Assessment of polymeric flow in micromouldings coated with nanocrystalline diamond

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ABSTRACT: With the increased production of microcomponents, it is necessary to overcome various technological challenges existing in the micro-injection moulding process: the wear of the microfeatured moulding tool; the perfect filling of high aspect ratio paths; the rheology and heat transfer mechanism in such conditions; among other factors. To address some of these challenges, appropriate moulding surface coatings, displaying high hardness, high thermal conductivity, high thermal shock capacity and low friction coefficient may be of great importance. In this work, a moulding insert was coated with nanocrystalline diamond films. This insert, especially designed to evaluate the flow front of two pathways, was then used for the production of polypropylene microparts with the scope of analysing the relative position of the welding line, and therefore, evaluate the polymeric melt flow in the microimpressions. The morphology, quality and stress developed in the obtained diamond film was analysed, showing an average grain size of about 100 nm, in which their crystals are homogeneous, forming a coalescent film. The coatings present a typical Raman spectrum. Through the moulding path with the diamond coating, it was found that the melt temperature is the variable that has the greatest influence on the advance of the front flow. The front flow appears to benefit from the coating, leading to a more controlled filling process, replicating the findings presented formerly. It is suggested that the diamond coating can act as a heat buffer, weakening the heat transfer mechanism in the polymer/mould interface at the flow stage, reducing the importance of the design of the temperature control system.

1 INTRODUCTION

1.1 *Problem contextualization*

The injection moulding of thermoplastics is a process that has been developed on a large scale in the last decades, being currently applied for various applications. The increased miniaturization of the technological systems is leading manufacturers to adapt the injection moulding process to the production of microcomponents. Nevertheless, the simple miniaturization of conventional injection moulding is not valid, due to various problems such as the wear of the moulding tool, the aspect ratio of the cavities to fill, the rheology and heat transfer mechanisms, among others (Neto 2009). The polymeric flow through microimpressions leads to a rising of the shear heating, contributing to an increase of the wear of moulding surface and compromising the tool life service. These problems increase the number of maintenance stops and influence negatively the overall quality of the moulded parts. Moreover, at the micrometre scale, many phenomena known from conventional injection moulding process of thermoplastics are not directly applicable, the rheology of materials on the nanoscale being dissimilar of those at the macroscales scale (Neto 2012).

1.2 *Objective*

Moulding surface coatings, displaying high hardness, high thermal conductivity, high thermal shock capacity and low friction coefficient may be of great importance. Nanocrystalline diamond film presents the properties aforementioned (Kulisch 2006).

In this paper, a moulding insert was coated with a commercial chromium nitride film in the moulding pathway and coated with a nanocrystalline diamond film in the opposite pathway. This insert was after used for the production of polypropylene (PP) microparts, with the scope of analysing the relative position of the welding line, and therefore, evaluating the polymeric melt flow in the microimpressions.

2 EXPERIMENT DETAILS

2.1 *Moulding block*

It was used a micromoulding block of AISI P20 steel (Fig. 1) to produce PP microparts that geometrically consist in a 16 × 10 mm plate with a central rectangular orifice (Fig. 2).

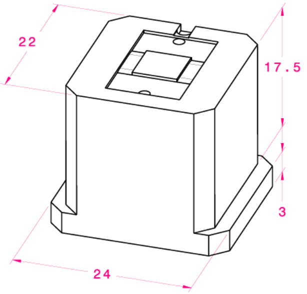

Figure 1. Main dimensions of micromoulding block.

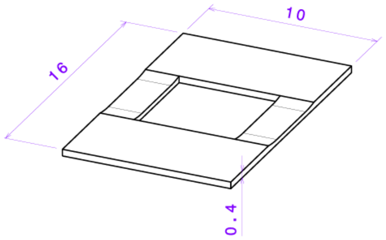

Figure 2. Main dimensions of PP micropart.

