Highly hydrophobic and durable plasma coatings to replace PFAS

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Abstract: Per- and poly-fluoroalkyl substances (PFAS) are still applied in large quantities for coating applications, although their health and environmental hazards are well documented. In particular, plasma coatings are suited to replace PFAS in many applications, where hydrophobicity and durability are required. Based on siloxanes, high-performing ultrathin coatings can be applied on 3D materials such as textiles and membranes.

1. Introduction

Newly produced per- and poly-fluoroalkyl substances (PFAS) are used mainly in textiles, medical devices, food-related packaging, and cookware [1]. For such coatings, fluorosurfactants are largely applied, adding up to quantities of ~30 kt per year alone in the European Union. In particular, fluorosurfactants, comprising a hydrophilic group and a perfluorinated, hydrophobic tail, are considered as toxic, since they are persistent, soluble in water and can thus be distributed in the environment. They have been linked to cancers and damage to immune systems, supporting allergies and obesity. Studies show that every year about 25% of all PFAS as used in textiles are emitted by wearing, laundering, and waste.

Hence, replacing PFAS in such applications is an urgent need. PFAS-free, so-called C0 (C-zero) coatings, however, lack in performance mainly regarding durability. Plasma coatings, on the contrary, enable enhanced durability due to covalent bonding on the substrate material by saving large amounts of chemicals compared to conventional solution coatings. Comparing surface energies of different compounds to PFAS, most of all, methylated siloxanes allow highly hydrophobic properties, whereas they do not provide oleophobicity as PFAS.

2. Methods

Different RF-driven low pressure plasma reactors are available at Empa, optimized for the deposition of functional plasma polymer films (PPFs). Pilot-scale plasma reactors have been developed, allowing roll-to-roll (R2R) treatment of web material including membranes as well as fiber materials such as yarns. Monomers such as hexamethyldisiloxane (HMDSO) are used to deposit siloxane PPFs functionalized with methyl ($-CH_3$) groups. Working pressure is 4-10 Pa, while power input and gas flow rate is varied to deliver sufficient energy for plasma activation in the gas phase. The detailed methodology how to optimize PPF deposition conditions has been published recently [2].

3. Results and Discussion

Most plasma coating processes are optimized to treat surfaces that are fully exposed to plasma-surface interaction. This way, the low pressure plasma provides energies of tens of eV in the gas phase for plasma activation (excitation and dissociation of molecules) as also at the surface by ion bombardment supporting film growth. The coating of complex geometries as in scaffolds, membranes, and textiles, however, require slightly adjusted strategies. Still, the generation of film-forming species is optimized by gas phase processes, i.e. the energy invested per molecule. The interaction with the substrate material, however, should be mainly based on neutral radicals able to diffuse into 3D structures [3]. Plasma deposition of optimized hydrophobic films from HMDSO enables uniform coating of all fiber surfaces of a yarn material resulting in strong capillary depression. Textiles made of the plasma-coated yarn thus outperform PFAS coatings in terms of fast drying and durability (Figure 1).

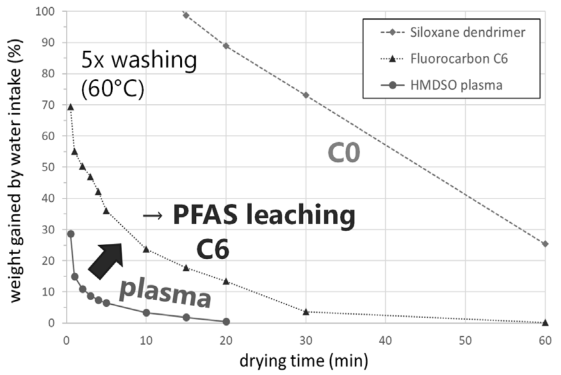

Fig. 1. Fast-drying performance of plasma-coated fabrics compared to PFAS-containing and PFAS-free conventional textile finishings (after 5 washing cycles).

4. Conclusion

Dry and sustainable plasma technology has proven its potential for the functionalization of complex materials, which can make an impact on health and environment.

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References

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