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Advanced coating systems towards the analysis of polymer flow within microcavities

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ABSTRACT: It is known that the production of polymeric micro components by injection moulding presents technology challenges that differ from the ones of conventional macro parts. High shear heating is known to occur in microcavity flows and may significantly contribute to increase wear within the microimpression compromising both tool life service and overall quality of the moulded parts. Advanced coating systems, detaining high hardness, high thermal conductivity, high thermal shock capacity and low friction coefficient may help to reduce the aforementioned problems. In this paper, a micromoulding insert is coated with a nanocrystalline diamond film on one side and a chromium nitride film on the opposite one. The coatings have been characterized as deposited and after the moulding runs. The coated micromoulding block was then used to produce polypropylene parts and specific quality signatures (i.e. weld line relative position) were established in order to assess the coating performance on semicrystalline polymer flow behaviour. It was found that polymeric flow at lower melt temperature may benefit from a diamond coating, which seems to be related with the thermal shock resistance capacity of diamond. The latter may act as a temperature buffer, fading the high influence of the polymer/mould interface heat transfer mechanism.

1 INTRODUCTION

The demand for small and accurate parts to equip electronic and mechanical devices is an increasing demand. Although conventional moulding is a well-known process, the simple miniaturization/rescale of the conventional injection moulding process is not valid due to problems related with the rheology of the polymer flow in the micro cavity/channel.

The flow of the polymer material through microcavities is known to give rise to high shear heating that may significantly contribute to increase wear of the moulding surface, therefore compromising the tool life service, i.e. requiring a higher number of maintenance stops, and the overall quality of the moulded parts.

Nanocrystalline diamond film detains a number of extreme properties that may help to reduce the abovementioned problems. It presents high hardness, high thermal conductivity, high thermal shock capacity and low friction coefficient.

In this paper, a micromoulding block was coated with a nanocrystalline diamond film on one side and a chromium nitride film on the opposite one. The coatings are characterized as deposited and after the moulding runs.

Polypropylene microparts were produced and specific quality signatures were established to assess

the coating performance upon moulding this semicrystalline polymer. To establish the latter, the weld line relative position was selected and analysed.

2 EXPERIMENTAL DETAILS

2.1 Moulding block and polymeric part

The micromould tool used to carry out the injection moulding supports interchangeable moulding blocks, shown in figure 1. This moulding insert is able to produce a 16×10 mm plate with a central orifice, as presented in figure 2.a. Figure 2.b and figure 2.c display the dimensions of the plate.

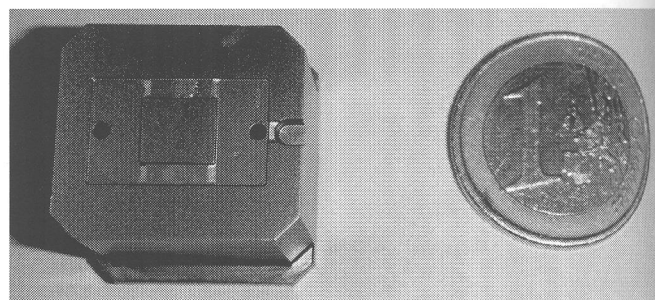
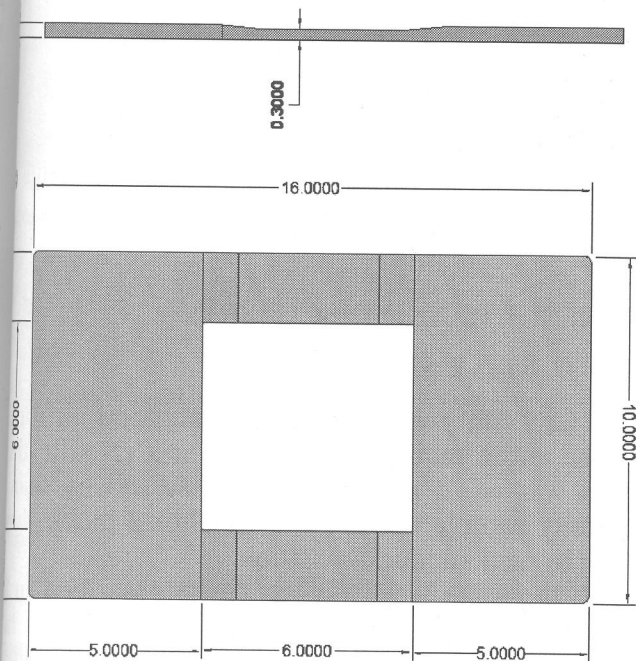
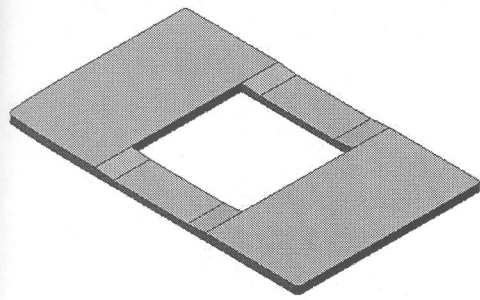


