Optimization of the wet and dry adhesion of organic plasma polymerized coating on polymers for biomedical applications

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Introduction:

Plasma surface modification is commonly used in biomedical field, for example to enhance cells adhesion and growth implants without affecting their bulk properties. In particular, plasma polymerization is used to create thin coatings rich in functional groups, e.g. primary amines, known to enhance the cellular response and allow grafting of actives biomolecules. An important issue regarding coatings for biomedical application is however adhesion on the substrates, especially in the wet physiological environment. The aim of this project was to evaluate the adhesion of a primary-amine rich plasma polymer on poly(tetrafluoroethylene) (PTFE) and poly(ethyleneterephtalate) (PET) in dry and wet conditions. Thereafter, optimization of adhesion on PTFE was carried out using ammonia plasma surface pre-treatment. A simple and cheap method of evaluation of adhesion was used in order to study the effect of the operating plasma conditions.

Materials and Methods:

The low-pressure plasma polymer studied here (referred to as "LP") is prepared from a mixture of ethylene (C_2H_4) and ammonia (NH_3) with a ratio of R=0.75 as detailed in previous publications (Ruiz et al, 2010). It was deposited on different substrates in PET and PTFE. The interfacial adhesion between the LP coating and each substrate was evaluated by a Peel-test 180° with cross-hatch according to ASTM F1842-09. Samples were tested dry or after immersion in deionized water. LP staining using fuchsin acid, followed by image analysis, was performed to determine the percentage of removed coating. Adhesion optimization using NH_3 plasma pretreatment was then carried out by changing pressure, power and treatment time. Chemical composition and wettability were characterized by XPS and contact angle measurements.

Results:

As shown in Figure 1, the adhesion of LP on PET was found to be excellent in a dry environment, but much lower in wet medium. Moreover, 5±10% to 69±13% of the LP was removed from virgin PTFE in a dry and wet environment respectively; this can be substantially improved by plasma pretreatment (0% and 8±3% delamination in air and after 30min immersion, respectively). This was achieved using NH_3 plasma pretreatment for 15s at 100 mTorr and 50W. N_2 plasma pretreatment proved much less effective.

Plasma pre-treatment also improved the peel test strength by a factor of 6 (6.4 ±0.2 N/cm for PPTFE vs. 1.2 ± 0.2 N/cm for PTFE). XPS analysis showed a significant reduction of F/C ratio after surface pretreatment compared to virgin PTFE. The free surface energy also almost doubled with plasma pretreatment (38 ± 5 dynes/cm vs. 20 ± 4 dynes/cm) while the contact angle with water decreased (77 ± 2 ° vs. 101 ±5 °).

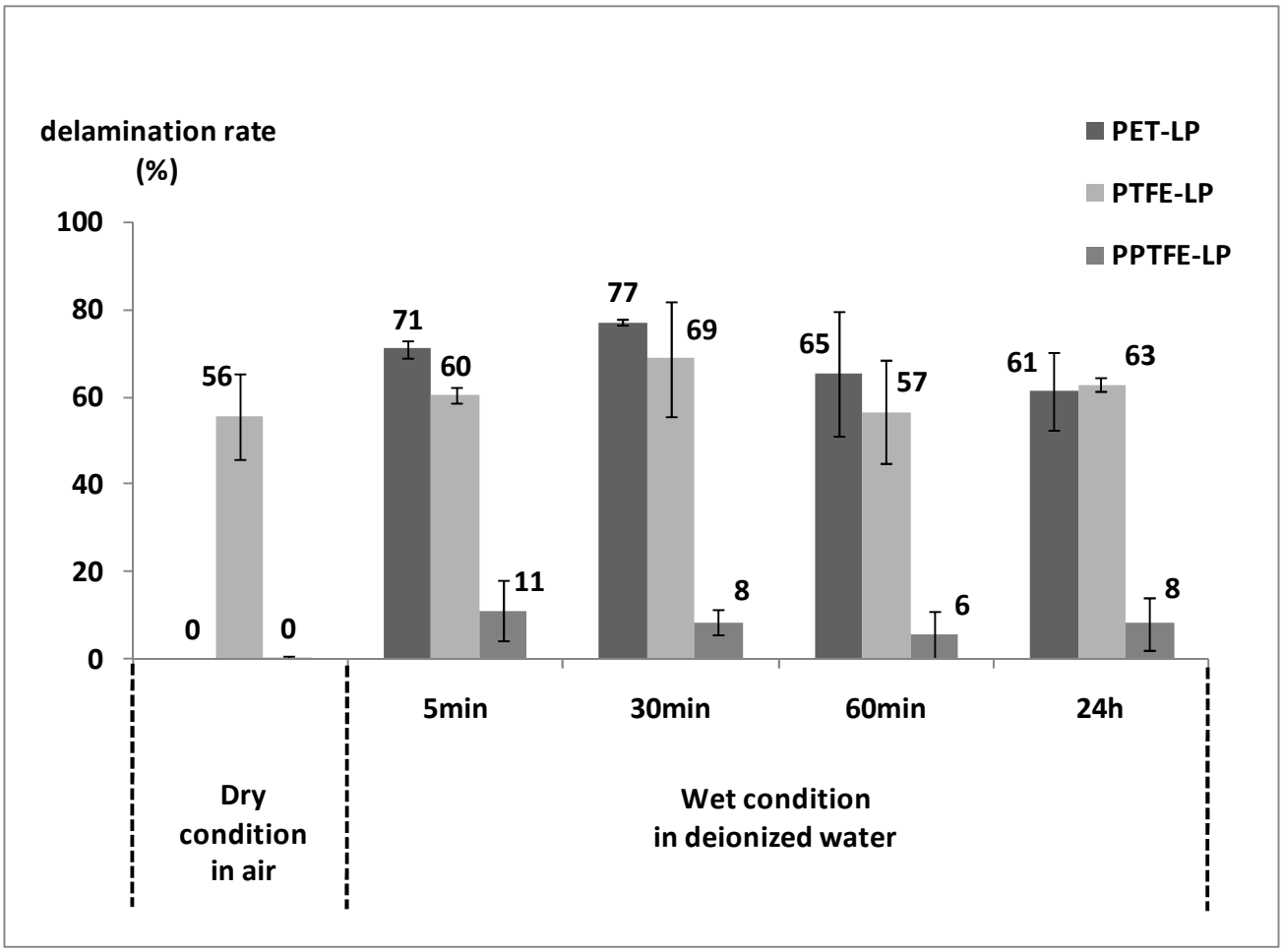

Figure 1: Delamination rate of LP on PET and PTFE virgin and pretreated in dry and wet conditions at different time of immersion in deionized water (PPTFE means pretreated PTFE)

Discussion:

In accordance to previous studies, the adhesion of LP on PTFE is low but can be considerably improved by NH_3 plasma pretreatment. The improvement was observed both in dry and wet conditions. LP chemical composition and cell growth on LP-PTFE were not significantly affected by this pretreatment. Further investigations are required to explain the LP/PET low adhesion in wet conditions and to define plasma pretreatment to overcome this weakness. These results however emphasize the importance to test coatings adhesion in wet conditions when biomedical applications are targeted.

References:

Ruiz, Juan-Carlos, Amélie St-Georges-Robillard, Charles Théresy, Sophie Lerouge et Michael R. Wertheimer. 2010. « Fabrication and characterization of amine-rich organic thin films: Focus on stability ». *Plasma Processes and Polymers*, vol. 7, n° 9-10, p. 737-753.

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