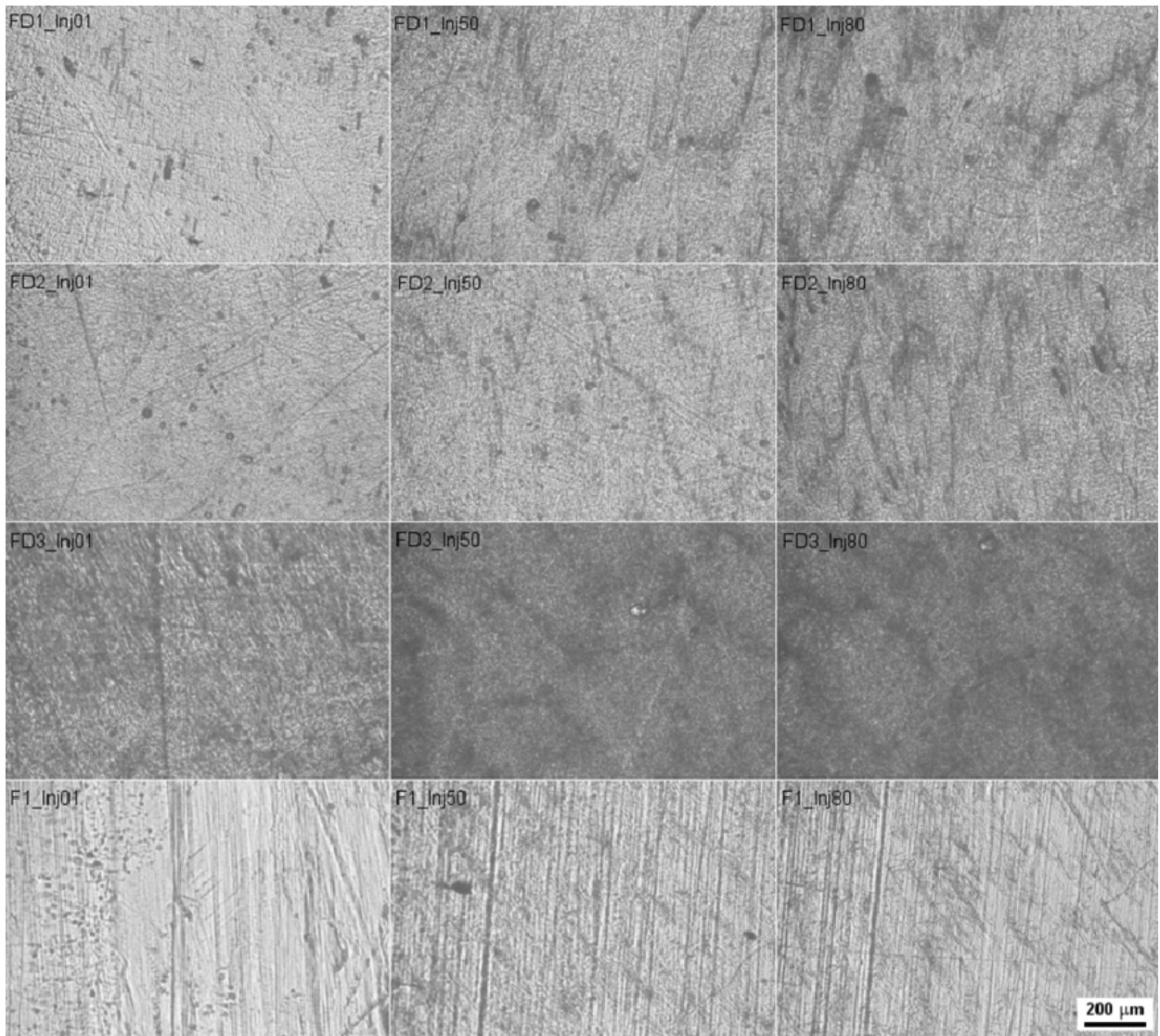


Fig. 9. Optical microscopy images of the HDPE molded surfaces, by the different inserts, in run numbers 1, 50 and 80