Figure 1. Cavity moulding block.



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Figure 2. a) Overview of the micropart. b) Lateral view dimensions. c) Top view dimensions. Dimensions are in millimeters.

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This geometry creates two pathways with different characteristics, which will display its influence on the flow behaviour and consequently in the weld line of the part.

The moulding block is produced in AISI P20 steel.

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2.2 Diamond film deposition

Figure 3 outlines the steps to achieve the diamond film on one of the polymeric flow pathways.

Prior to the steps described in figure 3, the moulding block surface was coated with chromium nitride (CrN) as described by Neto et al. (2009). The deposition of a CrN layer has two roles in this work. The first role is to be used as a surface enhancement of the moulding surface in order to compare its performance with the one of the diamond film. CrN is a tough thin film coating with high hardness, good oxidation resistance, and a low coefficient of friction for a ceramic coating, making it ideal for metal and plastic forming applications. The second role is to serve as a buffer layer between the steel surface and the diamond coating. Diamond cannot be directly coated onto ferrous substrates. Carbon, the precursor element of diamond, easily diffuses in-

to the ferrous matrix, leaving behind no matter to start the diamond nucleation process. The use of a CrN interlayer 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. (Neto, 2009)

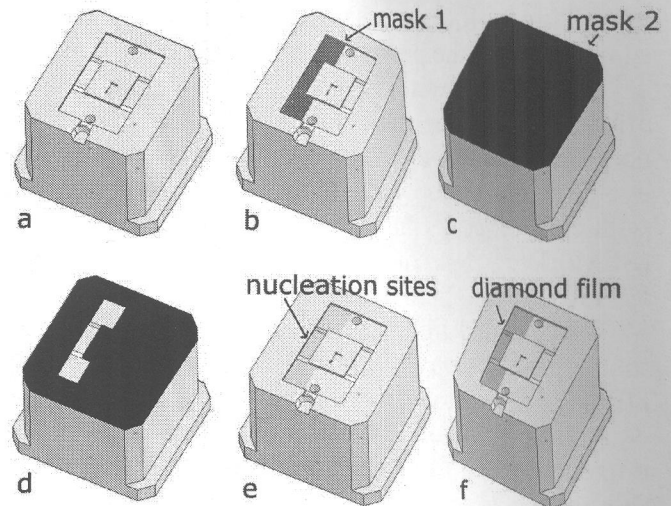


Figure 3. Sketch of the steps to achieve a diamond film on a half of the moulding impression. a) Bare moulding block. b) Placement of mask 1 (parafilm mask). c) Impregnation of the moulding surface with mask 2 (black wax). d) Removal of mask 1 to reveal the surface to be coated. e) After the nucleation pre-treatment and the removal of the black wax. f) After the deposition process.

