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Rutherford backscattering spectrometry and computer simulation for the in-depth analysis of chemically modified poly(vinylidene fluoride)

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The alkaline treatment of poly(vinylidene fluoride) (PVdF), in the presence of phase transfer catalysts (PTCs) has been investigated. Rutherford backscattering spectrometry (RBS) has been used to determine the depth of modification achieved and to provide compositional depth profiles of modified PVdF samples. The complex chemical nature of the modified substrate, and the overlap of the elemental scattering edges within the depths involved (up to 1.4 μm), create RBS spectra which are difficult to interpret. The DataFurnace software has been applied to the data, leading to excellent results. Defluorination and oxygenation of PVdF occurs on treatment with NaOH and PTC. Through the use of samples prepared with the aim of establishing the kinetics of the modification, a mechanism concerning elimination of fluorine followed by oxygenation, is shown to occur. The RBS analysis indicates that the kinetics of the defluorination reaction follows the Case 1 (Fickian) diffusion law, and that the depth of treatment is of the order of 1.4 μm.

1. Introduction

Poly(vinylidence fluoride) (PVdF) is well known for its high chemical resistance properties and can be processed by the standard routes used for thermoplastics. It is also known to be susceptible to attack from concentrated sodium hydroxide, however commercially it is known that resistance to such environments is improved by treating the surface with alkaline solutions of very high pH. The kinetics of this process can be accelerated with the addition of a catalyst to the treatment solution. There have been a number of investigations [1–7] concerned with the composition of such surface layers formed as a result of alkaline degradation of PVdF; all conclude that the following reaction occurs:

$$\text{–(CH}_2\text{–CF}_2\text{)–} + \text{XOH} \longrightarrow \text{–(CH=CF)–} + \text{XF} + \text{H}_2\text{O}$$

Where X = Li or Na.

Brewis *et al.* [2] and Kise and Ogata [6] did however expand this mechanism to include formation of hydroxide and carbonyl groups on the polyene chain. A more

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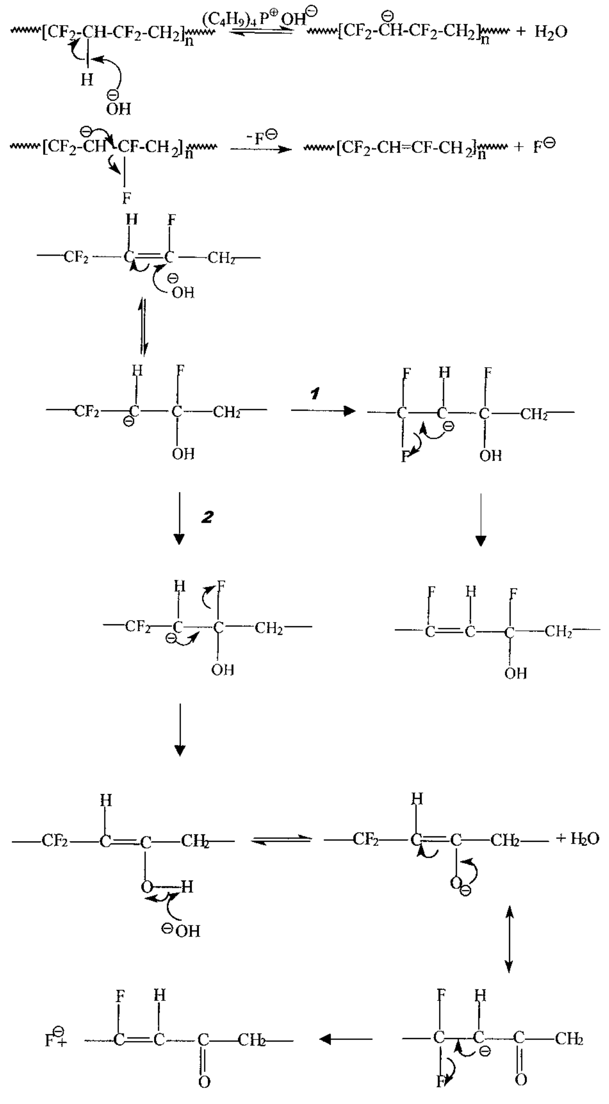
detailed mechanism has been provided by four of the current authors from previous work on this material [8–11] showing the formation of hydroxyl, HO−C−F, and carbonyl functionalities. The reaction mechanism is summarised as follows:



The mechanism is based on information obtained from surface specific techniques, XPS and ToF-SIMS, and Raman spectroscopy. So far the extent of modification (i.e. the depth) as a factor of exposure time has not been studied. For an insight into the depth of penetration and kinetics of the growth of the modified layer Rutherford backscattering spectrometry has been used.

