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# Proposal of a New Law for the Evolution of the Wetting Properties of Polymer Blends as a Function of the Content of Fluorinated Additives

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### Abstract

This work aims to develop polymer surfaces with improved hydrophobic properties. Films containing various contents of commercial Polystyrene (PS) and own-synthetized tailored Fluorinated Additives (FA) were elaborated by the solvent casting method. The influence of the fluorinated additives on the wettability properties of PS/FA blends, via the measurement of the dynamic contact angle with water, was evaluated. It was shown that the use of these synthetized tailored additives significantly improves the hydrophobicity of polystyrene, even at low percentages, variations which can be predicted by the proposed law.

**Keywords:** Polystyrene; Fluorinated additives; Copolymers; Blends; Wettability; Hydrophobic

**Abbreviations:** PS: Polystyrene; FA: Fluorinated Additives; dACAW: Dynamic Advancing Contact Angles with Water

## Introduction

Improving the hydrophobicity of commercial polymers is of a strategic interest in many industrial sectors, such as energy [1], biomedical [2] or food [3]. In this context, a study has been carried out to improve the hydrophobicity of polystyrene, following two guidelines of research: (i) the first one consists in synthetizing custom-made additives [4,5] and then mixing them to the polymer matrix at different contents, (ii) the second way consists in structuring the surface of the polymer parts, using (nano)particles [6] or by plasma treatment [7] or by reproducing the texture of an insert on a polymer surface [8,9]. In this work, the first route will be explored by incorporating random copolymers of fluorinated polystyrene [5] in a polystyrene matrix. We have previously shown that the latter improve the texture replication rates on the surface polymers [8]. The aim of this study is therefore to show not only the influence of additives on the dynamic wetting properties of blends but also to be able to predict their effect.

## Materials and Methods

### Materials

The polymer matrix chosen for this study is a polystyrene commercialized by Total Energies Refining & Chemicals under the trade name “Crystal polystyrene grade 1160” ($M_w$=250kg/mol, $M_n$=125kg/mol). Three additives, named POISE-a-4, POISE-a-20 and POISE-a-37, were synthetized in a previous work [5], based on a random copolymer architecture with different molar percentages of perfluorinated styrene comonomer: 4 mol.%, 20 mol.% and 37 mol.% (corresponding to 11 wt.%, 34 wt.% and 44 wt.% of fluorine, respectively). The polymers blends were then elaborated via a solvent route.

### Method

Wettability measurements were performed using the DSA25 drop shape analyzer (Krüss®, Hamburg, Germany). To improve the visibility of the contact line, the camera was tilted from the horizontal plane with an angle of 2°. The surface wettability was measured using demineralized water (resistivity of 18 MΩ.cm). The Dynamic Advancing Contact Angles with Water (dACAW) were obtained according to the proposed protocol of Huhtamäki et al. [10]. Five measurements were made per sample.

## Results and Discussion

The evolution of the dynamic angle of contact with water (called "dACAW") as a function of the fluorine content is presented in Figure 1 for the three blends analysed (PS/POISE-a-4, PS/POISE-a-20 and PS/POISE-a-37). It can be seen that whatever the blend considered the dACAWs increase progressively with the fluorine content, from a minimum value (called dACAWmin) close to 93° corresponding to PS, to a maximum value (named $dACAW_{max}$) close to 123°, corresponding to a surface made up exclusively of $-CF_3$ groups [11]. To predict the evolution of the dACAW with the fluorine content, the following law was then used:

$$dACAW = dACAW_{max} + \frac{dACAW_{min} - dACAW_{max}}{1 + \left(\frac{wt.F\%}{wtF50}\right)^n} \quad (1)$$