Figure 9 displays micrographs of the polymeric molded surface by the different inserts, in run number 1, 50 and 80. Apart from the first set of samples, that present marks of the demolding spray used in the beginning of the processing work, the injected parts are identical. All samples presented a good finishing surface, not showing the tarnished surface that the microcrystalline diamond coated insert originated. From the images, it is evident that the molded objects with the diamond-coated inserts, present more homogeneous surfaces than the ones molded by the insert without coating. It should be noted that insert F1 has the same or better surface finish than the samples that were used to deposit diamond, because their surface was not diamond abraded as the ones pre-treated for diamond coating. The initial steel samples were not surface polished to achieve a mirror surface, in order to obtain optical smooth surfaces and, hence, good quality plastic components/parts. Therefore, the results indicate that polishing time may be saved when using diamond-coated surfaces.

For the evaluation of the degradation of the molding surface, the injected parts by the different systems were analyzed. These parts had simple features which were measured throughout the injection process. Samples molded by diamond coated inserts showed a degradation trend of 0.0001 mm/injection, but the samples molded by samples with only the CrN film or without film presented a degradation trend of 0.0004 mm/injection. This may be due to the polymer aggregation to the cavity.

4.4 Performance of diamond coatings on steel substrates

Silicon (Si) and silicon carbide (SiC) samples were prepared to be diamond coated and then tested to be used as molding blocks. The diamond growth was performed using conditions to achieve both microcrystalline and nanocrystalline diamond morphology. Microcrystalline conditions can be seen in Neto et al. (2008c). Nanocrystalline was achieved by adding Argon gas to the reactor chamber. The full deposition conditions for the latter can be seen in Neto et al. (2011).

Figure 10 presents the SEM images of the as coated diamond films on Si and SiC with the nanocrystalline conditions. Si (a) is a low magnification image showing the rip and the nearby surface of the featured Si substrate. Si (b) is a high magnification image from the top surface and Si (c) from inside a feature. SiC (a) is a 600 times magnified image of one of the SiC samples, and SiC (b) and SiC (c) are also from the top surface from inside one of the rips, respectively. All films are almost fully coalescent and are composed of nanocrystalline diamond particles with a size inferior to 100 nm. The roughness assessment by means of a profilometer lead to an average surface roughness of 0.12 and 0.19 μm for the deposited diamond films on Si and SiC, respectively.

From the coated samples, 100 of HDPE parts were molded. It seems to replicate the molding surface in a proper way, displaying a fine shining surface.

The Si samples coated with microcrystalline diamond presented similar results as the ones presented by the steel coated substrates.

Different coated systems were tested to reproduce high-density polyethylene (HDPE) components, namely microcrystalline, sub-microcrystalline and nanocrystalline diamond films. Each coated systems were tested for a number of injection cycles in order to evaluate

the polymeric produced parts and also the degradation of the coated inserts. All coated samples presented good stability at least till 500 runs (the maximum that a single diamond coated insert was subjected to, under laboratory conditions). The HDPE thermoplastic molded objects presented good quality and reproduced well the molding surface. Microcrystalline diamond coated inserts produced slightly tarnished plastic parts. The latter, seems to be considerably dimmed with the use of sub-microcrystalline or nanocrystalline films. The diamond coated featured inserts presented a good performance and a reduced degradation trend comparatively to the non-coated surfaces.

