

Surface Modification and Electrochemical Metallization Of Advanced Polymers For Energy Application

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Introduction

For some demanding applications, the peculiar properties of polymers, as lightweight, flexibility and chemical resistance, need to be enriched with additional characteristics that are intrinsically associated with metals, such as thermal and electrical conductivity, barrier to fluids, high hardness, tribological resistance and reflectivity. Applications, requiring this coupling of different properties, include flexible electronics, barrier layers and alternative energy (1–3). For these applications, a layer of metal (whose thickness depends on the application), on top of the polymeric substrate, is sufficient to assure the required properties. The main concern for these multilayers is the level of adhesion between the two materials that is related to the low surface energy of polymers (4).

To overcome adhesion issues between the polymeric and metallic layer, several dry and wet processes have been proposed (5–7) that imply the utilization of expensive equipment or aggressive and hazardous chemicals. Chemical etching of polymer surface usually improves adhesion of the metallic layer, deposited by electroless process, due to mechanical interlocking; the growing metal penetrates in the highly crazed and porous surface of etched polymers thus increasing the adhesion between the two layers (8). Plasma treatment is being more and more considered as a viable alternative to wet

etching of the surface. This is due to the possibility of inducing chemical modification of the polymer surface without affecting bulk properties (9, 10); roughness variation can be minimized or enhanced depending on treatment conditions.

Plasma modification is particularly interesting when considering fluorinated polymers, due to their intrinsic chemical inertness. For this reason a two steps process is considered, based on plasma treatment of Halar[®] ECTFE surface followed by conventional electroless deposition. Plasma treatment is fundamental to increase wettability due to the introduction of polar groups, thus allowing the deposition of a metallic layer with good adhesion to the substrate. The possibility of exploiting this process to produce flexible concentrator mirrors for solar thermodynamic is being explored. For this purpose some preliminary studies were performed on reflection properties of copper coated Halar[®] films, obtained with the proposed process.

Experimental

Halar[®] 500 (ECTFE) films, with a thickness of 50 μ m, were supplied by Solvay Specialty Polymers. Before plasma treatment, surface cleaning was performed with cloths soaked with Isopropyl alcohol in order to remove grease and contaminations. Electroless metallization was performed with commercial electrolytes based on three steps: (I) activation with a PdCl₂ based solution, (II) reduction of adsorbed Pd²⁺ ions to metallic palladium and finally (III) copper autocatalytic deposition. Dipping times, in the copper deposition bath, were varied in order to obtain continuous and flawless metallic deposits and ranged between 1 and 3 minutes with an average growth rate of 100nm/min.

To obtain samples with higher thickness of copper deposits, electrodeposition was performed on the electroless layer of metal using acidic copper bath with soluble Cu-P counter electrode and current density 15mA/cm².

Characterization was performed on the plasma treated ECTFE in order to determine variation in wettability and surface morphology. Contact angle and surface free energy measurements were performed with Kruss DSA 25 instrument in static sessile drop mode. Determination of surface free energy was performed using water and diiodomethane with the Fowkes model. AFM measurements were performed on different areas, ranging from 4 μ m² to 50 μ m², using a NT-MDT Solver Pro instrument in tapping mode. Characterization was performed on the metal-polymer bilayer in order to determine adhesion properties; cross-cut testing was executed on the metallic side of the assembly, respecting the procedure reported in the ASTM 3359. Bending test was performed on the samples using BYK cylindrical mandrel tester ISO version, respecting the ISO 1519 standard.

SEM imaging was performed both on ECTFE/ electroless Cu (250nm) samples and on ECTFE/electroless Cu (250nm)/ electrodeposited Cu (3 μ m) samples with a Zeiss Leo Supra 35 field emission microscope; imaging was performed on the surface and in cross section to determine metallic deposit structure and homogeneity. Finally testing was executed in order to determine properties for the possible application as solar concentrator mirrors. Studies were performed measuring the evolution of light transmission properties of films of Halar[®] ECTFE with ageing under QUVB conditions. Reflection properties were determined using Perkin Elmer Lambda 2 spectrophotometer in reflection mode with integration sphere; measures were performed using incident radiation on the polymeric side of the sample. Collected data are relative to the reference sample of BaSO₄.

Results and Discussion

For sake of clarity, discussion is divided between characterization performed on the Halar[®] ECTFE film and characterization on the polymer-metal bilayer. This helps the discussion keeping in mind the two steps of the process; distinction is indeed done between test on the polymeric substrate and on the final bilayer after electroless metallization.