After the CrN deposition (figure 3.a), in order to achieve the diamond film just on one of the moulding impression pathways, it was necessary to carry out an appropriated methodology. A first mask (figure 3.b) was produced of parafilm, a plastic paraffin film, with the shape of the desired diamond coating, and placed in the moulding block. This is then followed by the application of a second mask (figure 3.c), a liquid solution of black wax (Apiezon). After the solidification of the black wax, the parafilm mask is removed, revealing the moulding surface (figure 3.d). The moulding block is then submitted to a pre-treatment in order to enhance the diamond nucleation. The pre-treatment consists of the sonication of the sample for 1 hour in a diamond suspension solution, composed of 1 carat of 0,25 μm grain size of commercial diamond powder, dissolved in 20 ml of pure methanol. This treatment creates nucleation sites on which the diamond film will nucleate. After this treatment the black wax mask is dissolved with limonene in an ultrasonic bath and then cleaned in pure methanol (figure 3.e).

The diamond deposition is then performed. For the deposition process, the substrates were placed 5 mm from an array of horizontal tantalum filaments, with 0,25 mm of diameter and 100 mm of length. The deposition temperature was measured by a type K thermocouple, touching the top side of the mould-

ing block and kept at 700 ± 50 °C. The filament temperature was kept at 2100 ± 50 °C and was measured by an optical pyrometer (IMPAC IS140). The deposition was performed in a homemade HFCVD system for 14 hours, with a gas mixture of argon, hydrogen and methane, with a flow of 100, 98 and 2 sccm, respectively (1 sccm = 1 mln/min). The deposition was performed at a constant pressure of 30 Torr (~4000 Pa). The latter led to a diamond film grown on the pre-treated site (figure 3.f).

The coatings were characterized as deposited and after the moulding runs. Scanning electron microscopy (SEM) and optical microscopy were used to evaluate the films, with a SEM system equipped with an Energy dispersive X-ray spectroscopy (SEM/EDS - Hitachi 4100) and a Nikon Eclipse LV150 Optical Microscope, respectively.

The diamond film was also assessed with a Raman spectroscopy system (JOBIN YVON HR800UV) operated at room temperature and equipped with an ion laser with wave-number of 325 nm. Appropriate filter for spectrum acquisition was selected and an acquisition time of 0,2 s was used.

2.3 Injection moulding

The mouldings were produced with a Boy 12 A injection moulding machine with $\varnothing 14$ mm injection screw (Dr Boy, Germany) that combines technical characteristics required for microinjection and affordability. The injection moulding cell also includes a mould temperature regulator and an external control unit for the cartridge heaters used in the temperature control system of the mould. The Boy 12 A machine is able to meter an injection volume of 0.1 cm^3 at a high flow rate, up to $15.6 \text{ cm}^3 \text{ s}^{-1}$. The injection pressure is limited to 240 MPa.

A semi-crystalline polymer polypropylene (PP) HP500N by Basell Polyolefins Europe was used. It is an easy flow grade with MFR of 12g/10 min (230°C , 2.16 kg).

During the injection moulding experiments, the injection pressure was kept at 100 bar, the packing pressure at 10 bar for 2 s, and a cooling time of 20 s. The mould temperature, melt temperature and injection velocity were the three variables of the full factorial experiment, using two levels of each parameter, as presented in table 1. The mould temperature was varied between 50 and 65 °C; the melt temperature between 220 and 240 °C; and the injection velocity between 72 and 144 mm/s. This led to 8 different experimental setups.

Table 1. Details of the DOE experiments.

Experiment	T mould	T melt	V inj
	°C	°C	mm/s
DOE 1	50	220	72
DOE 2	50	220	144
DOE 3	50	240	72
DOE 4	50	240	144
DOE 5	65	220	72
DOE 6	65	220	144
DOE 7	65	240	72
DOE 8	65	240	144

In order to minimize the natural variation of the process, at least 30 mouldings were produced keeping a consistent cycle time.

The weld line location in the micromouldings was observed with an Olympus BH2 microscope.

3 RESULTS AND DISCUSSION

3.1 Deposited films

The CrN film was deposited with a good uniformity in the entire moulding surface. The CrN film thickness was ca. 2 μm . This was assessed by using a dummy sample next to the moulding block during the physical vapour deposition.

