

# Computational analysis of polymer molecular structure effect on nanocavities replication via injection moulding

J. Pina-Estany\*<sup>1</sup> and A.A. García-Granada<sup>1</sup>

<sup>1</sup>IQS-Universitat Ramon Llull, Via Augusta, 390. 08017, Barcelona (Spain)

*Análisis computacional del efecto de la estructura molecular en la copia de nanocavidades mediante inyección de plástico*

*Anàlisi computacional de l'efecte de l'estructura molecular en la còpia de nanocavitats mitjançant la injecció de plàstic*

RECEIVED: 7 JUNE 2017. REVISED: 30 OCTOBER 2017. ACCEPTED: 7 NOVEMBER 2017

## SUMMARY

The purpose of this work is to study how the molecular structure of a polymer affects the replication of nanocavities when injection moulding manufacturing process is used. Even though the process and geometrical factors that affect the replication of nanocavities have been studied by several authors, the effect of the polymer molecular structure on the injection result is less studied.

In order to study through simulation the molecular structure influence, Computational Fluid Dynamics methods are not valid because they consider the matter a continuum. This limitation is overcome by means of Molecular Dynamics simulation method, in which each atom movement is tracked in a sort of n-body problem.

With a self-made model, the effect of degree of polymerization and tacticity are successfully quantified in the replication of nanocavities of down to 2.2nm<sup>2</sup>. It is concluded that the degree of polymerization has a negative effect on the nanocavity replication due to the easier entanglement of longer polymer chains. Concerning the tacticity effect, it is found out that syndiotactic polystyrene replicates less than atactic or isotactic polystyrenes because of the larger entanglement of the phenyl groups when in alternate positions along the chain.

**Keywords:** Computational Fluid Dynamics; injection moulding; Molecular Dynamics; nanoscale simulation; submodeling.

## SUMARIO

El objetivo de este trabajo es estudiar cómo la estructura molecular de un polímero afecta la copia de

nanocavidades cuando se utiliza inyección de plástico. Si bien distintos autores han estudiado los factores geométricos y de proceso que afectan a la replicación, el efecto de la estructura molecular del polímero en el resultado de la inyección no se ha analizado tan en detalle.

Con el objetivo de estudiar el efecto de la estructura molecular mediante simulación, la dinámica de fluidos computacional no es válida porque considera la materia un continuo. Esta limitación se supera usando la dinámica molecular, de forma que el movimiento de cada átomo se simula como si fuese un problema de n-sólidos.

Mediante un modelo propio, el efecto del grado de polimerización y la tacticidad se cuantifican con éxito en nanocavidades de hasta 2.2nm<sup>2</sup>. Se concluye que el grado de polimerización tiene un efecto negativo en la copia de nanocavidades debido al menor entrelazamiento de las largas cadenas de polímero. Referente a la tacticidad, se prueba que el poliestireno sindiotáctico copia en menor cantidad las nanocavidades que el atáctico o el isotáctico, debido al mayor entrelazamiento de los grupos fenilo cuando se ubican en posiciones alternadas de la cadena.

**Palabras clave:** Dinámica de fluidos computacional; inyección de plástico; dinámica molecular; simulación a escala nanométrica; submodelado.

## SUMARI

L'objectiu del treball és estudiar com l'estructura molecular d'un polímer afecta la còpia de nanocavi-

\*Corresponding author: jordipinae@iqs.url.edu

tats quan s'utilitza la injecció de plàstic. Si bé diversos autors han estudiat els factors geomètrics i de procés que afecten la replicació, l'efecte de l'estructura molecular del polímer en el resultat de la injecció no s'ha analitzat tan en detall.

Amb l'objectiu d'estudiar l'efecte de l'estructura molecular mitjançant una simulació, la dinàmica de fluids computacional no és vàlida perquè considera la matèria un continu. Aquesta limitació se supera fent ús de la dinàmica molecular, de manera que el moviment de cada àtom se simula com si fos un problema de n-sòlids.

