A new reagent for surface treatment of polytetrafluoroethylene

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Solutions of solvated electrons in the presence of magnesium offer many advantages for the surface treatment of PTFE when compared to the classical solutions of solvated electrons in the presence of alkalis: the polymer remains white instead of black, its surface is not destroyed and presents a controlled hydrophilic character.

Perfluorinated polymers such as polytetrafluoroethylene [PTFE, $-(CF_2)_n-$] are well known for their good chemical and thermal inertness, their low coefficients of friction and their high electrical resistance.[1,2] However, these remarkable properties impede the use of such polymers in any applications that require a good bondability to other materials, for example, adhesive bonding, lamination, painting, printing metallisation. Much effort has therefore been devoted to various polymer surface pretreatments which may improve their bondability.

Electrochemical or electrochemically generated pretreatments are already known, such as the extremely reductive solutions of sodium naphthalene complexes, radical anion naphthalene complexes or alkali metals in liquid ammonia.[3] Such solutions are highly reductive and often have the disadvantage of leaving the treated sample porous and blackened. We have developed similar magnesium solutions by electrochemical dissolution although magnesium was thought to be insoluble in liquid ammonia.[4] Here, the potential of this method is investigated in the case of PTFE by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and the measurement of the wettability of the polymer surface.

Magnesium is generally described as insoluble in liquid ammonia. However, the formation of a magnesium solution containing solvated electrons in the presence of the magnesium cation can be achieved by an electrochemical procedure which consists of two steps. In the first one, the electrolysis of an ammonium tetrafluoroborate solution is performed under conditions of controlled current using a stainless-steel cathode and a magnesium anode. The balance of the two electrochemical half-reactions corresponds to eqn. (1).

$$2\ NH_4^+ + Mg \rightarrow NH_3 + 1/2\ H_2 + Mg^{2+} \qquad (1)$$

In the second step when there are no more ammonium cations present in the medium, solvated electrons are generated at the cathode and magnesium cations at the anode acording to eqn. (2).

$$Mg \rightarrow Mg^{2+}, NH_3, 2e^- \qquad (2)$$

PTFE samples (area 2–3 cm^2 and 1 mm thick) were treated in solutions of solvated electrons (0.3 mol dm^{-3}) in the presence of magnesium in liquid NH_3 for different periods of time. In order to compare such treatments with the classical treatments using sodium, solutions containing both magnesium and sodium were also made by adding sodium tetrafluoroborate (0.3 mol dm^{-3}) to the magnesium solutions.

Before treatment, the appearance of PTFE was white and after treatment by the magnesium solution there was no visible change. However, when sodium was added to the solution of magnesium, the sample changed dramatically and appeared black and porous.

By SEM analysis of the backscattered and secondary electron emissions from untreated and treated samples, images of the surface morphology could be obtained. For the untreated sample the image shows the surface to be fairly homogeneous. However, a regular series of parallel lines across the surface can be observed, which may be due to machine finishing. The images of the sample treated by the magnesium solution for 15 min show that the lines present on the surface of the untreated sample have completely disappeared. The surface is also no longer homogeneous and thin white 'scars', due to accumulations of charge and indicating where surface modification has occurred, can be seen every 30–80 μm. After 19 hours of treatment with the magnesium solution, the appearance of the sample did not change further. The images of the sample treated by the sodium solution for 15 min show that the surface has been attacked to a much greater extent since large white scars cover nearly all the surface. The distance between the defects (taken from one centre to the next) is also ≈ 80 μm, suggesting that the modification begins at similar sites on the surface as during the treatment by the magnesium solution and is possibly the average distance between the naturally occurring random structural defects of the surface.

By analysing the X-rays emitted from a cross section of the sample, it is possible to estimate the depth of attack. The depth of attack for the sample treated by the magnesium solution for 15 min is smaller than the size of the X-ray probe (1 μm), whilst it is considerably greater with the sample treated by the sodium for 15 min (≈ 8 μm).

