

# Atomic force microscopy characterization of polyethylene terephthalate grafting with poly(styrene sulfonate)

Tuan Ngoc Nguyen<sup>1</sup>; Vincent Humblot<sup>2</sup>; Véronique Migonney<sup>1\*</sup>; Raphaël Lévy<sup>3\*</sup>

<sup>1</sup>Laboratory of Chemistry, Structures, Properties of Biomaterials and Therapeutic Agents (CSPBAT), UMR CNRS 7244, Sorbonne Paris Nord University, France

<sup>2</sup> Institut FEMTO-ST UMR CNRS 6174, Université Bourgogne Franche-Comté, 15B Avenue des Montboucons, 25030 Besançon, France

<sup>3</sup>Université Sorbonne Paris Nord and Université de Paris, INSERM, LVTS, F-75018 Paris, France

## Supporting information

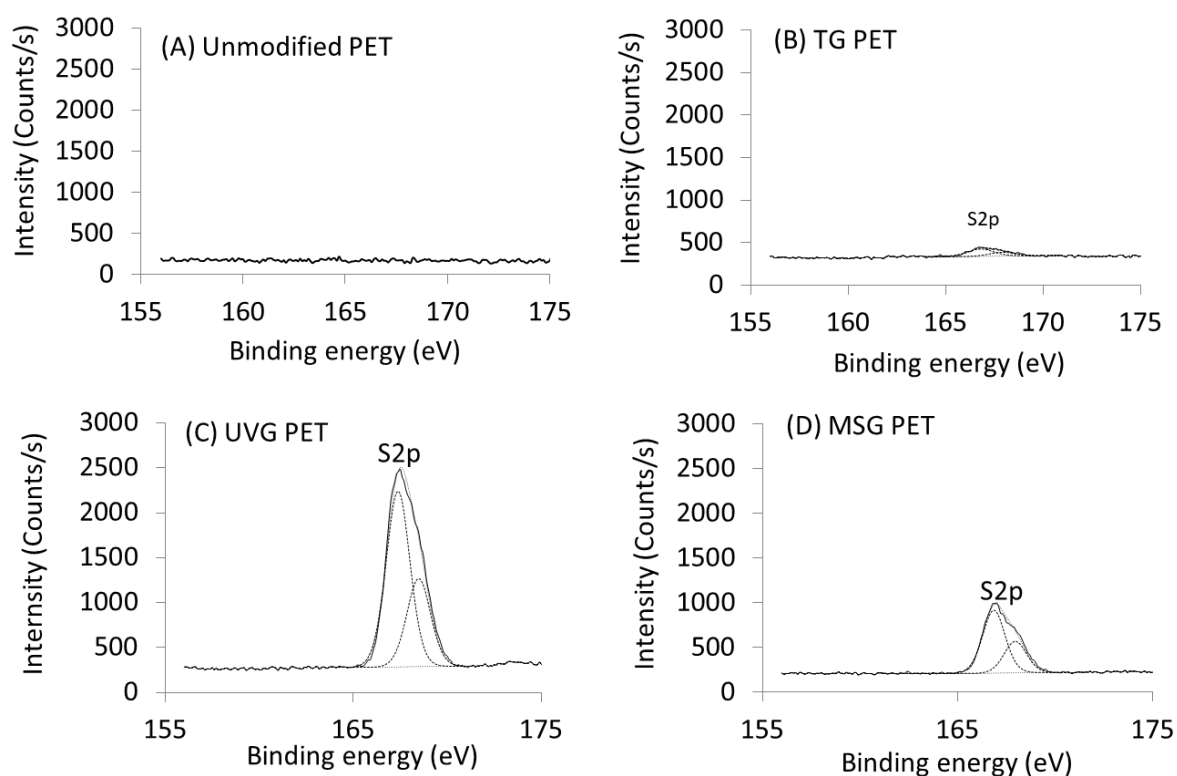


Figure S1. XPS spectra of functional PCL and PET: (A) non-grafting PET surface, (B) thermal graft PET surface, (C) UV graft PET surface, and (D) MS graft PET surface