The DataFurnace software has been used successfully in a number of cases [12–16] to determine the most likely elemental components of layers of material from the Rutherford backscattering spectrometry (RBS) data. Not only is an elemental concentration of a layer determined, but also the depth and width of that layer in the sample in question can be evaluated.

As a result of the simplicity of the PVdF structure, the DataFurnace programme can be used to fit the spectra quite satisfactorily, despite the fact that the fluorine and carbon edges overlap. However when considering a low mass matrix containing many different components, such as PVdF treated with alkaline media, the data analysis becomes more complex, as more elemental edges overlap. Oxygenation of the samples along with incorporation of catalysts and reaction media create more possible varieties of substrate layer chemistry, and therefore more possibilities for an incorrect fit of the RBS data.

By using a set of data from samples generated with the aim of establishing the kinetics of the modification process, a standard solution can be used to fit all the samples, thereby reducing the likelihood of an incorrect fit. The concentration of elements present at the surface is determined by X-ray photoelectron spectroscopy (XPS), and time of flight secondary ion mass spectrometry (ToF-SIMS) provides information concerning the surface molecular structure. This knowledge can then be used towards providing an accurate chemical description of the surface, as it provides evidence of expected elemental concentrations at this level [8–11]. This pattern of fitting the spectra can be utilised at any penetration depth in a set of samples prepared with the intention of establishing the kinetics. A layer structure of elemental concentration has been achieved in this matrix in such a manner.

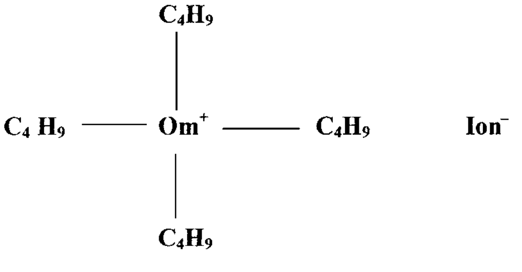
In this work the kinetics of the modification process has been investigated through the use of RBS. The mechanism of modification suggested in previous publications [8–11] indicates a diffusion controlled process. The rate of the reaction is controlled by the accessibility of the hydroxide to the organic media. Diffusion mechanisms in polymers are discussed elsewhere [17].

2. Experimental

PVdF film samples (100 μm in thickness) were mounted in polypropylene frames fixed with nylon screws to ensure no curling of the film, to reduce contamination through handling and to prevent problems due to surface proximity effects. The films were cleaned with isopropanol followed by rinsing in milli-Q water (conductivity = 0.18 S m^{-1}). The samples were treated with 2.5 × 10^{-4}m^3 4 M NaOH (Analar grade NaOH), and 0.0025 moles of PTC at 80°C in a shaking water-bath at 110 revolutions per minute, for between 1 and 24 hours. The PTCs used were as follows:

1. Tetrabutyl phosphonium bromide (TBPB): $(C_4H_9)P^+ Br^-$
2. Tetrabutyl ammonium hydrogen sulphate (TBAHS): $(C_4H_9)N^+ HSO_4^-$

The generic structure of the catalysts is shown below:



Where Om$^+$ = onium cation N$^+$ or P$^+$ and Ion$^-$ = Br$^-$ or HSO_4^-. On removal from solution the samples were rinsed in milli-Q water to quench the reaction.

The RBS analysis equipment at the University of Surrey was used with a 1.5 MeV $^4He^+$ beam, detected at a 145° scattering angle in the IBM geometry (beam, normal to the surface of the sample, and detector all in the horizontal plane). The samples were mounted on a liquid nitrogen cooled finger to reduce radiation damage induced by the He beam. Spectra were collected by serial acquisition, this means that the evolution of the sample under the beam can be determined, that is, the radiation damage can be studied. The analysis was integrated over an area of several square millimeters. A second area (sometimes a third) was analysed in order to check homogeneity of the sample. In general, the initial spectrum for the different spots on the sample were very similar in each case, i.e. no inhomogeneity problems were observed. However degradation of the samples under radiation occurred rapidly therefore short exposure times were used.

3. Rutherford backscattering spectrometry and simulated annealing

RBS is a well established and powerful technique for determining the elemental composition of thin films using an energetic light ion beam (typically 1 to 2 MeV H^+ or $^4He^+$). Because the data analysis is very simple in principle, RBS can be used to obtain quantitative and traceable information about homogeneous films. It has been used in a round robin exercise organised by the National Physical Laboratory [18] to characterise the 100 nm Ta_2O_5 standard for electron spectroscopy. Another recent example of the use of RBS in standards work is the characterisation of a secondary implanted standard by the Institute for Reference Materials and Measurements in Geel, Belgium [19]. A 1% accuracy has recently been demonstrated in the determination of the In content of InGaAs films [20]. Depths of up to 10 μm can be analysed with the use of this technique, and RBS of fluorinated polymers has been reported for depths of up to 0.8 μm [21]. Therefore, combining RBS with the surface specific techniques discussed previously, a full appreciation of the degradation mechanisms and kinetics can be achieved.