Mitjançant un model propi, l'efecte del grau de polimerització i la tacticitat es quantifiquen amb èxit en nanocavitats de fins a  $2.2\text{nm}^2$ . Es conclou que el grau de polimerització té un efecte negatiu en la còpia de nanocavitats a causa d'un menor entrellaçament de les llargues cadenes de polímer. Pel que fa a la tacticitat, es demostra que el poliestirè sindiotàctic copia menys les nanocavitats que l'atàctic o l'isotàctic a causa d'un menor entrellaçament dels grups fenil quan s'ubiquen en posicions alternades de la cadena.

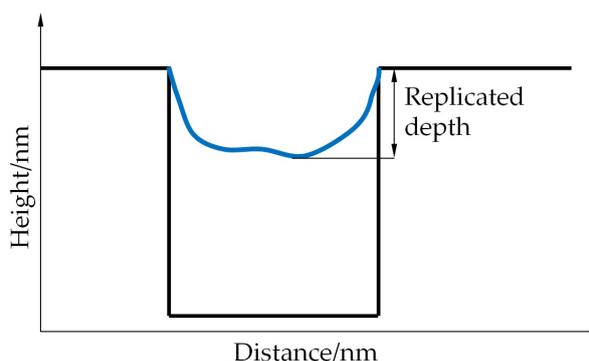
**Paraules clau:** Dinàmica de fluids computacional; injecció de plàstic; dinàmica molecular; simulació a escala nanomètrica; submodelat.

## 1. INTRODUCTION

Nanostructured surfaces are used for different applications such as lab-on-chips devices<sup>1</sup>, antimicrobial surfaces<sup>2</sup>, surfaces with self-cleaning capabilities<sup>3</sup>, water purification<sup>4</sup>, optical applications to achieve antireflection<sup>5</sup> or transmission enhancements<sup>6</sup>, etc. The vast majority of these parts are made of plastic and, from the different manufacturing processes, injection plastic is the most suitable one because of its low production costs. However, replicating a nanostructure is not straightforward because the large surface-area-to-volume ratio of the nanoscale tends to solidify the polymer before it has reached the bottom of the nanocavities, see figure 1 for an schematic figure of an incomplete replication.

In order to understand how the replication can be successfully achieved, several authors have studied how process and geometrical parameters can be tuned in order to improve the replication. The current available know-how was developed both experimentally<sup>7-11</sup> and also via simulation<sup>12-16</sup>. These works show which factors have a positive effect (cavity length, mould temperature, melt temperature, etc.) and which have a negative effect (filling time, for example). However,

<sup>1</sup>Abbreviations: BC=Boundary Condition. CFD=Computational Fluid Dynamics. DP= Degree of Polymerization. E=Energy. MD=Molecular Dynamics. NFT=No Flow Temperature. N=Number of atoms. P=Pressure. PE=Polyethylene. PS=Polystyrene. T=Temperature. Tg=Glass Transition Temperature. Tm=Melting Temperature. V=Volume.



**Figure 1:** Schematic image of an incomplete cavity replication.

these works simulate the polymer behaviour with Computational Fluid Dynamics approaches, which are not valid for dimensions smaller than 100nm because they consider the matter a continuum. Besides, they cannot consider the molecular structure because the fluid is modeled through bulk parameters (density, viscosity, heat capacity, etc.). In this work, the Molecular Dynamics algorithm published in "Molecular dynamics simulation method applied to nanocavities replication via injection moulding"<sup>17</sup> is used to study the effect of the degree of polymerization and the tacticity in the replication of cavities with dimensions smaller than 100nm.