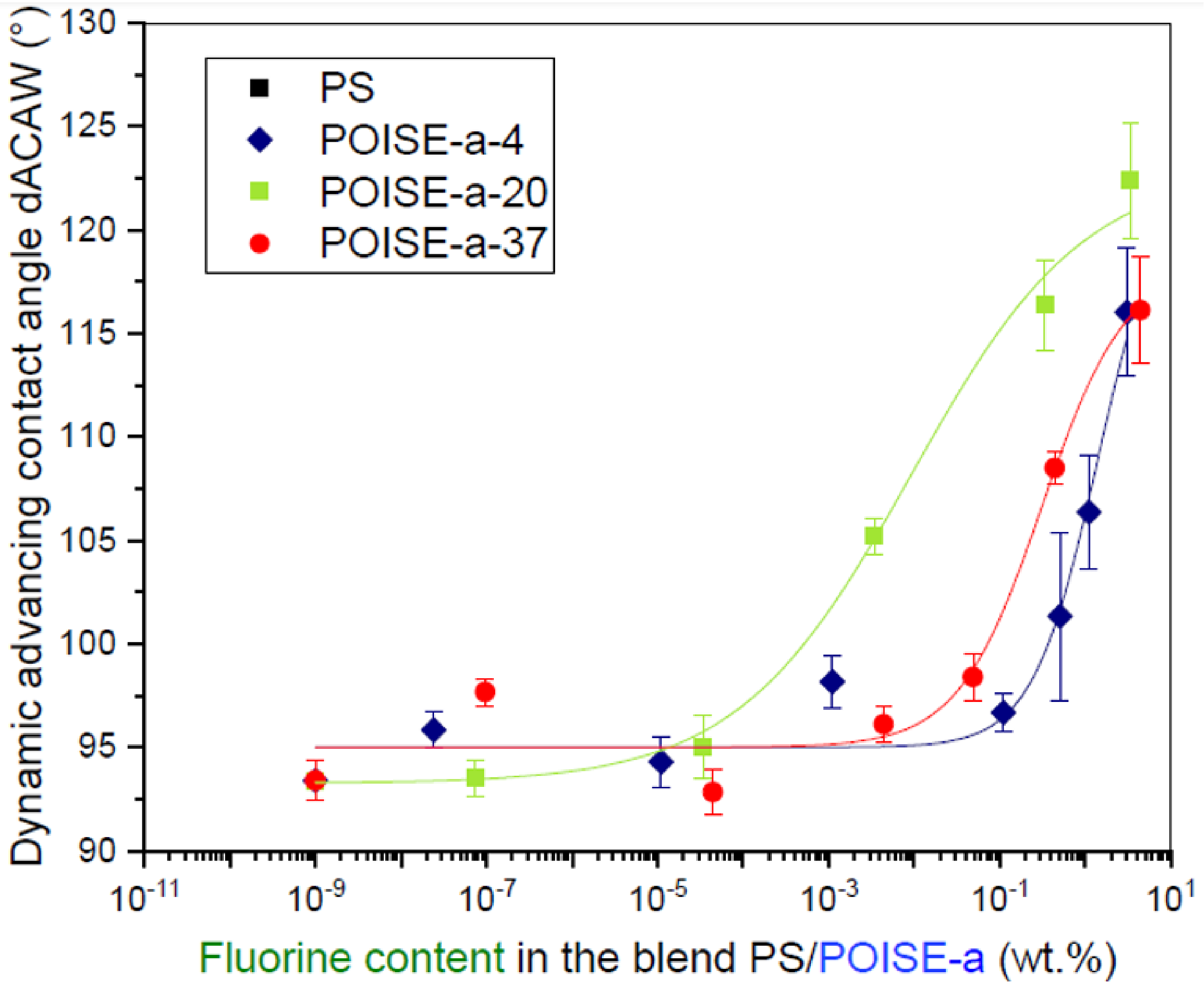


**Figure 1:** Evolution of the experimental dynamic advanced contact angle with water as a function of fluorine content (symbols) and predicted values using equation 1 (solid line).

With $dACAW_{min}$ and $dACAW_{max}$ correspond to the extremum values of dACAW, n the slope of the dACAW rise and wtF50 the fluorine content at 50% of the dACAW rise. The superposition of the experimental and predicted results confirms the relevance of the proposed approach. The analysis of the parameter values reported in Table 1 shows that the blend including POISE-a-20

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additive stands out from the others with an increase in dACAW at lower fluorine contents. This result may be related to the singular morphology of this blend, where an interdigitated structure of the fluorinated side chains has been shown previously [5].

**Table 1:** Optimised values of parameters from equation 1 (*: fixed values).

| Blend | $dACAW_{max}$ (°) | $dACAW_{min}$ (°) | n (°/wt.%) | $wtF50$ (wt.%) | $R^2$ adjusted |
|---|---|---|---|---|---|
| PS/POISE-a-4 | 123±25 | 95* | 1.1±0.7 | $1.4\times10^{0}$ | 0.79 |
| PS/POISE-a-20 | 123±3 | 93±1 | 0.4±0.1 | $9.2\times10^{-3}$ | 0.99 |
| PS/POISE-a-37 | 118±10 | 95* | 0.9±0.5 | $3.1\times\times10^{-1}$ | 0.87 |

## Conclusion

The influence of the presence and content of the own synthetized additives POISE-a on the hydrophobicity of polystyrene-based mixtures was studied using dynamic measurements of the contact angle with water. The sigmoidal variation of the dACAWs observed experimentally as a function of the fluorine content was predicted using a unique law composed of four parameters, which confirmed the singular behaviour of the blend containing the POISE-a-20, showing a much lower threshold value than the other blends.

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