However, most real films are not homogeneous. In such a case it is usually very hard to devise a computational method transparent enough to obtain depth profiles from the spectrum whose accuracy is traceable. Moreover, most spectra obtained from real samples are sufficiently complex to preclude manual extraction of any accurate depth profiles at all in a reasonable time. The general inverse RBS problem (obtaining the depth profile from the spectrum) can be efficiently solved by a new software package, DataFurnace, using a simulated annealing algorithm [22–24].

DataFurnace is unique in approach, as automatic analysis is achieved without the need for time consuming human iteration. The user inputs the experimental conditions, as well as the elements expected to be present in the sample. The input of this information need only take a few minutes, the fitting of the data can then be achieved without further intervention. The simulated annealing algorithm has two advantages, the first is that the solution is independent of any user-given initial input. The second advantage is the method of finding the minimum difference between the data and the fit, because the absolute minimum is reached, rather than a local minimum as in conventional minimisation algorithms. These features yield a higher quality solution.

The problem posed by the inverse transform of the RBS data has been described, previously by Barradas et al., as a discrete combinatorial optimisation problem [15]. All the possible RBS spectra can be represented by a finite solution space restricted by the finite sensitivity and resolution of the technique. The energy resolution of the technique is about 1% and therefore the number of layers, that can be distinguished is limited and in the region of 100. The use of this number of layers is computationally intensive and can lead to noisy depth profiles. To alleviate this problem the use of a small number of layers has been adopted in the current work. Also, if the sensitivity of the technique to a given element is represented by s, in a specific layer the possible number of different concentrations of the element is given by $1/s$. This justifies describing the structure of a sample by a specific number of layers, layer thickness and stoichiometry, which is known as a *state*.

For each of these structures a chi-squared value (χ^2) can be defined, which is the weighted distance between the proposed theoretical function and the data. In simulated annealing, transitions from one state to the next are achieved through the generation of a new structure from the previous calculated structure, in this way the layer thickness, stoichiometry and number of layers can be changed. Each transition is generated randomly, the probability (P) of the transition being accepted by the program is defined as:

$$P = \exp(-\Delta\chi^2/T) \qquad (1)$$

For conditions where $\Delta\chi^2 > 0$ (as $\Delta\chi^2 < 0$, when $P = 1$) and T is a control parameter. Equation 1 allows the escape from local minima of the χ^2 parameter and at high values of T almost all transitions are accepted. As T decreases, however, the probability of transitions with high increases in χ^2 also decreases. At very small values of T only transitions leading to a decrease in χ^2 are accepted.

The initial stage of the program selects a very high initial value T_0, such that the initial probability of the average transition is high, around 0.95. The value of T is then slowly reduced according to $T_{i+1} = kT_i$, where k is a positive constant less than 1. At each value of T, the number of proposed transitions L is very large, ensuring that at least a certain number of them are accepted. Given that T_0 and L are sufficiently large and k sufficiently close to 1, it can be proven that at $T = 0$ the absolute minimum of the function χ^2 (or indeed any continuous function) will be reached [24].

4. Results: Spectra and depth profiles

The two sets of samples treated with the different PTCs, TBAHS and TBPB, gave similar results indicating

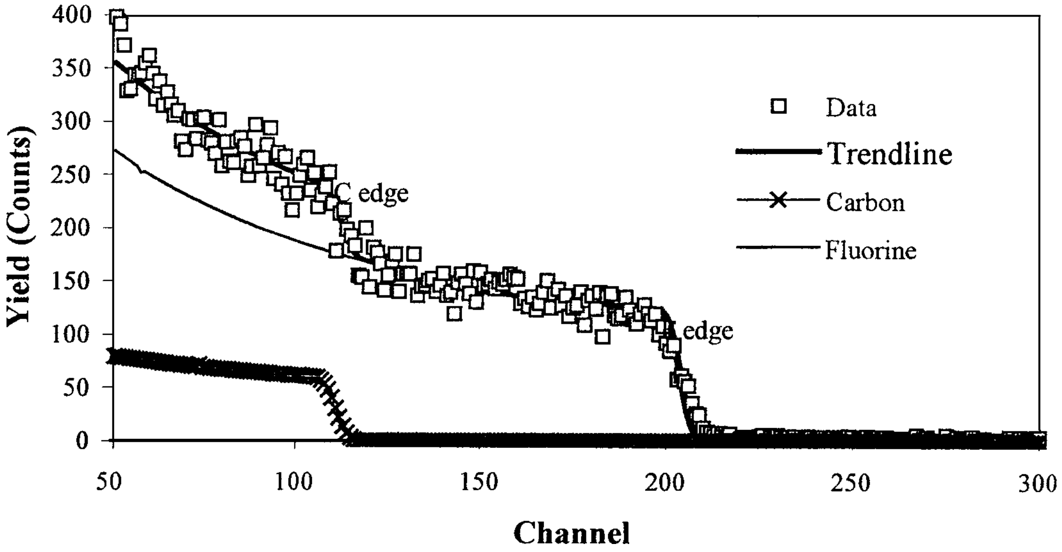


Figure 1 RBS spectrum of PVdF film, fitted with the Datafurnace software.