In the same way, the procedure described in figure 3 and the diamond deposition conditions have shown to be suitable to grow a tailored diamond coating. Figure 4 presents a high magnification SEM image of the nanocrystalline diamond film. The grain size of the diamond crystallites are below 30 nm. Nevertheless, it can be observed that the film is not complete, displaying nodules of nanocrystalline diamond of about 100 nm. Several authors report that the NCD films start the growing process with the growth of individual nodules, which eventually coalesce to form a continuous film. When the film is continuous and without NCD nodules, it gives indication of a very high nucleation density, on the contrary the presence of the nodules is due to a low nucleation rate (Kulisch, 2006). With the used conditions and the deposition time, it would be expected the film to have a thickness of about 1 μm .

Raman spectroscopy analysis was performed to evaluate the quality of the diamond film and the acquired spectrum is presented in figure 5. The spectrum presents the typical nanocrystalline diamond signature. A D and G band, that are due to sp^2 carbon structure are scattered at 1360 and 1580 cm^{-1} , respectively. The sp^3 carbon hybridization scattered at 1332 cm^{-1} is also present although masked by the presence of the 1360 cm^{-1} band. Also evident is the presence of nanocrystalline diamond to which the Raman line $1150\text{-}1190 \text{ cm}^{-1}$ is attributed (Wei, 2010).

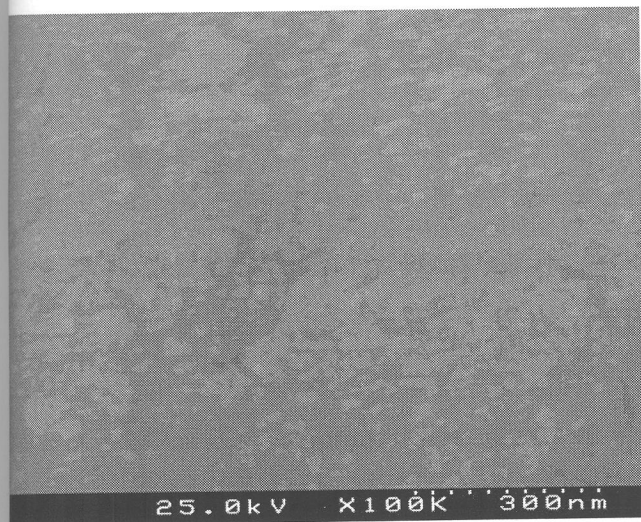


Figure 4. Scanning Electron Microscopy of the deposited film.

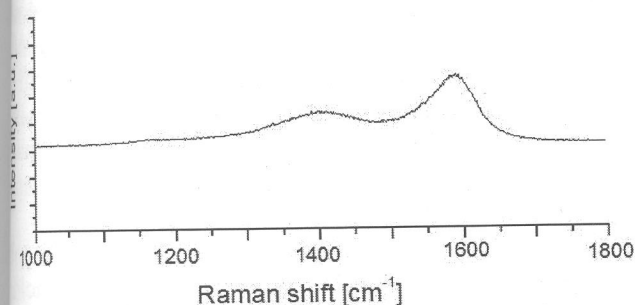


Figure 5. Raman spectroscopy of the deposited film.

During the injection process, the diamond coating was macroscopically observed for degradation. It should be said that the latter was not observed, not even at the end of the full process (more than 240 injection cycles). Nevertheless, it must be stated that this is a rather small number of runs to evaluate full wear rate of a diamond coating.

3.2 Polymeric parts

Figure 6 presents the zone with weld line of an injected PP micropart in experiment DOE1, by means of a polarized microscopy. From the eight different experimental sets, 3 samples were selected to be observed under the microscopy, in order to evaluate the weld line location.

In the image, two circle marks are observed. The one on the right corresponds to the extractor and the one on the left to the pressure sensor.