Characterization of Halar[®]ECTFE

Contact angle measurements revealed that after plasma treatment an increase in surface free energy always occurs. This is mainly due to the polar component while dispersive component is almost unchanged; the purpose of plasma treatment is indeed introducing polar groups on the surface, with the aim of increasing wettability with water. The entity of the surface energy increase depends on the plasma treatment conditions and is related to the amount of incorporated polar groups. It is well known in the literature that polymers, treated by plasma to increase surface free energy, are prone to hydrophobic recovery (11, 12), for this reason ageing studies were performed in order to determine time scales and mechanisms governing this phenomenon.

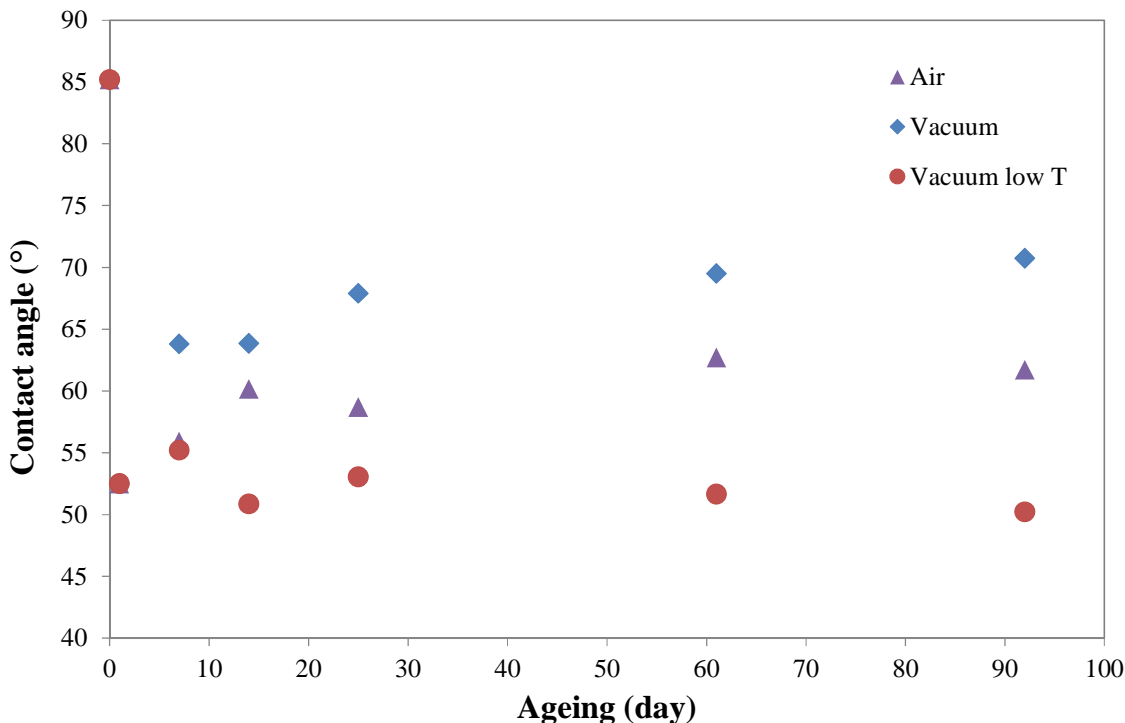


Figure 1. Water contact angle studies performed on plasma treated samples of Halar[®] stored in different conditions.

Ageing studies were performed monitoring the behavior of surface free energy and contact angle for plasma treated samples stored in three different conditions: under vacuum at room temperature, under vacuum at low temperature (-20°C) and at room temperature and pressure in air; the values reported for contact angle are averaged over

five measurements on individual drops. The results, reported in Figure 1, show the decrease in contact angle after plasma treatment (from 85° to 52°), moreover no hydrophobic recovery is observed for the samples stored at low temperature while the highest values are observed for those stored at room temperature under vacuum. This confirms that hydrophobic recovery is mainly governed by physical processes, related to chain reorientation to hide polar groups, grafted during plasma exposure, from the surface to the bulk of the polymer. Hence lower storage temperature implies lower free volume in the polymer and therefore lower chain mobility.