formation of the same products to the same depths and therefore the same reaction kinetics are assumed to occur. Previously it has been shown that the surface chemistry of the treated samples is the same in both cases [9]. Due to the similarity of the results, only those obtained from the samples treated with TBAHS will be described.

The data for untreated PVdF are shown in Fig. 1. For channels 1 to 50 the data are unreliable as the multiple and plural scattering effects are large at this analysis depth and distort the signal, therefore the data were only fitted from channel 50 onwards. The DataFurnace software package was then used to fit these data to produce the trendline shown, which corresponds to the fitted depth profile in the form of layers of specific percentages of the elements present. The sample treatment and identification details are described in Table I.

The untreated sample contains the elements carbon and fluorine; hydrogen is also present but is lighter than helium and therefore it cannot be detected. The amount of hydrogen present is inferred by deducing the percentage missing after accounting for all the other elements. The concentration of the carbon and fluorine do not change significantly with depth, indicating a uniform structure, this is expected for the untreated PVdF samples. The apparent rise in the yield for lower channels, is merely a result of the energy dependence of the backscattering cross-section as described elsewhere [25], and does not reflect changing elemental concentrations. The RBS spectra of the sample, treated for 24 hours at 80°C with 0.1 M TBAHS in the absence of NaOH, is the same as the untreated sample indicating that no subsurface reaction has occurred, as expected.

After 1 hour of treatment with the TBAHS with NaOH solution, at 80°C the fluorine edge drops slightly showing that the concentration of fluorine on the surface has decreased, see Fig. 2. Changes due to oxygen and sodium also begin to appear in the spectra. The oxygen edge occurs in between channels 150 to 175 and the sodium edge is apparent at channels 220 to 245.

After 4 hours of treatment (Fig. 3), the defluorination profile has extended further into the sample, with a simultaneous decrease in fluorine concentration in this region. The oxygen and sodium penetration depths and concentrations have also increased. This trend continues with the samples treated for 8, 12 and 24 hours (Fig. 4). The changes with treatment time of elemental concentrations over a range of depths are presented in depth profiles. These provide a simple comparison of the changes occurring in the samples with treatment time.

The depth profiles of fluorine as a function of treatment time are shown below in Fig. 5. It is evident that with increasing treatment time the fluorine concentration decreases from the original concentration of 33 at.% to 6.5 at.% after 24 hours. The fluorine concentration does not change when treated with the catalyst only.

Defluorination of samples 3 to 7 approaches depths from 0.3 μm to 1.36 μm. However 1.4 μm is the limit of the technique for this polymer and at this point the fluorine has not returned to 33% indicating that the defluorination depth is greater than this. To achieve an understanding of the kinetics of the process a graph of depth of the modified layer against square root time has been plotted, as shown in Fig. 6. The result is a linear relationship, which has been reported for a different system by Morrissey and Vesely [26]. This suggests that the treatment process is diffusion controlled, and that the diffusion process follows Case 1 (Fickian)

TABLE I Identification of sample treatment

Sample number	Treatment	Time (hours)
1	Untreated PVdF	0
2	0.1 M TBAHS, no NaOH, at 80°C	24
3	TBAHS[a]	1
4	TBAHS[a]	4
5	TBAHS[a]	8
6	TBAHS[a]	12
7	TBAHS[a]	24

[a] Samples were treated with 4 M NaOH at 80°C, with 0.0025 moles of TBAHS.