2.2 *Nanocrystalline diamond film deposition*

The diamond coating of steel substrates presents some difficulties and, despite some progress in this area, it still remains a complex problem. The diamond coating cannot be directly appliedonto the ferrous substrate, because carbon (the precursor element of diamond) easily diffuses into the ferrous matrix, leaving behind no matter to start the diamond nucleation process (Neto 2008). Moreover, the difference between the coefficient of thermal expansion of diamond and steel is too high, causing a residual stresses in the diamond film and negatively affecting its adhesion (Polini 2006). So, it is important to have an intermediate layer between the diamond film and the steel. Therefore, the moulding block was coated with chromium nitride (CrN) by PRIREV Lda, using the PVD process. The CrN thin film is a ceramic coating with high hardness, good oxidation resistance, toughness and ductility and a low coefficient of friction, preventing the diffusion over the block through the substrate material and allowing the adhesion between the diamond film and the moulding surface, not affecting the properties of the diamond coating or the moulding tool (Neto 2012; Warcholinski 2009).

After the CrN deposition, in order to achieve a diamond film just onto one of the moulding impression pathways, it was necessary to carry out an appropriated methodology, being used the procedure presented in (Neto 2012).

For the CVD process, three tantalum filaments of 0.25 mm of diameter and 100 mm length were prepared and inserted in a horizontal position into the HFCVD reactor. Then, the moulding block was left under a vacuum of about 10^{-3} Torr of pressure for 30 min, in order to avoid contamination effects with undesirable gases inside the rector. The deposition was then started, including the initialization of the filament temperature acquisition and the power source, in order to control the current and voltage according to the substrate temperature. After 7 h, the substrate temperature was decreased. When the substrate temperature reached 100 ˚C, the gas flow was turned-off, as well as the water cooling and then the air valve was open, in order to stabilize the pressure. All the procedures where repeated to achieve a total deposition of 14 h. The latter led to a diamond film grown on the pre-treated site. In Table 1, the conditions for the deposition are specified.

Table 1. Deposition conditions.

Parameters	Values	Units
Temperature of moulding block	700±50	˚C
Filament Temperature	2100±50	˚C
Time Deposition	14	hours
CH_4 flow	$3.30x10^{-8}$	m^3/s
H_2 flow	$1.66x10^{-6}$	m^3/s
Ar flow	$1.67x10^{-6}$	m^3/s
Pressure	4000	Pa

2.3 *Injection moulding*

The injection moulding was performed in a Boy 12A injection moulding machine. It is fully hydraulic equipment, projected for small moulds, allowing a high metering precision from 0.0001 to 0.01 mm^3. The injection unit features a screw of 18 mm diameter. The injection moulding cell is completed with a mould temperature regulator and an external control unit for the cartridge heaters used in the temperature control system of the mould. Table 2 shows some characteristics of the Boy 12A injection moulding machine. The material used to produce the microparts was semi-crystalline polypropylene (PP) HP500 N, produced by Basell Polyolefins Europe. It is a homopolymer very used in the injection moulding process, showing a good hardness and good flowability.

Table 2. Characteristics of the Boy 12 A injection moulding machine.

Characteristics	Values	Units
Screw diameter	18	mm
Screw L/D ratio	18:1	-
Injection pressure	240	MPa
Injection rate	30.6	g/s
Injection volume	0.1	cm^3

The injection of PP was carried out at a constant injection pressure of 100 bar. The packing pressure was of 10 bar for 2 s and the cooling time of 20 s. The mould temperature, the melt temperature and the injection velocity were the three variables that alternated between 2 levels, leading to 8 different experiments as indicated in Table 3.

Table 3. Details of the DOE experiments.

Experiment	T_{mould}	T_{melt}	V_{inj}
	˚C	˚C	mm/s
DOE1	50	240	72
DOE2	50	240	144
DOE3	65	240	144
DOE4	65	240	72
DOE5	65	220	72
DOE6	65	220	144
DOE7	50	220	144
DOE8	50	220	72

For each DOE experiment, at least 30 injection mouldings runs were performed, in order to minimize the natural variation of the process.

The injected parts where afterward analysed using an Olympus ILLC2 microscope to examine the weld line location.