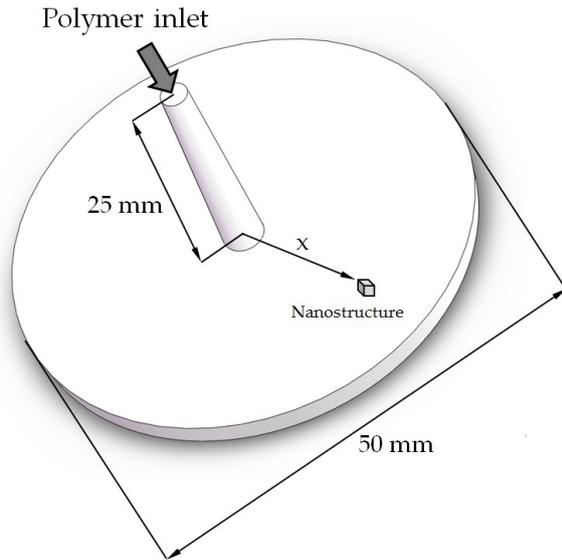
The use of Molecular Dynamics simulation method is growing along with the increase of the computational resources, indeed, MD is used to study different topics such as the heat transfer at the microscale<sup>18</sup>, the flow of liquids at the nanoscale<sup>19</sup>, the polymer crystallization from the melt<sup>20</sup>, the simulation of thread break-up and formation of droplets in nanoejection system<sup>21</sup>, etc. Related specifically to the replication of nanocavities via injection molding, Feng studies in "Molecular dynamics simulation of injection of polyethylene fluid in a variable cross-section nano-channel"<sup>22</sup> the effects of the nano-channel cross section and the external forces. Zhou analyzes in "Molecular dynamics study on polymer filling into nano-cavity by injection molding"<sup>23</sup> the effect of molecular weight and cavity size.

## 2. METHODS

Since it is computationally unaffordable to carry out a Molecular Dynamics simulation of a macro part, the submodeling approach is used to reduce the computational requirements. It consists in coupling a first macro-CFD simulation with a subsequent nano-MD simulation. The two simulation steps are summarized here under:

### *Macro-CFD simulation*

Using SolidWorks Plastic, an injection plastic simulation is performed in the geometry of figure 2 with 3 mm thickness.



**Figure 2:** Macro geometry used in the macro-CFD simulation.

The pressure profile is extracted at a point located at a distance  $x$  of the center and so an equation  $P/\text{MPa} = f(t)$  is obtained, where time  $t = 0\text{s}$  is defined when the polymer flow front first reaches the nanocavity. This equation and the temperature of the polymer when it reaches the nanocavity are the values used for the subsequent MD nanosimulation.

### Nano-MD simulation

The model used to perform the nano-MD simulation is the one published in “Molecular dynamics simulation method applied to nanocavities replication via injection moulding”<sup>17</sup>. It consists in the following steps: (i) generating an initial configuration of the polymer, (ii) compressing it until the target density, (iii) minimizing and equilibrating it and, (iv) performing the production run using the pressure equation transformed into force taking into account the nanocavity entrance area. Specifically for this paper, the mould is modeled with body-centered cubic (BCC) aluminium. The polymer is enclosed with a layer of frozen BCC atoms located above it, this is an alternative to the introduction of a vacuum layer done by other authors such as Zhou<sup>23</sup>.

The above exposed model takes into account two hypothesis:

- The replication takes place in the filling stage and the packing stage is of no influence in the degree of replication. It is stated in “3D filling simulation of micro and nanostructures in comparison to iso- and variothermal injection moulding trials”<sup>7</sup> that such hypothesis is acceptable as long as the mould temperature is below the No Flow Temperature of the polymer.

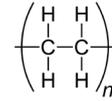
- Since the nanofeature is so small, the polymer initially goes through it as it was not present and, next, it gets inside the nanocavity due to the pressure profile. This was initially stated by Tofteberg<sup>12</sup> and experimentally proven by Pina<sup>15</sup>.

## 3. RESULTS AND DISCUSSION

This section is divided into two sections corresponding to the two studied factors, the degree of polymerization and the tacticity.

### 3.1 Degree of polymerization effect

The degree of polymerization is the number of monomers that constitute each polymer chain. Polyethylene is used in this section, see figure 3 for an image where  $n$  refers to the degree of polymerization of polyethylene. The reason for using PE is that it is the most simple polymer and, hence, the necessary computational resources are reduced.