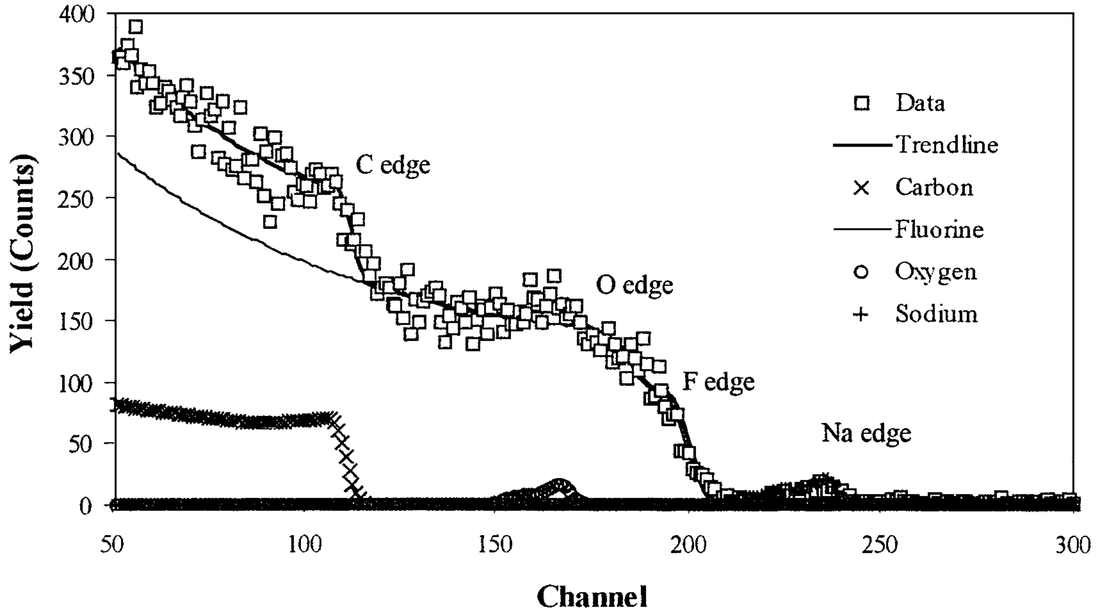


Figure 2 RBS data and fitted trendlines for samples treated with 0.0025 moles of TBAHS and 4 M NaOH at 80°C for 1 hour.

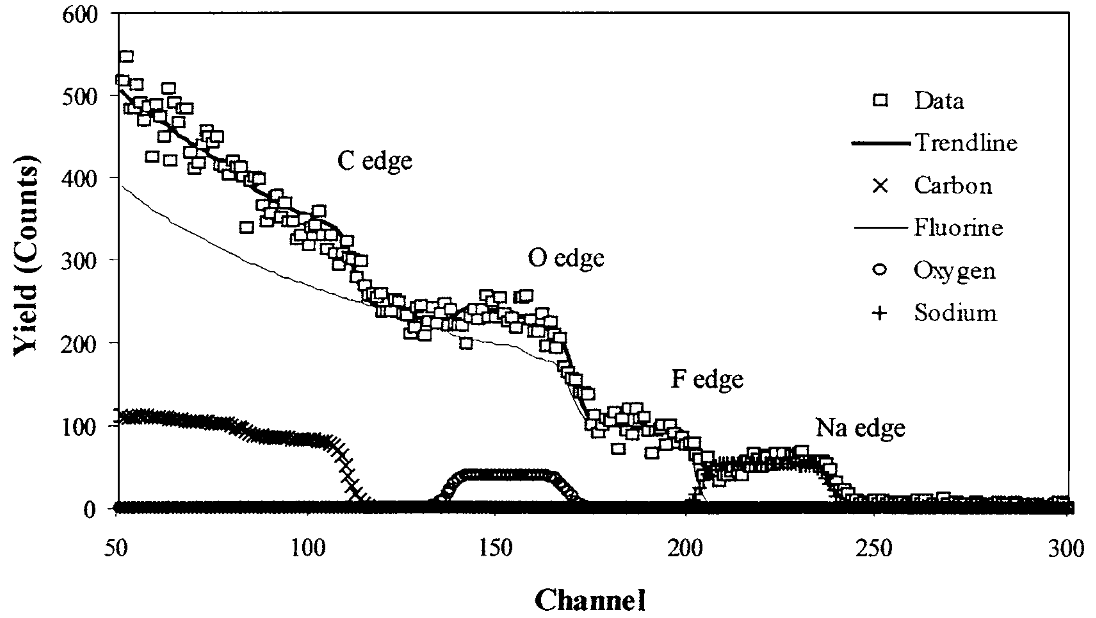


Figure 3 RBS data and fitted trendlines for samples treated with 0.0025 moles for TBAHS and 4 M NaOH at 80°C for 4 hours.