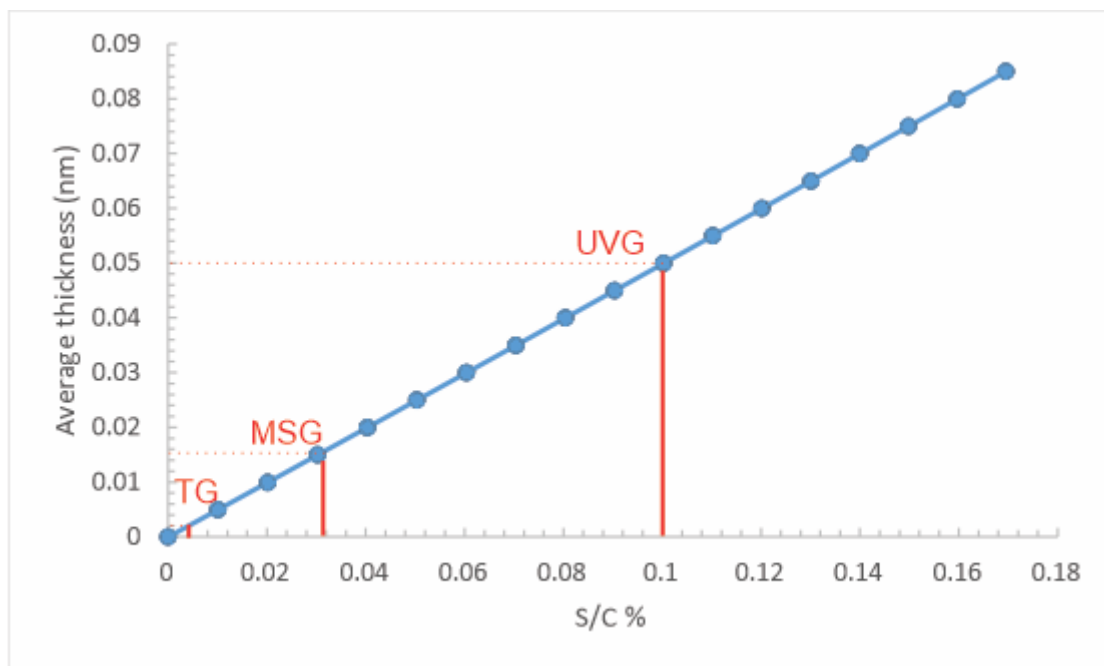


Figure S2: Theoretical estimate of average thickness as a function of %S/C for a layer of PNaSS on PET. The calculation is based on an estimated depth of PET of 10 nm being probed by XPS (PET =  $(C_{10}H_8O_4)_n$ ; PNaSS =  $(C_8H_7NaO_3)_n$ ; density of PET and PNaSS respectively 1.66 and  $2.38 \text{ g}\cdot\text{cm}^{-3}$ ). The red lines show the experimental results.

The equivalent thickness probed by XPS is estimated to be close to  $3\lambda = 10 \text{ nm}$  representing 95% of the signal,  $\lambda$  being the inelastic mean free path of electrons from the PET substrate in the organic PNaSS film; for electrons having a kinetic energy around 1200 eV (from the C1s atomic level),  $\lambda$  is estimated to be equal to  $3.23 \text{ nm}$ .<sup>1</sup>

The estimated thickness ( $d$ ) of PNaSS on top of PET can then be calculated using the following formula:

$$\frac{I_{S2p}}{I_{C1s \text{ 284 eV}}} = \frac{\rho_{PNaSS} M_{ET} \sigma_{S2p} T_{S2p} \lambda_{S2p}^{PNaSS} \left(1 - \exp\left(\frac{-d}{\lambda_{S2p}^{PNaSS} \sin(\theta)}\right)\right)}{\rho_{PET} M_{NaSS} \sigma_{C1s} T_{C1s} \lambda_{C1s}^{PET} \left(\frac{-d}{\lambda_{C1s}^{PNaSS} \sin(\theta)}\right)}$$

Wherein:  $\theta$  is the photoelectron collection angle. TC1s and TS2p are the relative sensitivity factors of C and S, respectively, provided by the spectrometer manufacturer. The Scofield

<sup>1</sup> Tanuma, S.; Powell, C. J.; Penn, D. R. Calculation of electron inelastic mean free paths (IMFPs) VII. Reliability of the TPP-2M IMFP predictive equation. Surf. Interface Anal. 2003, 35, 268–275.

photoionization cross-sections  $\sigma$  are equal to 1 for C 1s and 1.44 for S2p.<sup>2</sup>  $\lambda \times \gamma$  is the inelastic mean free paths of electrons  $x$  in the matrix  $\gamma$ . They were calculated using the Quases program based on the TPP2M formula 1.  $\rho_{\text{PNaSS}}$  and  $\rho_{\text{PET}}$  are the density of PNaSS and PET, respectively.  $M_{\text{NaSS}}$  and  $M_{\text{ET}}$  are the molecular weight of NaSS (sodium styrene sulfonate) and ET (ethylene terephthalate), respectively.