**Figure 3:** The degree of polymerization is the number  $n$  of monomers constituting each PE chain.

The degree of polymerization of PE can be controlled in the production process by adjusting the reaction conditions. D’Agnillo<sup>24</sup> shows a method to tune the degree of polymerization using soluble metallocene/methylalumoxane catalysts. Feucht<sup>25</sup> proves mathematically that the degree of polymerization decreases with increasing reaction temperature and is higher at higher residence times and smaller amounts of initiator in the feed.

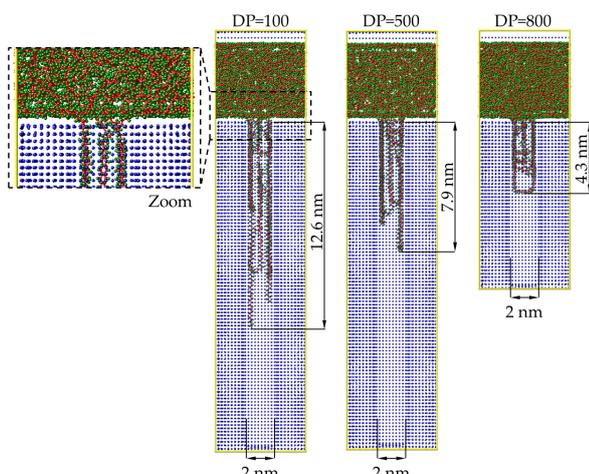
Using SolidWorks Plastic an injection plastic simulation to obtain the geometry of figure 2 is performed with polyethylene (PE-MD BASELL LUPOLEN 2410 of  $T_g = -125^\circ\text{C}$  and  $T_m = 117^\circ\text{C}$ ), where temperatures for the polymer and the mould are set to  $T_{polymer} = 230^\circ\text{C}$  and  $T_{mould} = 45^\circ\text{C}$ , filling time 2s and injection pressure limit of 134MPa. The pressure profile is extracted from SolidWorks simulation at  $x = 11.9\text{mm}$  and the equation  $P/\text{MPa} = 1.0643t^2 + 0.1202t$  is obtained. This equation and the temperature of the polymer when it reaches the nanocavity ( $227^\circ\text{C}$ ) are the values used for the subsequent MD nanosimulations.

The MD-nanosimulations consists of a set of three simulations performed with three different degrees of polymerization (100, 500 and 800). The contour length of the polymer chain with each degree of polymerization can be calculated taking into account that the angle between the C-C bonds is  $109.5^\circ$  and the C-C distance equal to  $0.154\text{nm}$ . Thus the apparent distance  $d$  (in nm) between two successive carbon atoms of the all trans chain is given by:

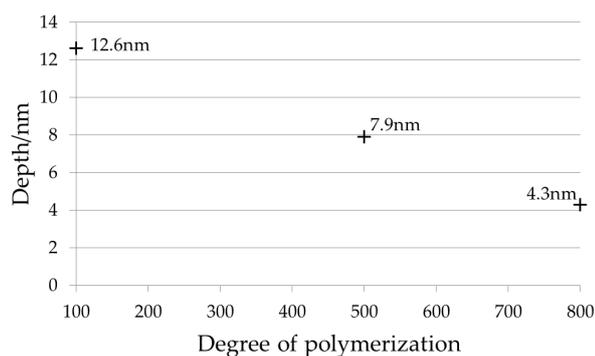
$$d = 0.154 \cdot \sin \frac{109.5^\circ}{2} = 0.126\text{nm} \quad (1)$$

The contour lengths of PE with a degree of polymerization 100, 500 and 800 are 25.2nm, 126nm and 201.6nm, respectively. The gyration radius are 0.73nm, 1.63nm and 2.06nm, also respectively. These dimensions, compared to the entrance area of  $2 \cdot 2\text{nm}^2$  give an idea of how difficult it is for the polymer to get into the nanocavities.

Figure 4 shows a front image of the polymer inside the  $2 \cdot 2\text{nm}^2$  cavity once it reaches the No Flow Temperature of  $147^\circ\text{C}$ . It is clearly stated that longer polymer chains lead to a smaller degree of replication. In fact, the replication is reduced linearly as shown in figure 5.