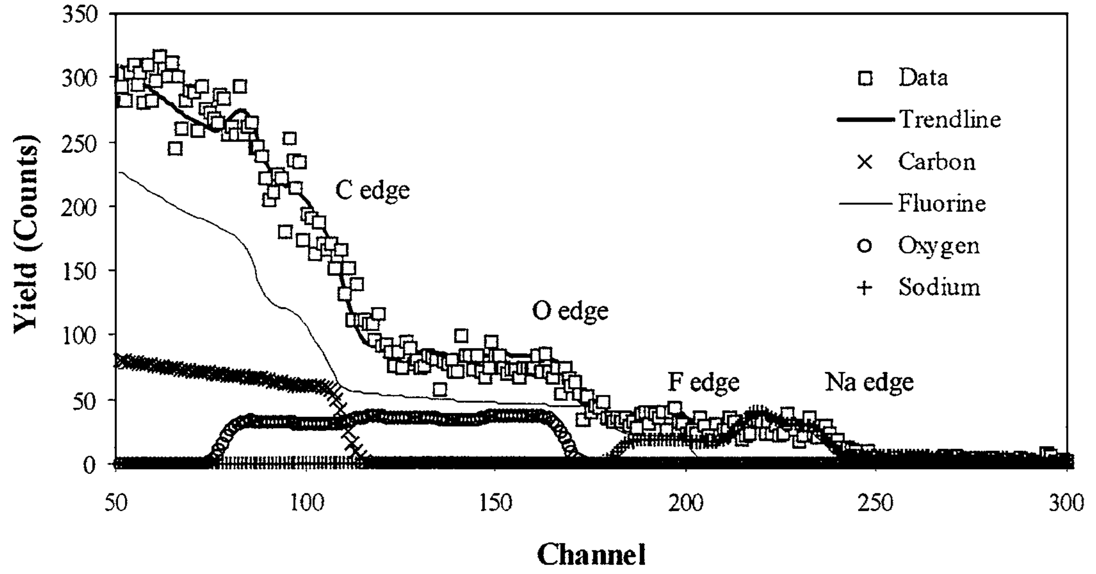


Figure 4 RBS data and fitted trendlines for samples treated with 0.0025 moles of TBAHS and 4 M NaOH at 80°C for 24 hours.

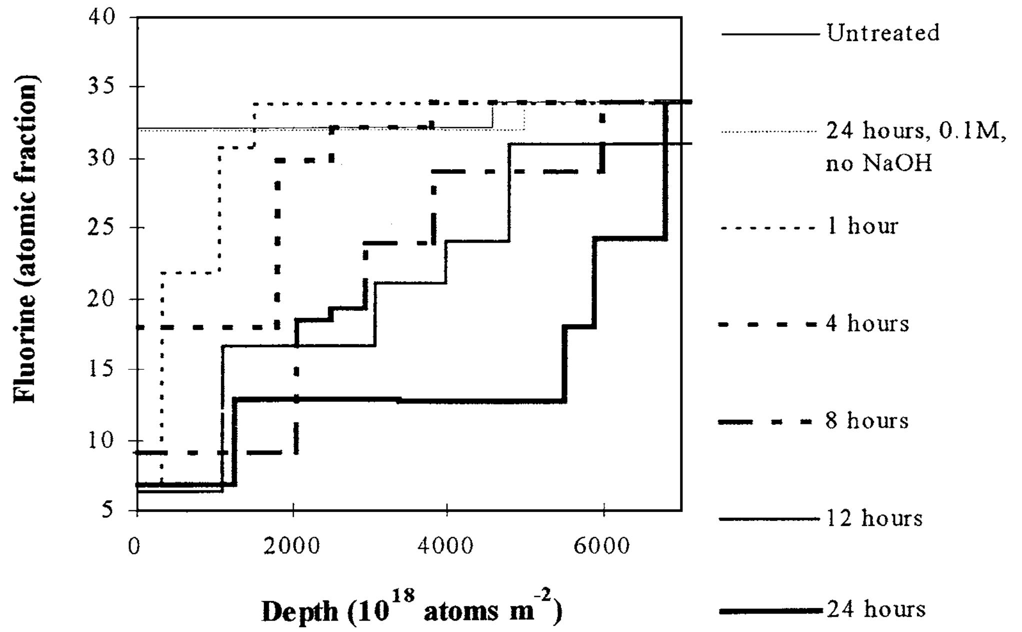


Figure 5 Fluorine depth profile of samples treated with 0.0025 moles of TBAHS and 4 M NaOH at 80°C for up to 24 hours (1000 × 10^{18} atoms $m^{-1} = 2 \times 10^{-7} m = 200$ nm).

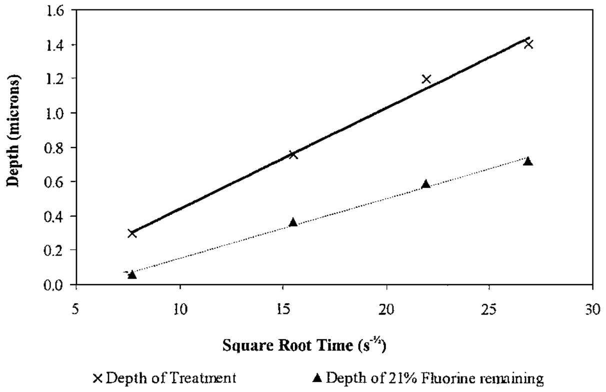


Figure 6 Depth of treatment of PVdF against square root times, to show Case 1 Fickian diffusion.

diffusion [17]. The depth of defluorination to 21% is also included in the graph, as this level of defluorination was reached in all the samples investigated within the depth of analysis. The effective analysis depth is 1.4 μm for the samples considered, as a result of the nuclear stopping characteristics of the material. This was reached after 12 hours of treatment.