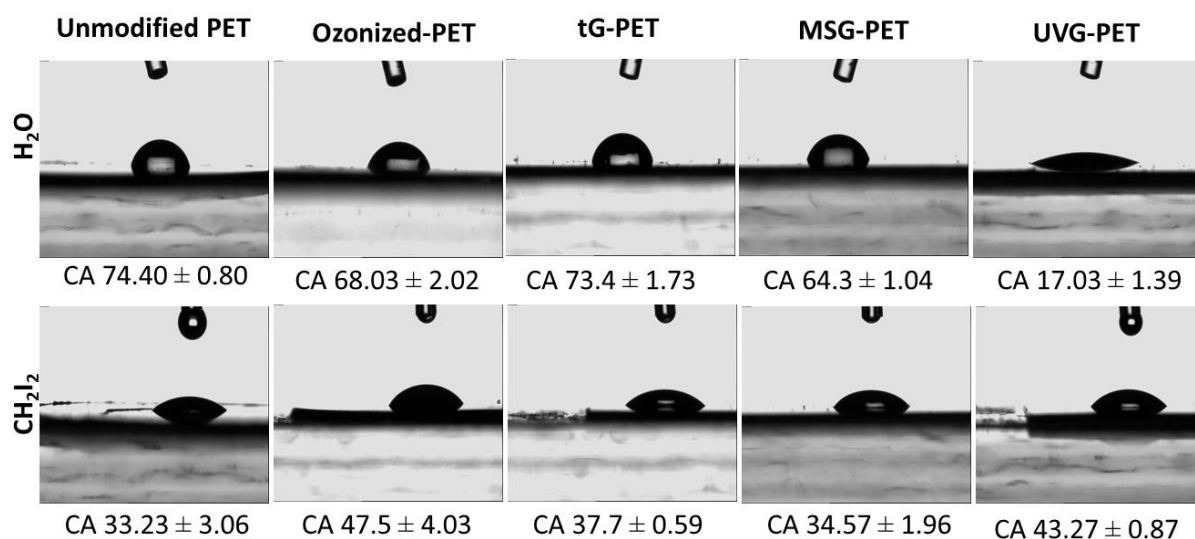


Figure S3. Contact angle measurement (2  $\mu\text{L}$ , 8s) for non-grafted and modified polyethylene terephthalate (PET)

<sup>2</sup> Scofield J (1976) Hartree–Slater subshell photoionization cross-sections at 1254 and 1487 eV. J Electron Spectrosc Relat Phenom 8(2):129–37

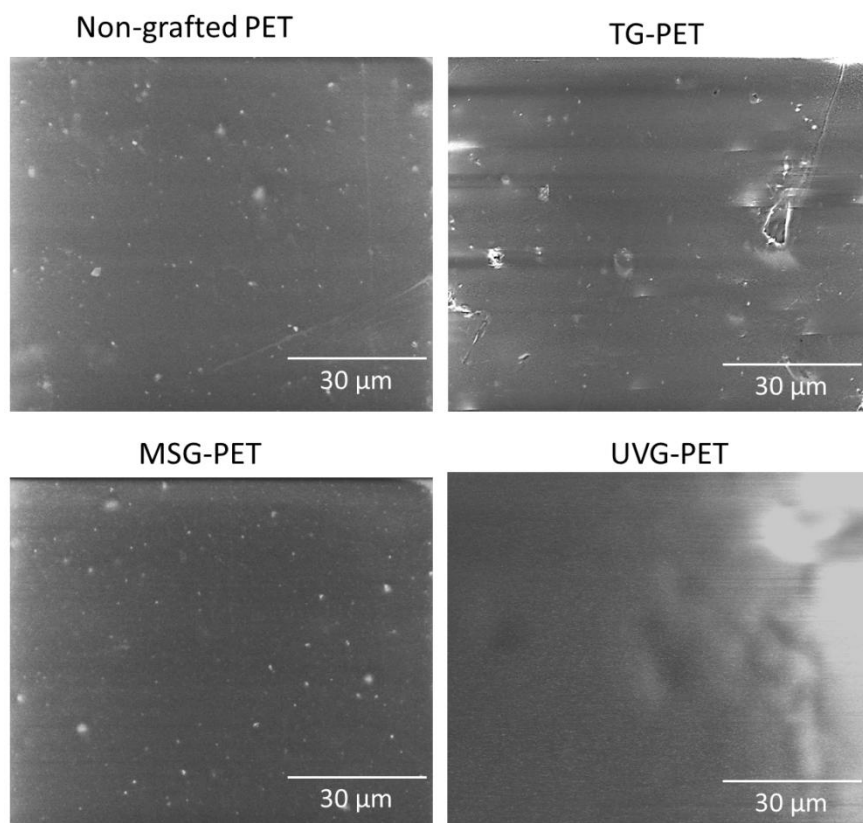


Figure S4. SEM images of non-grafted, thermal grafted, thermal grafting in the presence of Mohr's salt, and UV grafted PET; SEM HITACHI TM3000, magnification  $\times 20$