Due to the difference in the friction coefficient of diamond and CrN, that the literature places between 0,005 to 0,15 (Grillo, 2003) and 0,4 to 0,8 (Warcholinski, 2009), respectively, it is expected that the polymer flow may be subjected to a lower friction when flowing through the diamond pathway, therefore the welding line may not be in the geometrical center of the part but shifted to the opposite side of the diamond pathway. It must be noted that the diamond coated pathway has a slightly inferior aperture

than the opposite one, less $\sim 1\mu\text{m}$ (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 side of the press) has no coating, diamond or CrN.

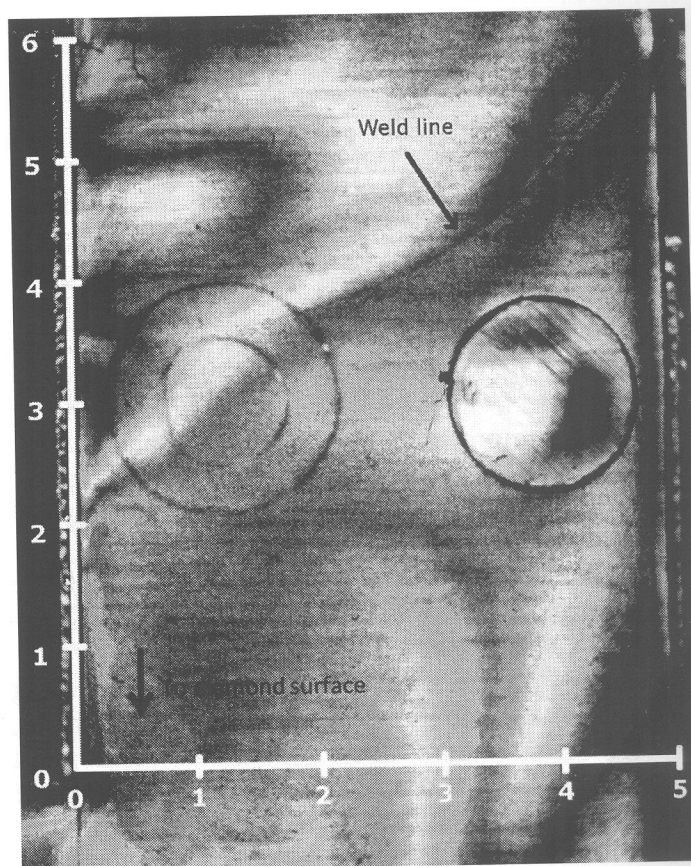


Figure 6. Weld line experimental observation in polarized light.

The average of the three weld lines per different experimental setup is presented in figure 7.

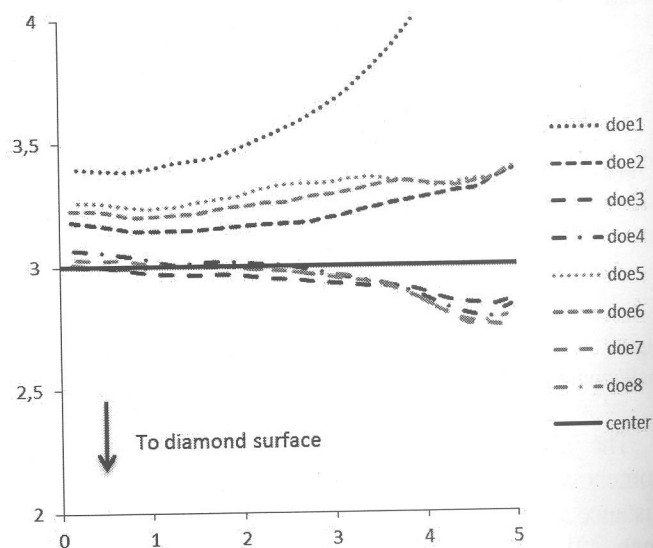


Figure 7. Weld lines location average for the different experimental setups.

For sure, the extractor position, at the right, has influence on all the welding lines locations, but this can be neglected because it is a constant influence.

The weld lines of samples DOE3, DOE4, DOE7 and DOE8 are very close to the geometrical centre of the part, where in similar surface condition it is expected to find the congregation of the flow fronts, therefore the diamond coating does not seem to have an influence on the melt flow.

