

# Complementary approaches for enhancing polystyrene hydrophobicity: additives development and replication of micro/nanotextures

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## Abstract

This work aims at developing polymer surfaces with enhanced hydrophobic behaviour by controlling both the surface chemistry and the surface structure. The chemical modification is given via the elaboration of polymers blends by incorporation of own-synthesized tailored fluorinated additives (FA) in commercial polystyrene and the physical approach is based on micro/nano-structuration of polymers surface. Different films containing various content of fluorine based on commercial polystyrene (PS) and FA were elaborated by solvent casting method. The nano-structuration of polymers surface was replicated from a Nickel insert using hot embossing technique with optimized processing conditions including, polymer/mold interfaces, micro/nano-textures, temperature and pressure. The impact of FA on both the wettability properties and the replication efficiency was evaluated, by water/polymer static contact angle and quantification of replication rate, respectively. It was evidenced that the use of this tailored additive, even at low percentages, associated with the structuration of the PS surface improves significantly the hydrophobicity of polystyrene and the robustness of the replication process.

**Keywords:** micro/nano-texturation, replication, hydrophobicity, functional surface.

## 1. Introduction

The replication of micro/nanotextures over polymer surfaces from metal inserts is a promising solution to add functionalities like superhydrophobicity [1], antimicrobiality [2], anti-relectivity [3] to manufactured plastic products.

For this purpose, there are viable processes at industrial scale, like hot embossing and injection molding [4,5]. But to ensure a compliant replication, two challenges must be overcome:

i/ depending on the chemical nature of the polymer and the viscosity of the polymer melt, some micro/nanostructures cavities can be hardly filled, leading to partial replication [6];

ii/ during the demolding of the part, solid state interactions between the part and the textured insert can lead to local adhesion and result in deformed or fractured micro/nanostructures [7].

Two solutions can be considered to avoid the above problems: the replication of micro/nanostructures with low surface energy materials (which limit the choice of materials that can be used) or the use of low surface energy coatings on the mold [8] (which can be non-uniformly coated or change the texture of the insert and be easily damaged over time).

The aim of this study is to evaluate the effectiveness of a new non-commercial fluorinated additive designed and synthesized specifically to improve the quality of replication by injection molding and hot embossing while providing additional functionality to the material surface, and ensuring compatibility with a commercial polymer matrix, like polystyrene. The solution proposed in this article could be applicable

for melt processed products like injection molding or hot embossing, and the results reported in this article are devoted to the enhancement of the replication for hot embossed products.

## 2. Experimental details

### 2.1. Material

#### 2.1.1. Textured insert

A Nickel insert was textured at the micro and the nanoscale by electroforming over a silicon wafer, giving three structures like a network of micro-holes with various dimensions, given in Table 1.

Table 1  
Dimensions of the micro-holes on the nickel insert.

Type of structure	A	B	C
Diameter of the holes (μm)	200	100	50
Spacing between the holes (μm)	200	100	50
Depth of the hole (μm)	0.9	0.9	1.0

A hierarchical structure is brought by nano-holes with diameters ranging between 300 and 400 nm in the aim of changing the wetting behaviour [9] (see Figure 1). The resulting textures take the form of micro cylindrical pillars of at most 1 micron height.

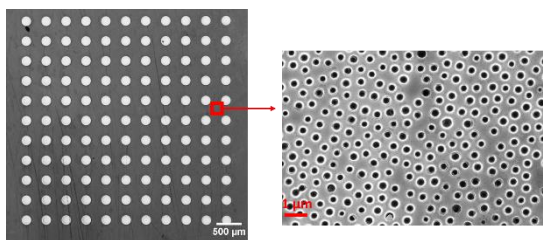


Figure 1. SEM imaging of micro and nano-holes of the nickel insert.

## 2.1.2. Polymer

### 2.1.2.1. Polystyrene

The polymer chosen for this study was an amorphous polystyrene commercialized by Total Petrochemical, under the trade name “Crystal” polystyrene ref PS1160 (see Table 2). This polymer has been chosen considering its medium viscosity (Melt flow index = 2.4 g/10 min (at 200°C-5kg)), and its limited brittle behaviour. The glass transition temperature ( $T_g$ ) and the different molecular weights ( $M_w$ ,  $M_n$ ) of the polymer are reported in Table 2.