3 RESULTS AND DISCUSSION

3.1 *Diamond deposition*

The CrN film was deposited with a good uniformity over the entire moulding surface, having as thickness about 2 µm.

During the diamond deposition on the HFCVD reactor, the different parameters were acquired, including the top process parameter: substrate temperature and filament power of with the growth rate and morphology will depend, in addition to the precursor gas feed.

The SEM images quality are slightly influenced by the electrostatic charges present in the samples, due to the fact that the SEM images acquisition was done after the production of the microparts, so the coating might have been contaminated by PP residues. Nevertheless, they allow the correct analyse of the crystalline morphology. Analysing Figure 3, it was possible to observe that the crystal structure is homogeneous, forming a coalescent film. It was also possible to observe that the average grain size is of the order of 100 nm.

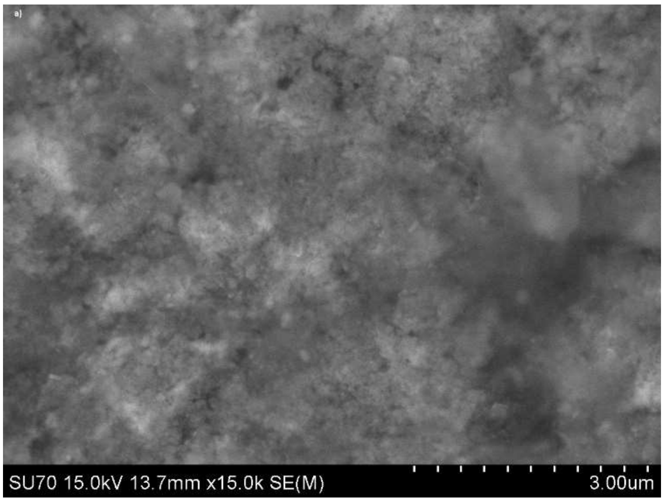

Figure 3. SEM image of nanocrystalline diamond film.

The Raman spectrum was obtained in the range 1000-1800 cm^{-1}, a wavelength of 532 nm being used. The Raman spectroscopic analysis was performed to assess the film quality. With the assistance of spectroscopy peak deconvolution software, the Raman spectra was subtracted from its linear background and then mathematically decomposed with Loreantzian functions for the diamond peak and Gaussian function for the non-diamond bands (Fig. 4). Therefore, the Raman spectrum exhibits the following power dispersion: nanocrystalline diamond (≈1178 cm^{-1}), polycrystalline diamond (≈1331 cm^{-1}), D and G band (≈1365 cm^{-1}) and microcrystalline graphite, D band (≈1587 cm^{-1}).

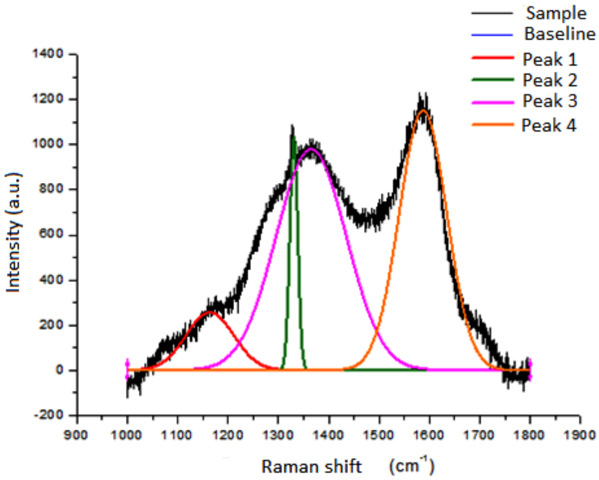

Figure 4. Raman spectroscopy of the deposited film and Deconvolution.