Following treatment, the samples were also analysed by XPS and a comparative study of the two reductive solutions is given below. XPS analysis enables us to distinguish between three different types of carbon atoms ([C–C, C=C, C–H], [C–OH, C=O, CO_2H, C–F] and CF_2) and to estimate the relative proportions of each type of carbon atom. Fig. 1 represents the rate at which the surface chemical composition was modified with the magnesium solution. For the first 4 min of treatment,

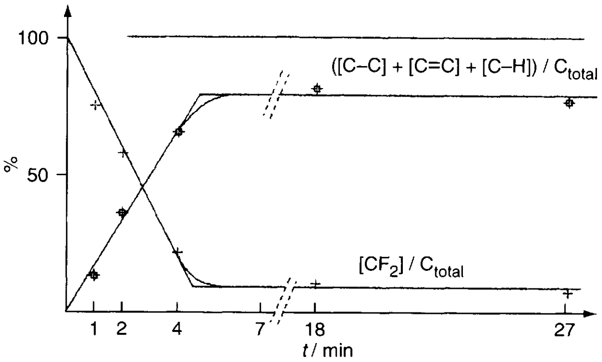

Fig. 1 Variation of the functionality of the surface carbon with time

the rate of surface modification is linear and the content of ([C–C] + [C=C] + [C–H]) increases by approximately 12% per min whilst the fluorine content decreases by about 15% per min. The proportion of ([C–C] + [C=C] + [C–H]) rises quickly to a maximum of 80–85%, whilst the CF_2 content decreases to about 10%. After 30 min of treatment the modifications appear to have terminated and no further change is apparent even after 18 h of treatment. By contrast, after just one minute of treatment in the sodium solution the sample is almost completely defluorinated and has a high ([C–C] + [C=C] + [C–H]) content. With both magnesium and sodium treatments, the oxygen content increases with time of treatment up to 25% of the total amount of carbon.

The compositions of the samples were qualitatively depth profiled by XPS using angle dependent measurements. For magnesium treatments > 10 min or sodium treatments > 1 min, the XP spectrum did not depend on the take-off angle of the photoelectrons (between 0 and 70° relative to the normal); this suggests an even greater depth of attack than that explored by XPS (15 nm).

A study of the surface free energy of samples treated by magnesium and sodium solutions was undertaken since this parameter is of fundamental importance when considering surface phenomena such as adsorption, wetting and adhesion. The method used consisted of measurement of equilibrium contact angles of small sessile drops of probe liquids (water, 1-bromonaphthalene and tricresylphosphate) deposited on the untreated and treated surfaces of PTFE. The solid surface free energy of the sample could be deduced from the contact angles using Young's, Fowkes' and Owens' and Wendt's equations.[5–7]

The dispersive component of the surface free energy of PTFE increases with treatment time from 22.7 mJ m^{-2} for the untreated sample to 40.1 mJ m^{-2} for the sample treated for 32 min in the magnesium solution and to 43.3 mJ m^{-2} for the sample treated for 1 min in the sodium solution. At the same time, the polar component increases with treatment time from 0.16 mJ m^{-2} (negligible) for the untreated sample to 7.0 mJ m^{-2} for the sample treated for 32 min by the magnesium solution and to 7.8 mJ m^{-2} for the sample treated for 1 min by the sodium solution. In all cases, the surface free energy and consequently the hydrophilic character of the surface increase with defluoration. The high values observed after treatment with the sodium solution have to be considered with care since an increase of the heterogeneous character of the surface may also affect contact angles to some extent.

In conclusion, the magnesium solution seems to be a milder reducing agent than the sodium solution. It reacts with PTFE to give a modified surface containing carbon–carbon double bonds, carbonyl, hydroxy and carboxylic functional groups, all of which make the surface much more hydrophilic. At the same time, the extent of the reduction is less severe than that of the sodium solution, resulting in a suitably modified surface without the extensive structural damage to a considerable depth observed for the classical sodium solution and which affects the strength of the material. The depth of attack with the magnesium solution is between 15 nm and 1 μm without any noticeable increase in the porosity of the material.

Different parameters of the treatment are currently under investigation: effects of the concentrations of the reactants and the nature of the C–O bonds obtained using chemical derivatization treatments. Subsequent modifications of the surface of treated PTFE samples are under investigation such as metallisation by electroless or chemical vapour deposition (CVD) procedures. Extension of the treatment to other fluorinated and chlorinated polymers (polyvinyldifluoride, Viton, Nafion, polyvinylchloride, polyvinyldichloride, *etc.*) is also presently being considered.

F. K. is a research fellow of the DRET, which is thanked for this collaboration. F. Lacour is thanked for her assistance in SEM measurements. This work was supported by EDF (contract no. 2L 508/AEE 1761) which is acknowledged.

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Received, 22nd September 1995; Com. 5/06253E