Table 2  
Properties of PS1160 grade

$T_g$ (°C) <sup>a,b</sup>	$M_w$ (g/mol) <sup>b</sup>	$M_n$ (g/mol) <sup>b</sup>
105	≈ 250 000	≈ 125 000

<sup>a</sup> DSC measurement conducted in the laboratory at a heating rate of 20°C/min.

<sup>b</sup> PS1160 datasheet.

### 2.1.2.2. Additive FA

The additive FA is synthesized at laboratory using multistep synthesis method consisting on partial and controlled fluorination of a polystyrene backbone. This synthesis route is inspired from literature [10] and the synthesis conditions to which solvents, temperature, and reaction time were adapted.

### 2.1.2.3. Additive FA/polystyrene blends

Polymers blends were elaborated via solvent route as described below.

## 2.2. Methods

### 2.2.1. Additivated polymers films processing

Films having thicknesses ranging from 80 to 100 μm were obtained by solvent cast. This involved first mixing the polymer and the additive in solvent phase followed by an evaporation step. Two mother solutions with a concentration of 20 g/L were thus prepared by dissolving PS1160 in dichloromethane and FA in acetone. Then, various volumes of FA solution are taken according to the target weight ratios (FA/PS polymers blends with weight ratio ranging from 1, i.e. 0,3 wt% of Fluorine to 10 wt.%, i.e. 3,3 wt% of Fluorine) and evaporated at ambient conditions during 24h. In order to ensure a total dispersion and final homogeneity of the films, the dried additives were then re-dissolved (into an ultrasonic bath during 30 minutes) in a volume of dichloromethane/polystyrene

solution according to the target weight ratios PS/FA. Finally, the solutions were transferred to PolyTetraFluoroEthylene (PTFE) molds ( $\phi = 75$  mm) and then the solvent was slowly evaporated at ambient conditions and confined atmosphere during 12h.

### 2.2.2. Textures replication process by hot embossing

The films were replicated using a laboratory press (Carver®) equipped with Specac Atlas Series heated platens and Specac Atlas constant thickness film marker accessory to control the thickness of the polymer samples. These processing conditions were inspired from the previously published work by Dubelley et al. [11]. An interfacial layer of Kapton was used between the films and the heating plate in order to reduce the adhesion during molding and demolding. The replication tests were conducted at 120°C (i.e. 10 °C above the polystyrene  $T_g$ ) and under a static load of 15 MPa corresponding to a compression strain of 68% (see Figure 2).

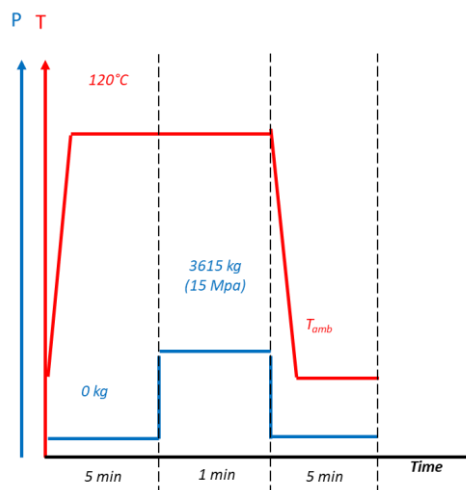


Figure 2. Heating/cooling and pressure cycles used for the hot embossing process.

### 2.2.3. Replication characterization

A confocal microscope (OLYMPUS LEXT OLS4000) was used to measure the height of the replicated pillars with the 3 different structures using the objective x100 (magnification x2160) exhibiting a height resolution of 0.06 μm (vertical resolution).

The height of the texture's micro-pillars was measured by averaging the height of the step between the top of the pillar and its base over a width determined by two cursors (see Figure 3). This width was of 60 μm for structure A and B (which correspond to the average over 480 values) and 20 μm for the structure C (which correspond to the average over 160 values). As we can see in Figure 3, the light part corresponds to the pillar, and the dark part the insert base.

