

## Controlling film topography to form highly hydrophobic waterborne coatings

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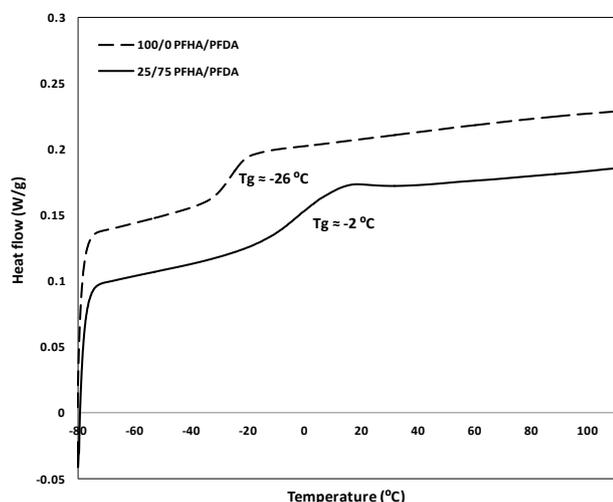
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### Electronic Supplementary Information (ESI)

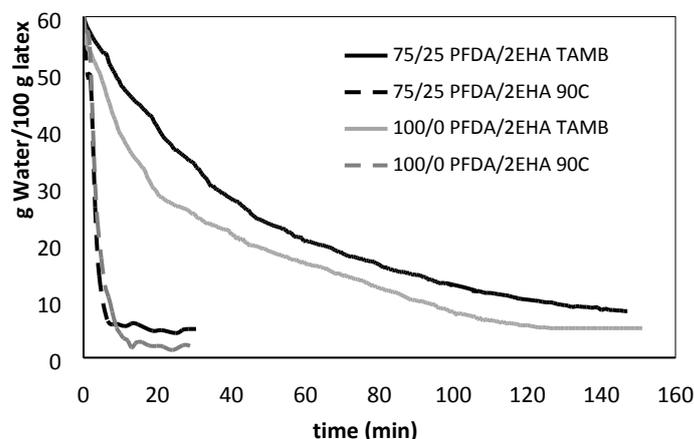
As the  $T_g$ s of the amorphous part of the polymers could not be determined from the data in Figure 1, a different approach was used. A completely amorphous copolymer of PFDA and PFHA (1H,1H,2H,2H-perfluorohexyl acrylate) was synthesized and its  $T_g$  measured. Then, the  $T_g$  of poly(PFHA) was determined from the DSC of its homopolymer. Finally, the  $T_g$  of poly(PFDA) was determined from these data (Figure S1) using the Fox equation. The value of the  $T_g$  for poly(PFDA) was 7 °C.



**Figure S1.** DSC thermograms of the PFDA/PFHA copolymer (75/25 wt/wt) and the PFHA homopolymer.

The latexes were cast on a glass substrate and introduced in a convection oven at either 23 °C or 90 °C in both cases at 55%

relative humidity. Obviously, a certain time was required to increase the temperature of the film and during this time water was evaporating. In order to analyze our experimental results in the framework of the Routh and Russell theory<sup>1</sup> the rate of evaporation and the evolution of the temperature are required. The rate of evaporation was measured gravimetrically and the results are presented in Figure S2 for the softest (75/25) and the hardest (100/0) films during drying at 23 and 90 °C (55% relative humidity).



**Figure S2.** Mass loss of the films when drying at 23 and 90 °C and 55% relative humidity.

As the evolution of the temperature of the film could not be measured, it was estimated by means of a mathematical model.

