Localized Graft Copolymerization of Polytetrafluoroethylene Following Carbonization by Scanning ElectroChemical Microscopy (SECM)

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Fluoropolymers are widely used in applications where their low chemical activity, elevated resistivity, low friction coefficient and high temperature resistance, make them primary choices as far as durability is concerned. However, the same properties are disadvantageous when the fluoropolymer is required to be in contact with another material. Therefore, surface modification of PTFE has to be carried out prior to most applications.

Here we describe the localized reductive modification of PTFE surface by SECM followed by graft copolymerization with acrylic acid.

On the first hand, (Figure 1), the PTFE surface reduction has been investigated by SECM.

Typically, a redox mediator, M, is reduced into a radical-anion, $M^{\cdot -}$, at a microelectrode. When approached to the PTFE surface, the microelectrode current evolution represents the regeneration of M. This feedback corresponds to the reduction of the PTFE surface according to :

$$-(CF_2-)_n + (2+\delta n)\ M^{\cdot -} + (2+\delta n)\ Cat^+ \rightarrow [-(C^{\delta -}-)_n, \delta n\ Cat^+] + 2n\ [Cat^+, F^-] + (2+\delta n)\ M$$

with Cat^+ the electrolyte cation.

This leads to a *n*-doped conductive carbonaceous material,[1] whose conductivity decreases with time.[2]

We have studied the different parameters (E^0_M, Cat^+) which influence this reduction process in the feedback mode of the SECM (Figure 2).

Transient techniques at constant electrode-PTFE distances (Figure 3) allowed to evidence the nucleation process, which occurred during the first stage of the reduction. Then an ellipsoid-shaped reduced zone grew in the 3 directions with an in-depth process much slower than the radial one.

On the second hand, the reduced PTFE surface was graft polymerised with acrylic acid by UV irradiation in aqueous solution (Figure 4). This process allowed the formation of a thin polyacrylic film (approx. 100 nm thick) on the modified PTFE surface.

This thin film allowed not only the stabilization of the reduced PTFE zone but also the formation of a cation exchange membrane of micrometric dimensions.

The cation exchange properties of the thin polyacrylate membrane have been characterized by UV, fluorescence spectroscopy and SECM in the generation-collection mode.

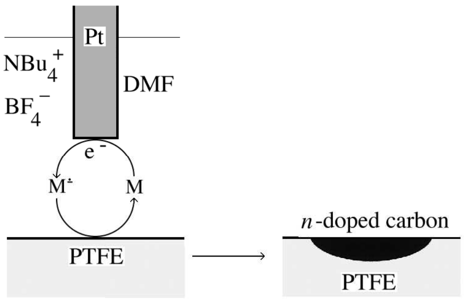

Fig 1. PTFE carbonization by indirect reduction

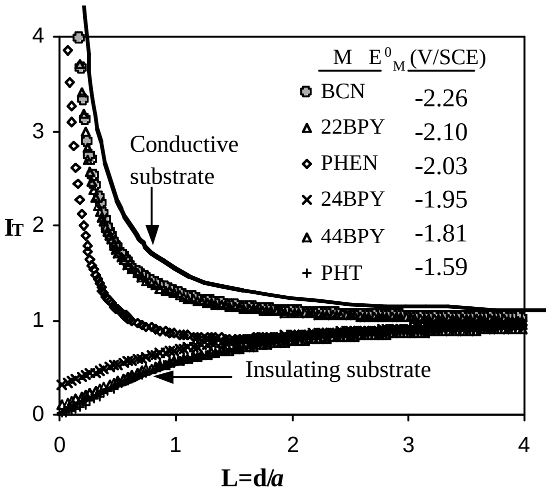

Fig. 2. Carbonization. Feedback experiments

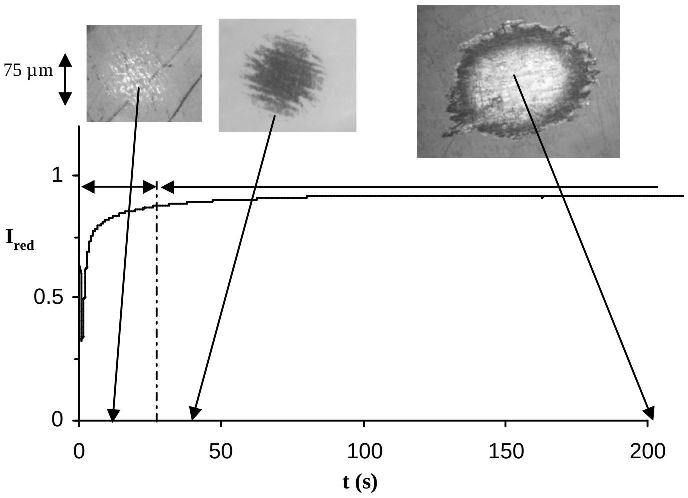

Fig. 3. Carbonization. Transient experiments

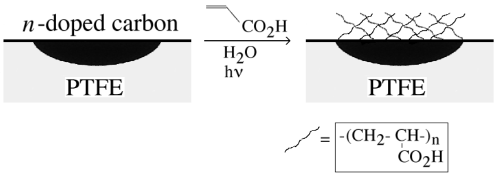

Fig. 4. Copolymerization of PTFE with acrylic acid

1 C. Amatore, C. Combellas, F. Kanoufi, C. Sella, A. Thiébault, L. Thouin, Chemistry- a European Journal, **6**, 820, 2000.

2 C. Combellas, F. Kanoufi, D. Mazouzi, A. Thiébault, Patrick Bertrand, Nicolas Médard, Polym, in press.