The oxygen depth profiles are shown in Fig. 7. There is no appreciable amount of oxygen present in samples 1 and 2, as expected, as no reaction has occurred. The concentration and depth penetration of the oxygen increases in samples 3 to 7 with increasing treatment time much in the same way that the fluorine decreases. The depth of oxygen penetration reached after 24 hours of treatment was approximately 1.1 μm.

The reaction mechanisms have been discussed in detail in a previous publication by the current authors [9]. The oxygen was also found to advance linearly with the square root of time, see Fig. 8, demonstrating Fickian behaviour. The profile is however behind the fluorine loss profile, indicating that the oxygenation reactions occur subsequent to the dehydrofluorination reaction. This supports the conclusions made in previous papers [8–11].

The other family of depth profiles of interest are those for sodium, Fig. 9. The results are similar to those for oxygen but the concentrations and penetration depths are lower (0.8 μm after 24 hours of treatment). The depth profiles of carbon and hydrogen (deduced) do not change significantly from the initial 33% that is present in the untreated PVdF. This is as expected, as the elimination and substitution reactions discussed in previous publications [8, –9] do not bring about any change in the overall concentration of the carbon and hydrogen present.

5. Discussion

The RBS results indicate that defluorination occurred to a depth of at least 1.2 μm. The oxygen and sodium penetrate the sample to depths of 1.1 μm and 0.8 μm respectively. The lack of complete penetration of the sodium ions into the polymer supports the argument that the PTC transfers the hydroxide into the organic medium, therefore behaving as a true phase transfer catalyst. In this manner the sodium does not need to be present in the sample at the depth of defluorination.

It was shown in previous publications by the authors of this paper [8–11], that the treatment process results in the formation of carbon double bonds through the elimination of hydrogen and fluorine atoms, as shown in the mechanism above. This is followed by oxygenation of the double bonds. The hydroxide transported by the PTC initially participates in the dehydrofluorination reaction, which results in the removal of the bulky fluorine atoms reducing the steric hindrance in the tightly packed crystalline PVdF structure. This facilitates further attack by the hydroxide on the newly formed double bonds. The data presented in this paper support's this mechanism, i.e., the dehydrofluorination front advances ahead of the oxygenation front.

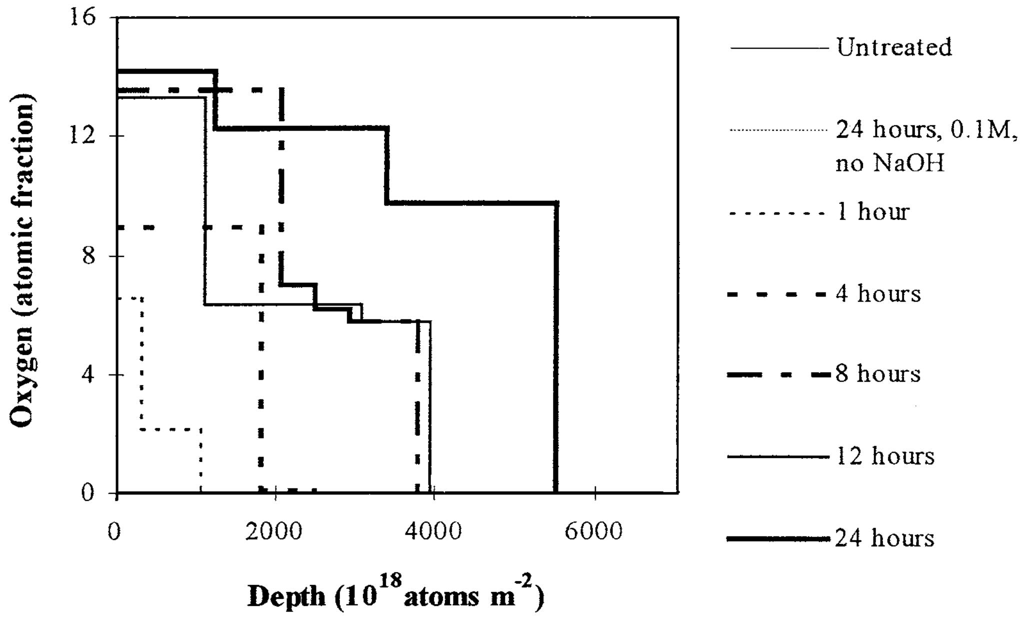


Figure 7 Oxygen depth profil of samples treated with 0.0025 moles of TBAHS and 4 M NaOH at 80°C for up to 24 hours (1000×10^{18} atoms $\mathrm{m}^{-1} = 2 \times 10^{-7}$ m = 200 nm).