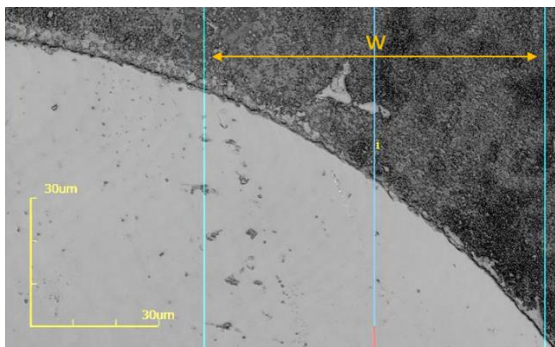


Figure 3. Confocal microscopy image illustrating the method of quantification of the pillar's height, where the light part is the replicated pillar (blue lines: width  $w$  considered to average the heights).

The height measurement was done on three pillars for each structure on the polymer films. The stamp micro-holes were characterized with the same method. The replication rate was calculated by the following equation (1):

$$R = \frac{h_p}{H_h} \times 100\% \quad (1)$$

where  $h_p$  is the average height of three pillars of the replicated films and  $H_h$  the average depth of three holes of the insert.

#### 2.2.4. Wettability measurements

The wettability measurements were made with a goniometer DIGIDROP composed of (i) a white light illuminating the sample, (ii) a moving plate in order to shift the sample and (iii) a camera of resolution 718 x 452 pixels linked to the computer with the software Visiodrop. The surface wettability was measured with the sessile drop method, using ultrapure water ( $R > 10 \text{ M}\Omega\cdot\text{cm}$ ), a drop of  $0.7 \mu\text{L}$  poured with a micropipette Transferpette S BRAND and 5s of drop stabilization time.

The films obtained by solvent cast were cut in order to obtain samples of 5 mm width and deposited onto a microscope slide with a double-sided adhesive in order to get a flat surface and limit the diffusion of the goniometer's light.

Twenty-eight measurements of the contact angle were performed on each solvent-casted micro-film on the side of the film exposed to air (large surface) and four measurement were carried out on the hot-embossed films (limited surface).

### 3. Results and discussion

#### 3.1. Effect of FA on hydrophobicity

The films based on PS/FA blends were formulated with fluorine content ranging 0.3 wt.% to 3.3 wt.%. The effect of fluorine content on the hydrophobicity is given in Figure 4, showing the static contact angle (CA) as function of the fluorine content. The contact angles increase with the fluorine content, as 0.3 wt.% of fluorine increases the CA by  $16^\circ$ , rising from  $92^\circ$  for the PS alone to  $108^\circ$  for the PS/FA. When the fluorine

content is increased by a factor 10 to 10% (3.3 wt.% of F), a slight increase is observed as the CA becomes close to  $111^\circ$ . This suggests that the hydrophobic enhancement with the fluorination rate is limited. Indeed, the maximum contact angle reachable for the lowest surface energy polymer is  $120^\circ$  and obtained for a polytetrafluoroethylene surface constituted of aligned  $-\text{CF}_3$  groups [12]. In order to reach higher contact angles and enhance the hydrophobicity, the topography of the surface must be modified with micro/nanotextures [13,14].

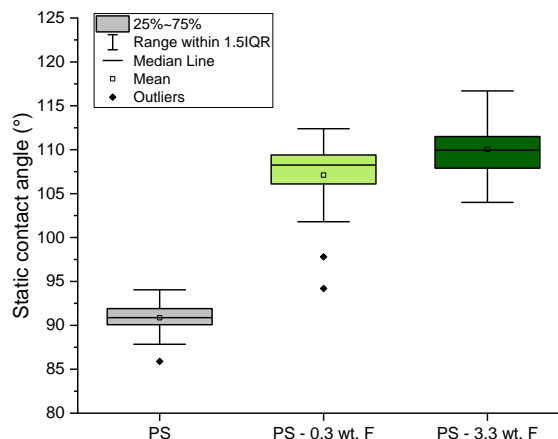


Figure 4. Water/polymer static contact angle for the additivated polymers (PS is given for comparison).