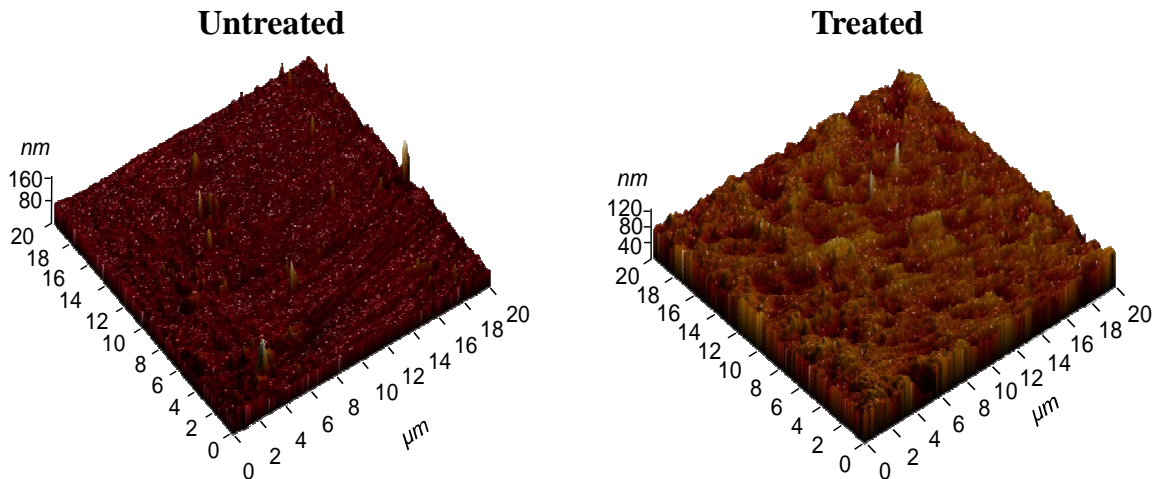


Figure 2. AFM measures performed on untreated and treated samples of Halar[®]

AFM measurements, performed before and after plasma treatment, revealed no change in surface morphology and roughness for several plasma treatment parameters. In the example, shown in Figure 2, it's possible to notice that morphology isn't affected; moreover average roughness is almost unchanged and varies from 56.4 nm for the untreated sample to 56.8 nm for the plasma treated one. This confirms that plasma is suitable to modify surface chemistry and wettability without altering morphological properties of the sample. This is fundamental for some demanding applications where the thickness of the metallic deposit is low and the roughness must be strictly controlled.

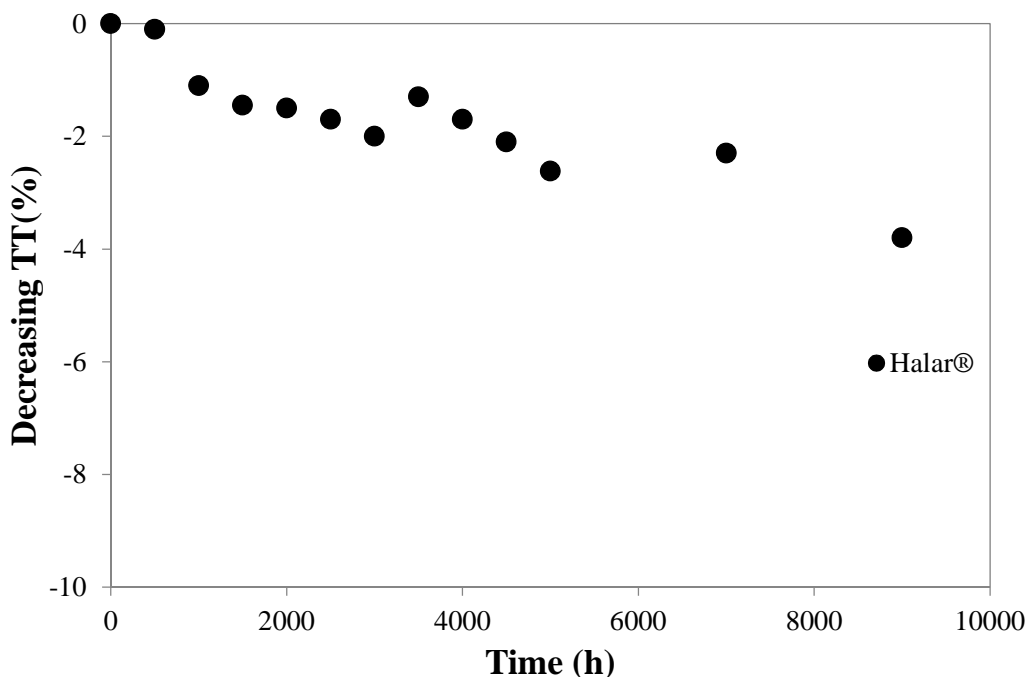


Figure 3. Reduction in light transmission for Halar[®] ECTFE under QUVB accelerated ageing.