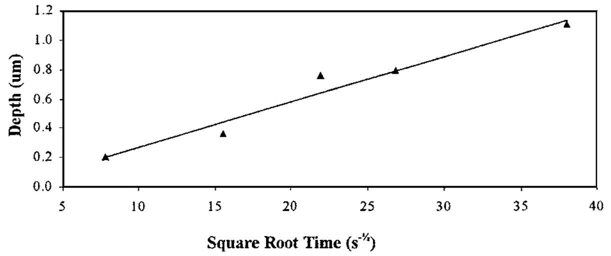


Figure 8 Depth of oxidation of PVdF against squuare root of time, to show Case 1 (Fickian) diffusion.

In order to assess the accuracy of the RBS data, it was compared to XPS data of the same sample [9]. The concentration of oxygen incorporated into the sample is 13 atomic percent from the RBS data compared to approximately 20 atomic percent from the XPS data. This however does not take into account the amount of hydrogen present in the sample, whereas the RBS data does. The RBS data indicates that there are approximately equal amounts of hydrogen and carbon present. This is in good agreement with the Raman results [9] which suggests that the treated surface has a high concentration of conjugated double bonds.In such systems one hydrogen atom is present per carbon atom as shown below.

$$-(\mathrm{CH{=}CH{-}CH{=}CH})_n-$$

This structure does not however take into account the oxygen present in the sample. In previous publications it was shown that the oxygen is mainly present in the form of hydroxyl groups. If we assume that there are an equal number of hydrogen atoms as carbon atoms present in a system where the oxygen concentration is 20 at.% and the carbon concentration is 70 at.%, as indicated by XPS, then there will be 70 hydrogen atoms for every 170 atoms. Therefore there will be 70/170 carbon atoms and 20/170 oxygen atoms, giving a carbon concentration of 41 at.%, a hydrogen concentration of 41 at.%, and an oxygen concentration of 11.8 at.%. This result is very close to that calculated by RBS (13 at.%), at the surface of the sample, demonstrating the accuracy of the results from the DataFurnace package.

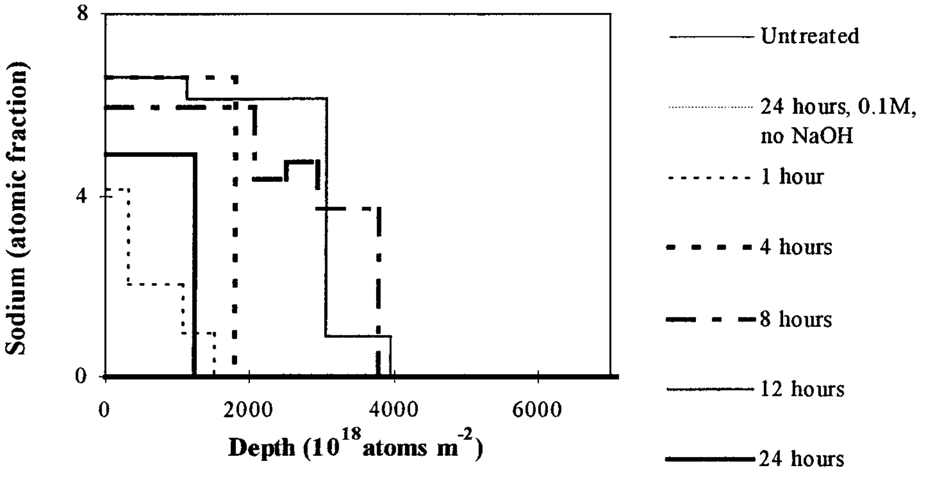


Figure 9 Sodium depth profile of samples treated with 0.0025 moles of TBAHS and 4 M NaOH at 80°C for up to 24 houurs (1000×10^{18} atoms $\mathrm{m}^{-1} = 2 \times 10^{-7}$ m = 200 nm).

6. Conclusions

The use of RBS in conjunction with surface specific techniques, such as XPS, SIMS and Raman has proved a valuable tool for assessing the mechanism and kinetics of the treatment process and the depth of resulting surface layer. The main conclusions can be summarised as follows:

1. Defluorination and oxygenation of PVdF occurs on treatment with NaOH and PTC.
2. The DataFurnace software package has been used successfully to fit RBS spectra of samples prepared with the intention of estblishing the kinetics of the polymer modification.
3. The concentrations, calculated as atomic percentage, generated from DataFurnace compare favourably to the values determined with XPS.
4. The generated depth profiles support the dehydrofluorination mechanism proposed in previous publications.
5. The results indicate that the kinetics of the defluorination and oxygenation reactions are diffusion controlled and obey the Case 1 (Fickian) diffusion law.
6. The defluorination layer advances ahead of the oxygenation layer.

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