Surface Modification of Poly(vinylidene difluoride) (PVDF) by LiOH

Robert Crowe and Jas Pal S. Badyal*

Department of Chemistry, Science Laboratories, University of Durham, Durham DH1 3LE, UK

Treatment of poly(vinylidene difluoride), PVDF, with aqueous lithium hydroxide solution results in defluorination and oxidation at the polymer surface, whereas all previously reported wet methods for surface modification of fluoropolymers have to be executed under a dry nitrogen atmosphere, this process can be performed in the open laboratory; the chemistry occurring at the solid–liquid interface has been isolated and investigated in detail by XPS.

Several methods are commonly employed to functionalize polymer surfaces, which can lead to an improvement in printability, adhesive bond strength or biocompatibility of the polymer, the most popular being surface oxidation by corona discharge,[1] oxidizing solutions[2] and surface grafting.[3] Fluoropolymers are generally renowned for their chemical and physical inertness. Indeed their hydrophobic character is extensively exploited for applications such as non-stick coatings. However, it is desirable to increase the wettability of the unexposed side of such films in order to improve the lamination and adhesive properties at the polymer–substrate interface. Existing techniques used to accomplish this are quite drastic; amongst those most frequently used are solutions of alkali metal–liquid ammonia[4] and sodium–naphthalene–tetrahydrofuran (THF)[5] solutions. Alternatively, surface functionalization can be achieved by phase-transfer catalysis.[6] All of these methods are air-sensitive and therefore require a nitrogen atmosphere. In this article we report a far milder treatment involving the application of aqueous lithium hydroxide in the open laboratory. X-ray photoelectron spectroscopy (XPS) measurements show a loss of fluorine from the PVDF surface with an accompanying enhancement in its hydrophilicity.

Samples were characterized in a Kratos ES300 surface analysis instrument using Mg-Kα radiation as the excitation source. Spectra were acquired in the fixed retard ratio (FRR) mode. The take-off angle between electron exit and the sample surface was kept constant at 60°. An IBM PC computer was used for data accumulation and component peak analysis. For any specific XPS region, all the different K$\alpha_{1,2}$ environments were assigned a constant full width at half maximum (FWHM) and the K$\alpha_{3,4}$ were assigned a different fixed FWHM. In calculating elemental ratios, the relative sensitivity factors have not been taken into consideration, since we are only interested in relative trends.

Clean PVDF (Pennwalt) exhibits two main C(1s) features at 291.1 eV and 286.6 eV, these correspond to $-\underline{C}F_2-$ and $-\underline{C}H_2-$ respectively,[7] Fig. 1(*a*). The tail towards lower binding energy is mainly due to overlap with the K$\alpha_{3,4}$ lines, however a small amount of hydrocarbon impurity was also apparent. As might be expected, only one peak is seen in the F(1s) region at 688.1 eV, Fig. 2(*a*). It should be noted that no O(1s) XPS signal was detected prior to chemical treatment.

PVDF pellets were dipped into a saturated solution of LiOH(aq.) (Aldrich) and left overnight at room temperature. The resultant material was washed in one of two ways: firstly, some of it was cleaned in distilled H_2O and subsequently dried in a vacuum dessicator. Two new peaks are evident in the C(1s) spectrum, the dominant one is at 285.2 eV (most likely $-\underline{C}_xH_y-$); but there is also an extra component at 287.4 eV [probably $>\underline{C}=O$ or $>\underline{C}<(OH)_2$]. Approximately 56% of the surface carbon atoms have been modified. The emergence of an O(1s) peak is consistent with the aforementioned interpretation of the C(1s) region, Fig. 3(*b*). A significant drop in the $\underline{F}$: $-\underline{C}F_2-$ peak area ratio from 5.0 for clean PVDF to 3.8 was seen, but there was no shift in the F(1s) binding energy. All of the LiOH(aq.) solution was assumed to have been removed since there was complete absence of any Li(1s) signal.

Some more of the LiOH(aq.) treated PVDF was rinsed in *iso*-propyl alcohol and then dried. Surprisingly this procedure managed to cleanse the polymer surface of excess LiOH(aq.) without disturbing the PVDF–LiOH interface. This was

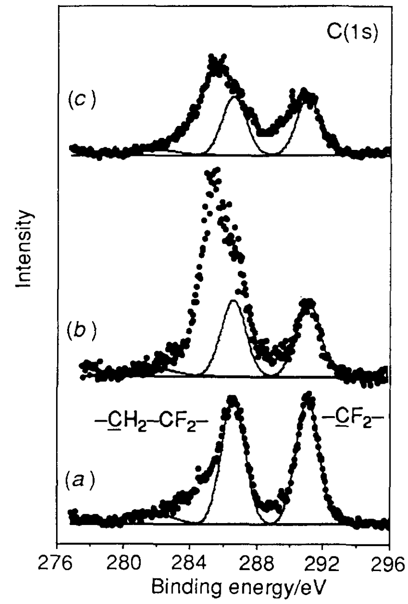

Fig. 1 C(1s) XPS spectra of: (*a*) clean PVDF; (*b*) LiOH(aq.) treated PVDF washed with H_2O; (*c*) LiOH(aq.) treated PVDF rinsed in *iso*-propyl alcohol. Solid lines represent gaussian fits for $(-CF_2-CH_2-)_n$