Finally QUVB accelerated ageing, associated to light transmission tests, confirmed the high weathering resistance of Halar[®] ECTFE, with a reduction in light transmittance below 4% after 9,000 hours (Figure 3). This is essential since the application of this material in solar concentrator films is being considered.

Characterization of Polymer-Metal Bilayer

Cross cut tests, performed on several samples showing homogeneous and continuous copper deposits, revealed that the level of adhesion between the polymer and the metal is excellent. After executing the procedure reported in ASTM 3359, in which six adhesion classes (from 0B to 5B) are defined depending on the amount (in %) of coating removed during the procedure, no metal was removed; therefore the samples can be classified in the highest adhesion class, i.e. 5B. Bending tests, done in compliance of the ISO 1519 norm, revealed that the polymer-metal bilayer is able to undergo deformation with a radius of 1mm (the lowest value available) without cracking and delaminating. Considering that AFM revealed no morphological modification, these results imply that chemical modification induced by plasma is sufficient to guarantee a high level of adhesion, between the partially fluorinated polymer and the metal, without mechanical interlocking. Moreover, such outcomes suggest that applications where adhesion is required to be maintained also during bending, as flexible electronics, are accessible using this technique.

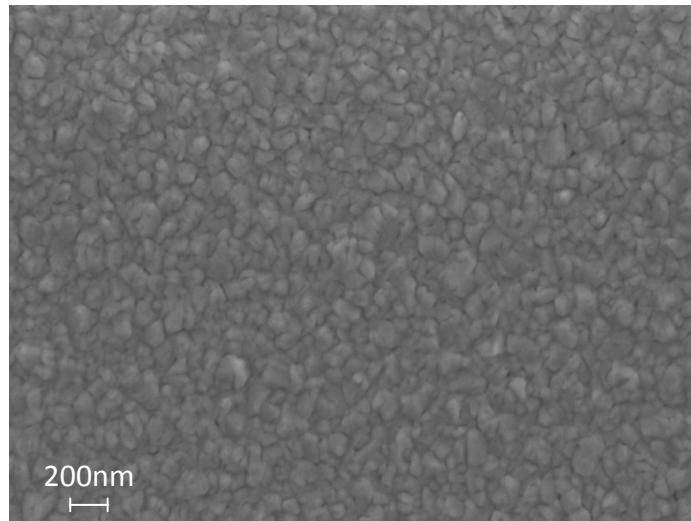


Figure 4. SEM image of electroless copper deposited for 3 minutes on plasma treated Halar[®].

SEM imaging shows that the Cu layer, grown for 3 minutes by electroless, is continuous and homogeneous with a grain size of about 80nm and thickness of about 250nm. Homogeneity in grain size and continuity of the deposit confirm that palladium adsorption, during the activation step of electroless process, is homogeneous on the polymeric surface (Figure 4). Consequently this is a proof that also chemical modification obtained by plasma treatment is homogeneous on the polymer surface. Reflectivity measurements (Figure 5) show promising results considering the application of the proposed technology for the production of solar concentrator mirrors.