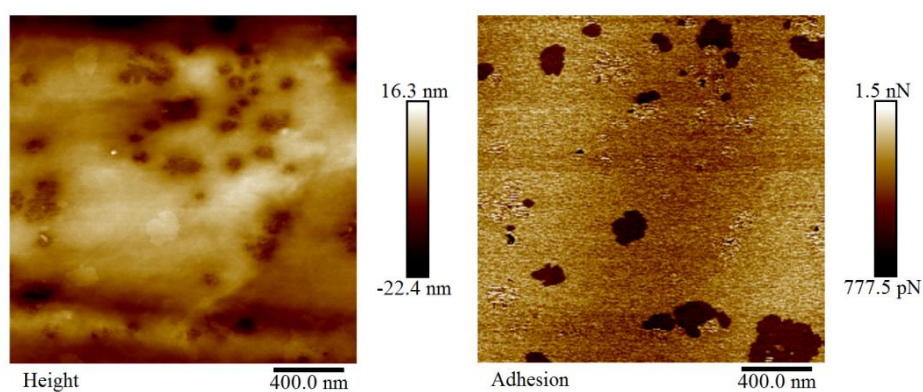


Figure S5. AFM image of UV grafted PET with scan size  $2 \mu\text{m} \times 2 \mu\text{m}$ , 256 points/line, scan rate 1 Hz, PF-QNM. The fraction of surface area occupied by the low adhesion patches is 8% (measured with Image J).

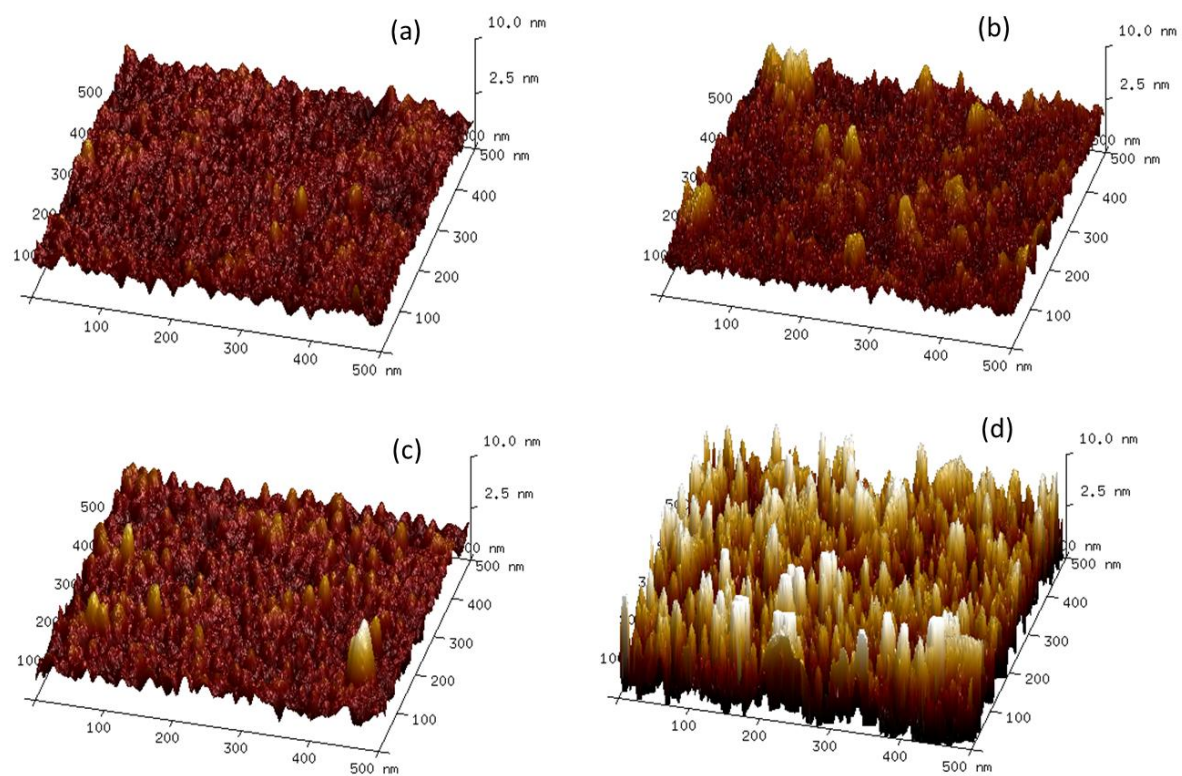


Figure S6. 3D AFM images of (a) non-grafted PET, (b) ozonized PET, (c) thermal grafted PET (tG), and (d) thermal grafted PET in the presence of Mohr's salt (MSG)