Because the latex films were very thin (90 μm) it was assumed that there was no temperature profile in the film. Under these conditions, the heat and mass balances are

$$m\bar{c}_p \frac{dT}{dt} = h(T_{oven} - T) - r_{vap}\Delta H_{vap} \quad (S1)$$

$$\frac{dm}{dt} = -r_{vap} \quad (S2)$$

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where  $m$  is the mass of the film per unit of surface area;  $\bar{C}_p$  the average heat capacity of the film,  $h$  the heat transfer coefficient,  $r_{\text{vap}}$  the rate of vaporization per unit of surface area, and  $\Delta H_{\text{vap}}$  the heat of vaporization of water.  $\bar{C}_p$  was estimated as

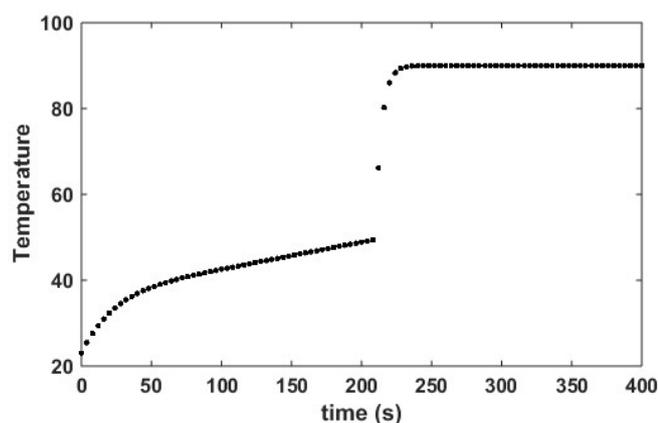
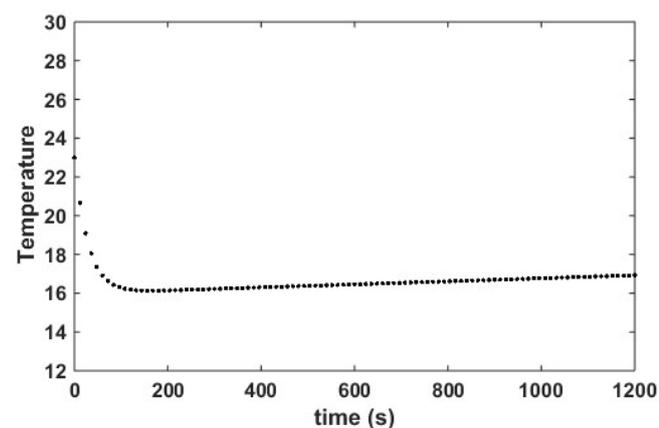
$$\bar{C}_p = 0.4m_0C_{\text{ppol}} + \frac{C_{\text{pw}}(m - 0.4m_0)}{m} \quad (\text{S3})$$

where  $C_{\text{ppol}}$  is the heat capacity of the polymer,  $C_{\text{pw}}$  that of the water and  $m_0$  the initial mass of the film per unit area.

Figure S3 presents the estimated evolution of the film temperature calculated using the rate of water evaporation experimentally determined (Figure S2) and the parameters given in Table S1.

**Table S1.** Parameters used in the calculation of the evolution of the film temperature during drying.

		reference
$m_0$ (kg)	0.104	
$C_{\text{ppol}}$ ( $\text{J kg}^{-1} \text{K}^{-1}$ )	1000	2
$C_{\text{pw}}$ ( $\text{J kg}^{-1} \text{K}^{-1}$ )	4180	
$\Delta H_{\text{vap}}$ ( $\text{J kg}^{-1}$ )	$2.33 \times 10^6$	3
$h$ ( $\text{W m}^{-2} \text{K}^{-1}$ )	12 (oven at $90^\circ\text{C}$ ) 8 (oven at $23^\circ\text{C}$ )	4



**Figure S3.** Estimated evolution with the oven at  $23^\circ\text{C}$  and  $90^\circ\text{C}$ .

Figure S3 shows that during drying the temperature in the film is substantially lower than the oven temperature and that for  $90^\circ\text{C}$ , only when most of the water was evaporated (see Figure S2) the temperature of the film reached  $90^\circ\text{C}$ . The reason was that during water evaporation, the heat provided by convection was counteracted by the heat used to evaporate water.

The temperature profile in Figure S4 is particularly significant when the results in Figure S1 are considered because for most of the drying the temperature of the film dried at  $90^\circ\text{C}$  was below the melting temperatures of latexes 90/10 and 100/0.

## References

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