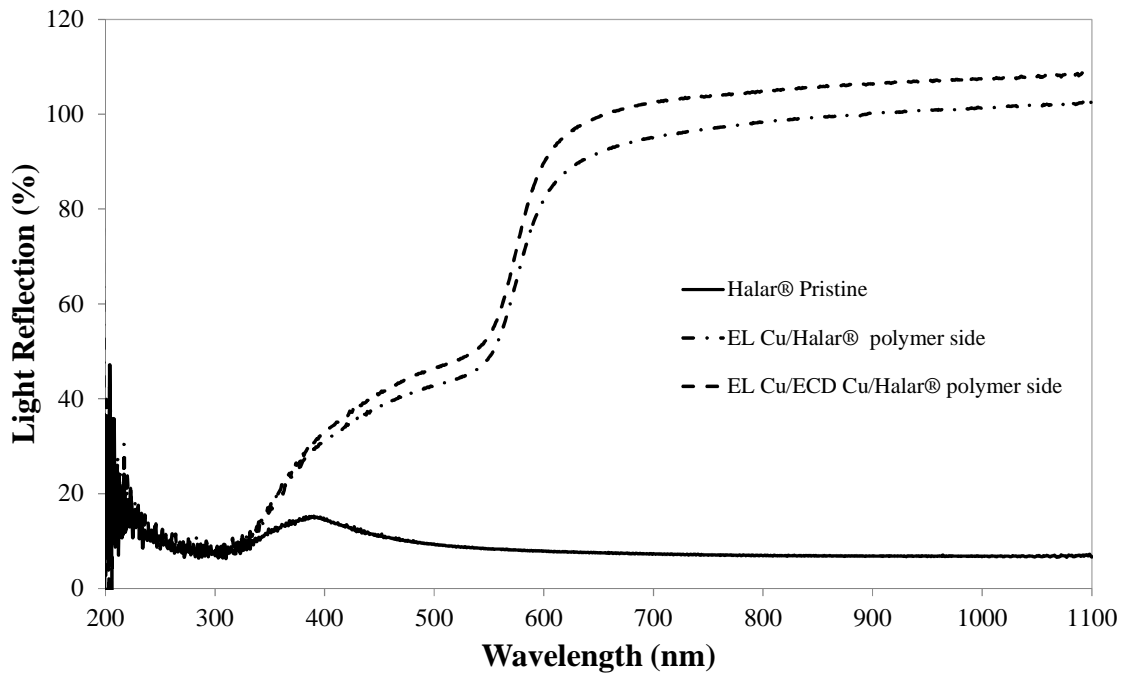


Figure 5. Light reflection properties measured on the polymeric side of: bare Halar[®], electroless Cu on Halar[®] electroless Cu/electrodeposited Cu on Halar[®]

Reflection properties are improved when a thicker layer of copper is used. The low reflection properties at high photon energies (low wavelength) are typical of copper; this limitation can be overcome by using another metal as reflective layer. Silver is a good candidate for this purpose. It should be noted that, in the near-IR, reflection values measured for both metallized samples exceed 100%. This is due to the higher reflectivity of copper coated Halar[®] with respect to the reference material (BaSO₄).

Conclusions

Surface energy of Halar[®] ECTFE samples was successfully increased by plasma treatment without inducing morphological modification of the surface. This allowed the execution of electroless copper deposition on the plasma modified surface, obtaining good results in terms of deposit adhesion and homogeneity. The possibility of exploiting this process to produce solar concentrator mirrors is being investigated; preliminary results show that Halar[®] ECTFE is suitable for this purpose due to its excellent weathering resistance. Moreover reflective copper layers were deposited. It should be considered that to produce samples with superior reflection performances Copper should be replaced with a metal owning higher reflectivity.

References

1. G. Garnier *et al.*, *Polym. Adv. Technol.* **22**, 847 (2011).
2. Y. Su *et al.*, *Int. J. Solids Struct.* **49**, 3416 (2012).
3. J. Vanfleteren *et al.*, *MRS Bull.* **37**, 254 (2012).
4. J. M. Burkstrand, *J. Appl. Phys.* **52**, 4795 (1981).
5. K. L. Mittal, *J. Vac. Sci. Technol.* **13**, 19 (1976).
6. K.-W. Lee, A. Viehbeck, *IBM J. Res. Dev.* **38**, 457 (1994).
7. P. Bertrand, P. Lambert, Y. Travaly, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms.* **131**, 71 (1997).
8. R. R. Rye, A. J. Howard, A. J. Ricco, *Thin Solid Films.* **262**, 73 (1995).
9. M.-J. Wang, Y.-I. Chang, F. Poncin-Epaillard, *Langmuir.* **19**, 8325 (2003).
10. A. Kaynak, T. Mehmood, X. Dai, K. Magniez, A. Kouzani, *Materials (Basel).* **6**, 3482 (2013).
11. R. Morent, N. De Geyter, C. Leys, L. Gengembre, E. Payen, *Surf. Coatings Technol.* **201**, 7847 (2007).
12. J. Larrieu, B. Held, H. Martinez, Y. Tison, *Surf. Coatings Technol.* **200**, 2310 (2005).