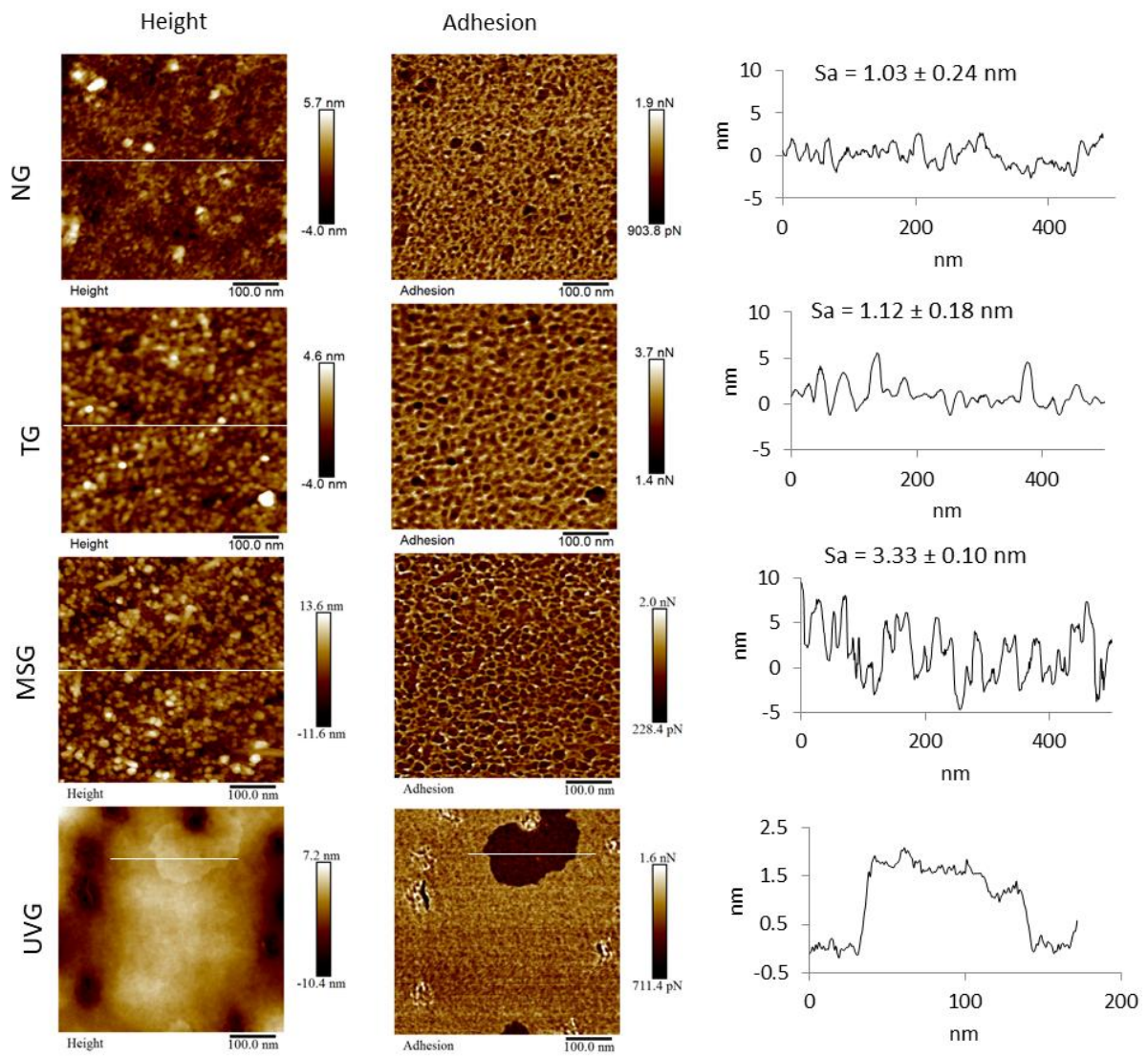


Figure S7. Summarization of AFM images of different PNASS grafting methods on PET