**Figure 4:** Front image of the polymer once it reaches the NFT. The blue points are the aluminium atoms. A zoom is shown in order to show the atomistic detail level of the simulation.



**Figure 5:** Depth vs. degree of polymerization plot for the cavities with  $2 \cdot 2\text{nm}^2$  sectional area. It is observed how larger degrees of polymerization hinder the polymer replication due to the entanglement of the polymer chains above the hole.

The reason for the negative effect of the degree of polymerization in the replication is the larger entanglement that takes place with long polymer chains. Nevertheless, the replicated depth is considerable compared with the sectional area, indeed, even with the larger degree of polymerization of 800, 4.3 nm are

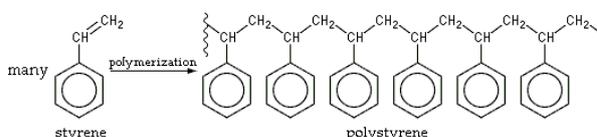
replicated, approximately the double of the nanocavity dimension.

The calculation time of each simulation was of approx. 75h with Intel(R) Core(TM) i5-3320M CPU @ 2.60 GHz) with 4 cores parallelization.

### Tacticity effect

The purpose of this section is to study the tacticity effect on the replication. Tacticity is the relative stereochemistry of adjacent chiral centers within a macromolecule, i.e., the way the substituents are arranged along the backbone chain of the polymer.

Polystyrene is used in the simulations of this section because the phenyl substituent is voluminous and, hence, the tacticity effect can be doubtless proved. Polystyrene is manufactured by styrene polymerization. See figure 6:



**Figure 6:** Polymerization reaction of styrene.

According to the reaction conditions, the three usual different tacticities can be obtained as shown in figure 7:

### Atactic

In atactic polystyrene the phenyl groups are placed randomly along the chain. It is the commonly commercialized form of polystyrene and the polymerization is initiated with free radicals. The random positioning of the phenyl groups prevents the chains from aligning and, hence, none crystallinity is obtained, generating an irregular and amorphous polymer. Due to its amorphous characteristic, it has no  $T_m$  and  $T_g=100^\circ\text{C}$ .

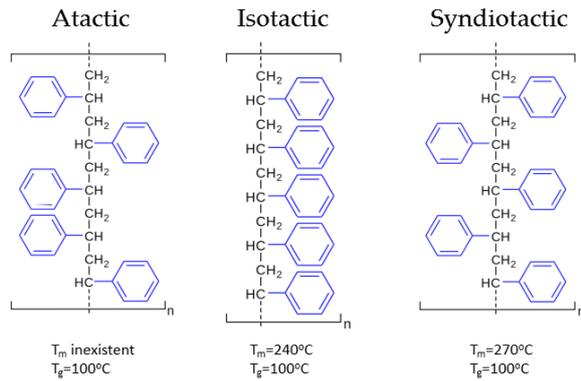
### Isotactic

In isotactic polystyrene all the phenyl groups are located on the same side of the macro-molecular backbone. It leads to a semi crystalline polymer with  $T_m=240^\circ\text{C}$  and  $T_g=100^\circ\text{C}$ .

### Syndiotactic

In syndiotactic polystyrene the phenyl groups have alternate positions along the chain. Syndiotactic polystyrene is obtained with Ziegler-Natta polymerization. This form is highly crystalline with a  $T_m$  of  $270^\circ\text{C}$  and a  $T_g=100^\circ\text{C}$ . It is produced under the trade name XAREC.

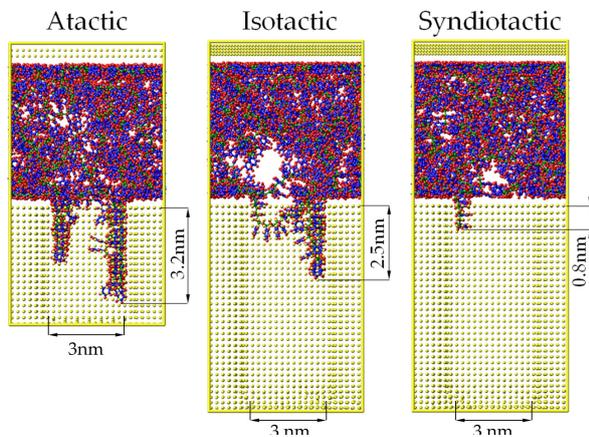
In this section, three simulations are performed with the submodeling approach in order to study the effect of tacticity in the replication of a  $3 \cdot 3\text{nm}^2$  cavity with a single polymer chain of DP=550. The cavity length is increased in comparison with the  $2 \cdot 2\text{nm}^2$  of the previous section because the voluminous phenyl