Analysing Figure 4, it was possible to obtain important information to better characterise the coated film on the moulding surface. To quantify the diamond proportion, f_q, it was used the relation of the area below the diamond peak ($A_{diamond}$) to the total area of the peaks:

$$f_q = \frac{75A_{diamond}}{75A_{diamond} + \sum 75A_{other\ bands}} \tag{1}$$

To calculate the film quality, Q, it was used the relation between the intensity of diamond ($I_{diamond}$) peak and the sum of this intensity with the intensity of the graphite peaks:

$$Q = \frac{I_{diamond}}{I_{diamond} + I_{graphite}} \tag{2}$$

Therefore, observing Figure 4 and using equation 1, the diamond proportion (f_q) is about 14 % and using the Equation 2, the diamond quality is about 39.35%. The values of f_q and Q are relatively low, because the film exhibits two non-diamond bands (microcrystalline graphite). Moreover the film suggests being subjected to tensile stress due to the influence of non-diamond phases at the grain boundaries.

3.2 *Polypropylene microparts*

For the production of the microparts it was used a micromoulding block with a diamond film in one moulding pathway and a CrN film in the opposite pathway. As described in the experimental procedure, they were considered 8 different injection conditions, 30 microparts being produced for each processing condition. Posteriorly, 3 microparts of each DOE were selected to be analysed by means of polarized light microscopy, in order to evaluate the weld line location.

Figure 5 exhibits a micropart with the axis system considered: the y-axis represents the interval [0, 6] (mm) and x-axis represents the interval [0, 5] (mm). The left pathway of the micropart corresponds to the moulding pathway coated with diamond film and the right pathway corresponds to the moulding pathway coated with CrN film.

The Figure 5 shows two centred circles. The top circle corresponds to the extractor and the bottom circle corresponds to the pressure sensor. Both features are neglected for the evaluation of the welding line, since their effect is balanced and constant. It is also important to note that the diamond coated pathway has a slightly inferior aperture than the opposite one, less than 1 µm (the thickness of the diamond film). Additionally, it must also be noted that the coatings are only in the moulding block. The fixed cavity plate (the half of the mould that is attached to the fixed platen of the injection moulding machine) has no coating.

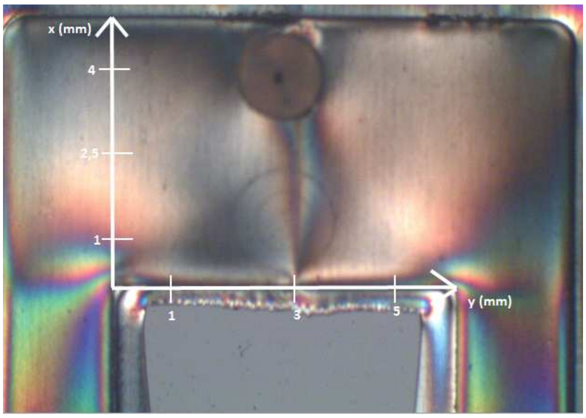

Figure 5. Micropart analysed in the optical microscope.

Analysing the weld lines in polarized light and with the aid of software for data acquisition, the lines were plotted for each injection condition. Then, a weighted average of weld lines provided by 3 microparts for each DOE was performed to get one single average line per DOE experiment, as displayed in figure 6. Analysing figure 6, it was possible to observe that the weld lines are located above the micropart centre (y=3 mm), i.e. the weld lines are located in the opposite side to the pathway coated with diamond film. However, for each injection condition, there are weld lines closer to the micropart than others. The weld lines of samples DOE1, DOE2 and DOE4 are located closer to the micropart centre, while the weld lines of samples DOE5, DOE6, DOE7 and DOE8 tend to move away of the micropart centre. The weld line of sample DOE3, initially, is farthest from the micropart centre, but then this weld line approaches of the centre.

The common parameter of DOE1, DOE2, DOE3 and DOE4 is the melt temperature. In the same way, the common parameter of the DOE5, DOE6, DOE7 and DOE8 is the melt temperature of 220 °C. Therefore, the melt temperature is the variable with more influence on the advance of the front flow, i.e. the flow front appears to benefit from diamond coating (Fig. 7) in more controlled injection conditions, especially when the melting is at a temperatures closer to the solidification point.