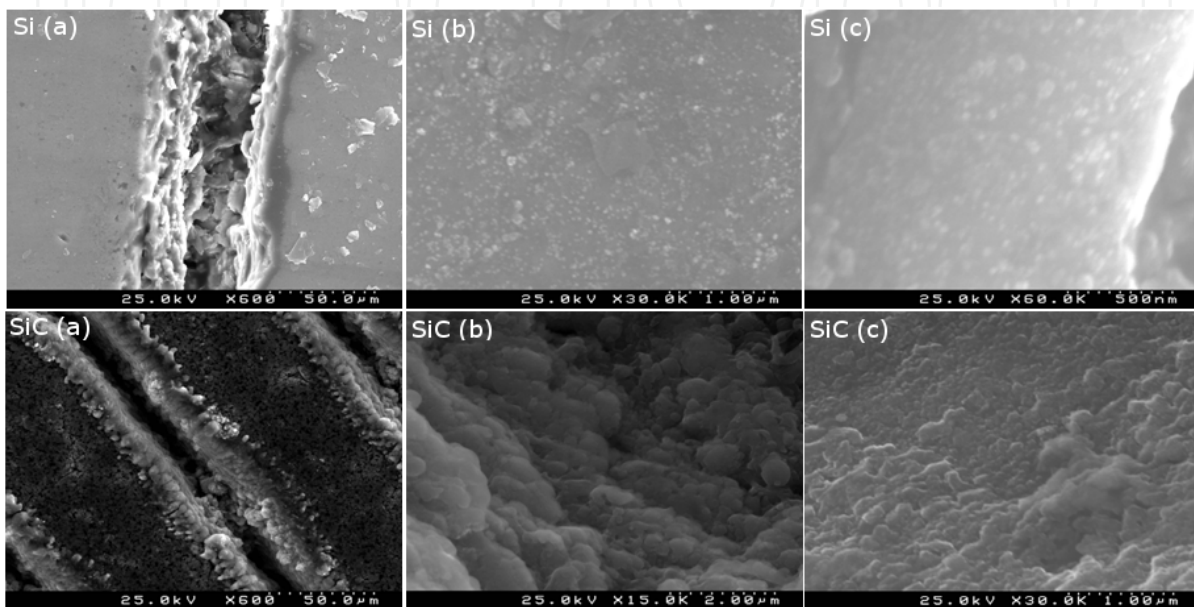


Fig. 10. Nanocrystalline diamond deposited on Si and SiC structured substrates

5. Conclusion

Injection molding enables the large scale production of polymeric components with accuracy. This technology has been progressively used for the production of micro-components in quantity and quality at low cost, which supports the development of micro-electro-mechanical systems. Nevertheless, the dimensional reduction of the components requires a higher control of the dimensional accuracy of these devices. It is also known that in the molding blocks of this type of objects, the wear is amplified due to the fact that the surface roughness is dimensionally very close to the dimensions being controlled. Reinforcing materials such as glass or metallic fibers, or carbon nanotubes in the polymeric matrix enhances the wear capability of the material being injected, compromising the service life time of the tools. Reinforced thermoplastics, the so called nano-composites, where developed in order to test the tools and the process, using carbon nanotubes as enhancers.

A gateway to reduce the deterioration of the molding impressions, increase their durability and reduce the need of corrective intervention on the tool may be by the use of appropriate surface engineering processes. The use of nanocrystalline diamond or other allotropic carbon coatings is considered a potential surface engineering coating for this type of application, since it detains high hardness and high thermal conductivity, being both properties very interesting to apply to the thermoplastic injection molding process. The

coating with thin carbon based films is possible by means of chemical vapor deposition techniques. The roughness of these films and the intrinsic characteristics of diamond lead to a reduced friction coefficient, which will be important to minimize the wear of micro-components on the extraction stage.

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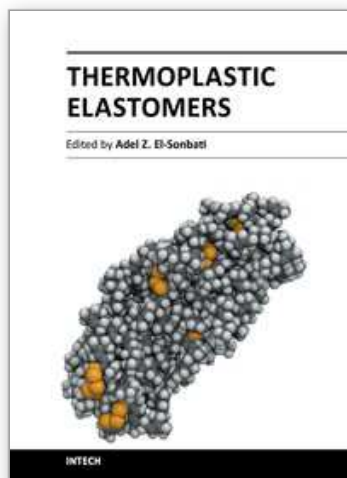
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Thermoplastics can be used for various applications, which range from household articles to the aeronautic sector. This book, "Thermoplastic Elastomers", is comprised of nineteen chapters, written by specialized scientists dealing with physical and/or chemical modifications of thermoplastics and thermoplastic starch. Such studies will provide a great benefit to specialists in food, electric, telecommunication devices, and plastic industries. Each chapter provides a comprehensive introduction to a specific topic, with a survey of developments to date.

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