#### 3.2. Effect of the additive on the replication rate

The micro/nano-structuration of polymer films was performed by replicating micro/nano-textures (Table 1) with the nickel insert (Figure 1). The figure 5 shows the replication rate for PS, PS/FA with 0.3 and 3.3 wt.% of fluorine on three textures (A, B and C). Qualitatively, all the textures can be replicated over the polymer surface with the chosen processing conditions. Some differences over the replication rates are observed and linked to the amount of fluorine additives. The replication rate exceeding 100% could be explained by:

- i/ the slight dimensional difference (0.9 to 1  $\mu\text{m}$ ) between the depth of the insert holes and the structured pillars on the polymer film.
- ii/ a potential demolding effect, involving possible strained structures.

The more the content of FA in the polystyrene matrix, the higher is the replication rate. Thus, FA seems to play a major role as a processing aid agent by contributing to the enhancement of the filling of the micro-cavities and consequently improve the replication quality. This positive effect can be linked to the reduction of the polystyrene chain's interaction at the interface due to the migration of the FA, leading to a reduction of the friction coefficient and the level of stresses at the wall.

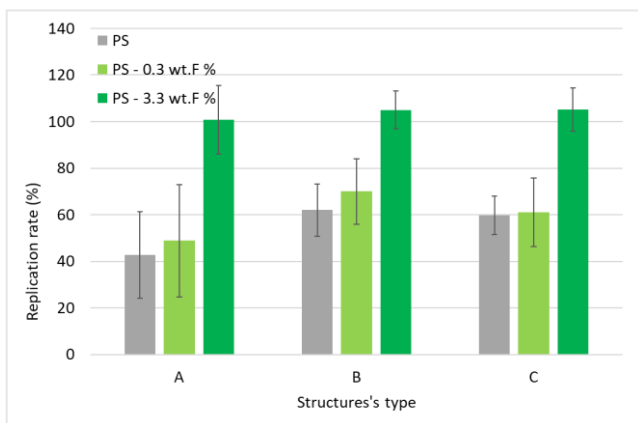


Figure 5. Bar chart of the replication rate by hot embossing of the formulated polymers performed on 3 micro/nano-structures (PS is given for comparison).

### 3.2. Effects of surface structuration and addition of FA

The final functional properties of the micro/nanostructured polystyrene surfaces were characterized by measuring the contact angles water/non-replicated (flat polymers), and water/replicated polymers (textured surface) with the three textures (Table 1). Figure 6 shows the water wettability comparison between PS and PS containing FA (0.3 wt.% of fluorine) and the effect of replication on the CA. In comparison with PS, it can be noticed a significant increase of CA by 16° when FA is added and by 37° when FA is added and the micro/nano-texture C is replicated over the polymer film. This evidences the synergy between the improvement of intrinsic surface properties by using of FA (chemical approach) and the nanotexturing of the surface (physical approach) for the achievement of a high hydrophobic behavior for a chosen polymer model: polystyrene.

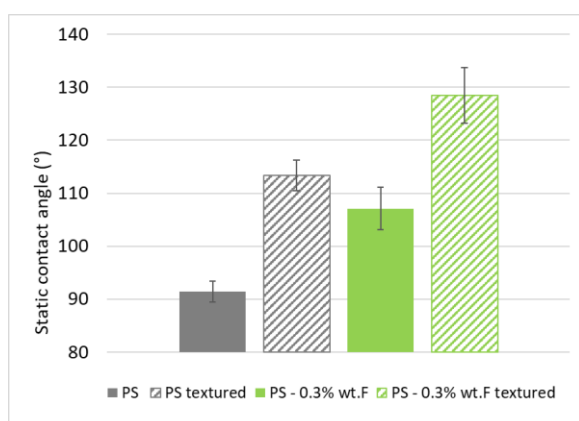


Figure 6. Bar chart: comparison of water/polymer static contact angles on non-replicated and replicated (structure C) films.

## 4. Conclusions

In this study, non-commercial fluorinated additives (FA) were formulated with commercial polystyrene (PS). It was shown that they are efficient on the functionality of the final product, as they enhanced the hydrophobicity of the polystyrene, but also on the process: the replication rate rises when

their amount rises too. Moreover, the combination of the effects of FA and micro/nano-replication has a positive effect on the enhancement of the hydrophobicity of the material. This study will be completed in the future by understanding how the fluorinated additives contribute to change the polymer wettability, at the solid state and even during the processing by injection molding, to enhance the hydro/oleophobic behavior of surfaces.

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