On the contrary, the weld lines of samples DOE1, DOE2, DOE5 and DOE6 are shifted to the opposite side of the diamond coating, which seems to indicate that the diamond coating somehow eases the polymeric flow.

The common parameter of DOE3, DOE4, DOE7 and DOE8 is the melt temperature, 240 °C. In the same way, the common parameter of the DOE1, DOE2, DOE5 and DOE6 is a melt temperature of 220 °C. Therefore, it seems that the diamond coating has a positive influence on the polymer flow at the lower investigated melt temperature, but has no influence at the higher melt temperature.

The literature highlights the importance of the heat transfer mechanism at the polymer/mould interface with a particular emphasis on microcavity polymeric flow. It seems therefore that diamond coating plays also an important role on that mechanism, since it is evident that for temperatures of the melt closer to that of the mould temperature, the polymer tendency to freeze in contact with the moulding wall rises. If the diamond coating works as a temperature buffer between the fluid and the mould walls, this behaviour may therefore be reduced, a situation rather interesting when a variotherm system is not used. The latter is illustrated on figure 8.

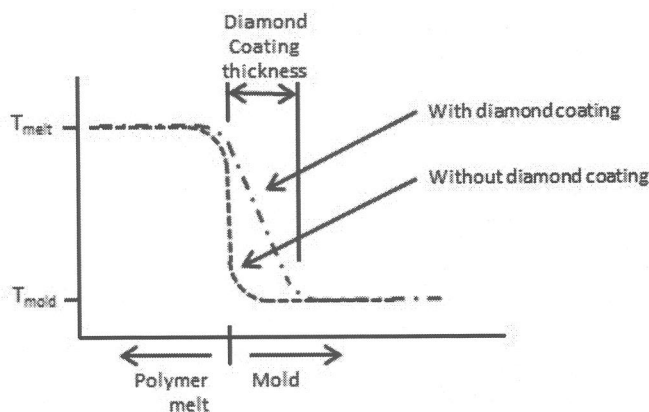


Figure 8. Illustration of the temperature profile in the melt/mould interface.

The above mentioned behaviour seems to be somehow consistent with the thermal shock resistance capacity attributed to diamond (Temmerman, 2011).

Nevertheless, this must be further investigated, increasing the number of studied levels for the melt

temperature and also the number of moulding blocks, and finally, increasing the number of polymer parts analysed.

It would also be interesting to extend this study to different thermoplastic materials, including amorphous polymers, although a new method to evaluate the weld line of the flow front would be required if the polymer is not transparent.

4 CONCLUSIONS

In this paper, a micromoulding block and mould tool were used to evaluate the influence of advanced coating systems on the polymer flow within microcavities.

The moulding block is able to produce a 16×10 mm polymer plate with a central orifice, that allows for the engineering of two pathways with different characteristics, which will display its influence in the flow behaviour and consequently in the weld line location. One pathway was coated with a commercial CrN coating and the other with a nanocrystalline diamond coating. Both coatings presented appropriate characteristics for the application.

A design of experiment was set to produce polypropylene (PP) parts. Injection pressure, packing pressure and time, and cooling time were kept constant for all the experiments. Mould and melt temperature and injection velocity were varied between two levels to construct a full factorial experiment. At least 30 moulding parts were produced for each experiment, keeping a consistent cycle time.

During the injection process, the diamond coating was analysed to evaluate degradation, which did not seem to occur. It must be stated that this is a rather small number of injection cycles to evaluate full wear rate of a diamond coating.

The PP mouldings were observed with polarized light to evaluate the weld line location.

It was found that lower melt temperature level (220 °C) experiments resulted in a positive contribution of the diamond film to the melt flow, but no influence at the high temperature level (240 °C) was encountered. The latter is believed to be related with the thermal shock resistance capacity of diamond which may act as a temperature buffer, diminishing the high influence of the polymer/mould interface heat transfer mechanism so important in micro-moulding.

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