**Figure 7:** Molecular structure of three different PS tacticities.

substituent of polystyrene makes necessary a larger entrance area rather than polyethylene.

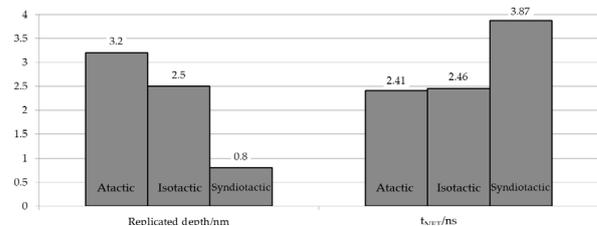
The macro simulation is performed with Solidworks Plastics with filling time=2.37s,  $T_{mould} = 50^\circ\text{C}$ ,  $T_{polymer} = 230^\circ\text{C}$  and maximum inlet pressure of 134MPa. From this simulation, the pressure in a point located 12.48mm of the center is exported and the pressure profile is obtained ( $P/\text{Pa} = -194991t^2 + 210580t$ ). The Molecular Dynamics simulation is performed and a snapshot of the polymer once it has reached the NFT is shown in figure 8.



**Figure 8:** Frontal image of PS once it has reached the NFT inside the nanocavity for atactic, isotactic and syndiotactic configurations. Yellow points correspond to aluminium.

Figure 9 shows a bar chart with the replicated depth and the time elapsed until NFT for each tacticity. It is concluded that the tacticity affects the replication of the nanocavities. This is a logical result because the entanglement of the polymer chains above the nanocavity are influenced by the position of the substituent groups. Indeed, syndiotactic configuration leads to a fewer replication of the nanocavity because the alternate position of the phenyl groups eases the entanglement. Atactic PS, which is commonly commercialized, has the higher degree of replication, not far away

from the isotactic configuration. It is observed that the replication gets worse with the degree of crystallization of the polymer, indeed, the atactic configuration is amorphous, isotactic is semi-crystalline and syndiotactic is crystalline. The time until NFT shows opposite results, fewer replications lead to larger time until the NFT. This is due to the fewer contact of the polymer with the walls that takes place with smaller replications.



**Figure 9:** Bar chart with the replicated depth and the time elapsed until the polymer reaches the NFT for atactic, isotactic and syndiotactic configurations of PS for  $3 \cdot 3\text{nm}^2$  sectional area.

The calculation time of each simulation was of approx. 100h with Intel(R) Core(TM) i5- 3320M CPU @ 2.60 GHz) with 4 cores parallelization.

## CONCLUSIONS

In this paper has been proved that Molecular Dynamics simulation method enables the study of the molecular structure effect on the replication of nanostructures.

The degree of polymerization is a factor with a negative factor. Indeed, longer polymer chains lead to a smaller replication of the nanocavities due to the larger entanglement of the chains above the nanocavities. For a nanocavity with an entrance area of  $2 \cdot 2\text{nm}^2$ , the replication depth was of 12.6nm for DP=100, 7.9nm for DP=500 and of 4.3nm for DP=800, as shown in figure 4, 5.

Concerning the tacticity factor, it has been proved that the polymer tacticity influences the nanostructures replication. Indeed, for a  $3 \cdot 3\text{nm}^2$  a syndiotactic polymer leads to a smaller replication (0.8nm) compared with an atactic (3.2nm) or isotactic (2.5nm) polymer due to the larger entanglement between adjoining chains as shown in figure 8 and plotted in the bar chart of figure 9.

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