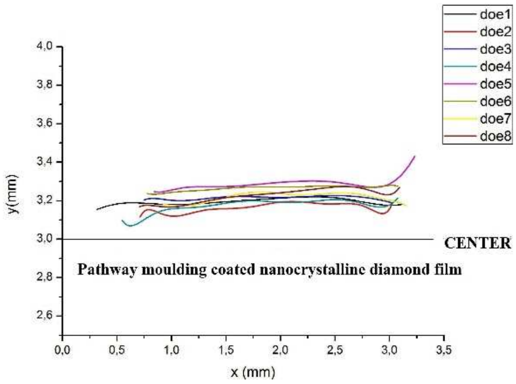

Figure 6. Weld line location average for the different experimental setups.

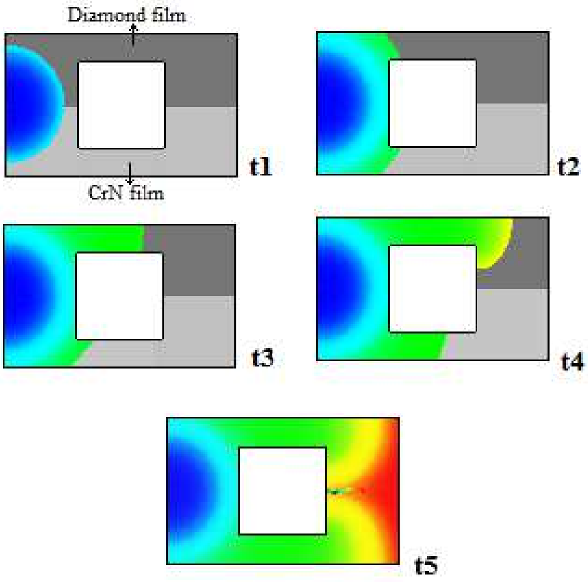

Figure 7 - Behaviour of polymeric flow during filling: t1<t2<t3<t4<t5, where t represents time.

The behaviour illustrated in Figure 7 can be influenced by the high thermal shock resistance capacity of diamond, which leads to heat buffer behaviour, weakening the influence of the heat transfer mechanism on the polymer/mould interface at the flow stage, allowing a less aggressive design of the temperature control system.

The results obtained in this study are in accordance with previous experiments reported elsewhere (Neto 2012).

CONCLUSIONS

In this study it was used a micromoulding block and a moulding tool to evaluate the influence of advanced coating systems in the polymeric flow in micro cavities. The moulding insert is able to produce thermoplastic parts of 16×10 mm with a central rectangular orifice. The moulding surface of the block was coated with commercial CrN and posteriorly, through HFCVD process it was coated with nanocrystalline diamond film in one of the moulding pathway, exhibiting two pathways with different characteristics.

The obtained coalescent diamond film has homogeneous crystals and an average grain size of 100nm. Moreover, the film shows a typical Raman spectre of nanocrystalline diamond, however this film displays still some internal tensile stress, most probably due to the influence of non-diamond phases. Parameters like low hydrogen flow and low substrate temperature can have influenced the quality and tensions of the film.

After the diamond deposition, the block was used to produce 30 microparts, for eight different DOE. The injection pressure, the packaging pressure, the packaging time and the cooling time were kept constant for all the experiments, while the mould temperature, the melt temperature and the injection velocity were varied between two levels. The PP parts were observed by polarized light microscopy, to observe the weld lines.

It was found that for lower levels of melt temperature, there is a significative influence of the diamond film on the polymeric flow. The front flow appears to benefit from the diamond coating, which may lead to a more controlled processing condition. Therefore, it is speculated that diamond can act as a heat transfer buffer, weakening the influence of the heat transfer mechanism on the polymer/mould interface at the flow stage, allowing less aggressive design of the temperature control system.

ACKNOWLEDGEMENTS

The authors acknowledge for the support through the project SUDOE (SOE4/P1/E793). The authors also acknowledge Prirev, Lda. (Vagos, Portugal) for the CrN film deposition. The authors acknowledge Professor S. K. Mendiratta for the use of the polarised optical microscope.

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