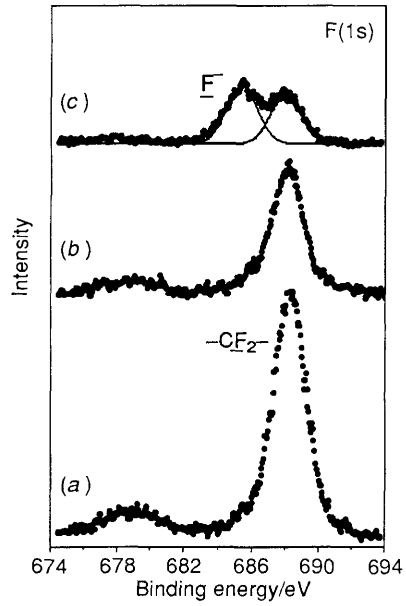

Fig. 2 F(1s) XPS spectra of: (*a*) clean PVDF; (*b*) LiOH(aq.) treated PVDF washed with H_2O; (*c*) LiOH(aq.) treated PVDF rinsed in *iso*-propyl alcohol. Gaussian lines represent ionic and covalent fluorine species.

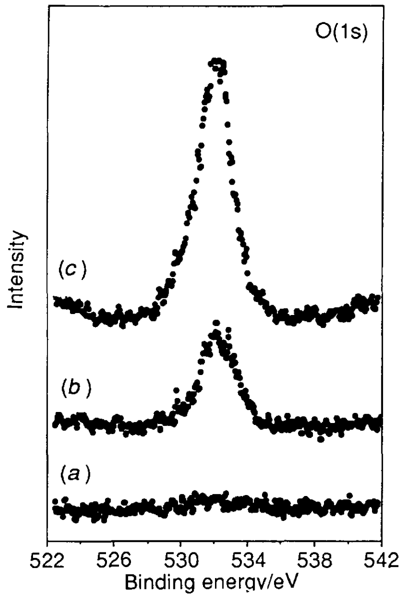

Fig. 3 O(1s) XPS spectra of: (*a*) clean PVDF; (*b*) LiOH(aq.) treated PVDF washed with H_2O; (*c*) LiOH(aq.) treated PVDF rinsed in *iso*-propyl alcohol

evident from the XPS results: firstly, both covalent (688.1 eV, 46%) and ionic (685.4 eV, 54%) fluorine species are seen, Fig. 2(*c*). Strong Li(1s) and O(1s) intensities at 55.7 eV and 532.1 eV respectively, are further evidence for a reaction occurring between PVDF and LiOH at the solid–solution boundary. Unfortunately due to the very low photoemission cross-section for the Li(1s) core level, it was not possible to differentiate between $\underline{Li}$-F and $\underline{Li}$-OH. Shoulders amounting to 53% of the total C(1s) signal also emerge towards the lower binding energy side of both the -$\underline{C}F_2$- and -$\underline{C}H_2$-peaks. Dehydrofluorination of the PVDF surface is probably occuring as depicted in eqn. (1). It is interesting to note that the amount of modified C(1s) for both types of wash (56 and 53% respectively) ties in well with the observed ionic fraction (54%) of the F(1s) spectrum. Therefore the chemistry occurring at the PVDF–LiOH interface has really been isolated by rinsing in *iso*-propyl alcohol.

$$\text{-CH}_2\text{-CF}_2\text{- + LiOH} \rightarrow \text{-CH=CF- + LiF + H}_2\text{O} \quad (1)$$

In contrast to many other reported processes,[4,5] no colour change was observed, this suggests that this is a relatively mild treatment and appears to be localized at the surface. Conventional treatments based upon alkali metals tend to lead to straightforward extraction of the fluoride ions, and therefore leave behind a reactive polymeric surface which may subsequently be functionalized.[8] In our method, the washing away of the PVDF–LiOH interface with H_2O must concurrently result in reaction of any freshly exposed reactive centres with H_2O to produce -C_xH_y-. These experiments were checked by using H_2O instead of LiOH(aq.), however no surface modification of the PVDF was found.

Simple tests with adhesive tape reveal that the modified polymer surface now has far superior adhesive properties than untreated PVDF. Present studies are aimed at evaluating the potential of using such alkali hydroxide solutions for attaching desirable functional groups and also to see whether other fluoropolymers can be modified by this method.

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