Surface modification of poly(tetrafluoroethylene) by gas plasma treatment

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Poly(tetrafluoroethylene) (PTFE) samples were surface modified in gas plasma atmospheres of air, oxygen, argon and water vapour in order to increase the surface energy. Its dispersive and polar components were determined by contact angle measurements after various treatment times. Plasma treatment times of only 15 s were sufficient in all gases studied for substantial surface modification of PTFE. The chemical composition of the surfaces was studied by X-ray photoelectron spectroscopy (X.p.s.). The main results of all the plasma treatments were the abstraction of fluorine and the production of surface crosslinks, whereas only a low level of oxygen-containing groups was attached into the surface layer.

(Keywords: PTFE; gas plasma treatment; surface modification; X-ray photoelectron spectroscopy)

INTRODUCTION

The surface of poly(tetrafluoroethylene) (PTFE) is extremely hydrophobic and not well suited to a number of potential applications; in particular, for adhesive bonding and for printing by polar inks the surface needs to be modified. A variety of techniques are useful for chemical modification of polymer surfaces; examples comprise acid etching, flame treatment, and corona treatment. For PTFE, however, the first two are not well suited, and the last is often non-uniform on a microscopic scale. Gas plasma, or glow discharge, techniques[1,2] appear more promising because evidently reactive species in a gas plasma may attack even the C–F bonds which are difficult to substitute by conventional chemical reactions. Plasma techniques, while applicable to most materials, appear especially attractive for polymers such as PTFE which are difficult to surface modify by conventional chemical methods. Plasma treatment is uniform and versatile[1,2]. Apparatus has been described for extended plasma treatment runs using moving substrates[3–7]; large scale, industrial plasma treatment of moving substrates thus becomes feasible provided adequate treatment can be obtained within reasonably short treatment times.

Surface modification of other polymers by treatment in gas plasmas is well known with many general applications[8] with an emphasis on replacement of some of the C–H bonds by polar, oxygen-containing new groups, but much less has been reported so far on plasma surface modification of PTFE. The effects on PTFE of plasmas from ammonia[9,10] and air[10], argon[1,11,12] and other inert gases[13], nitrogen[1,11], and hydrogen[14] have been studied, and X-ray electron spectroscopy (X.p.s.) has shown that these treatments lead to partial loss of fluorine[1,10,11,14], the production of C=C bonds[12], and, depending on the feed gas and impurity gases, incorporation of oxygen and nitrogen on the surface.

Our interest in plasma surface treatment of PTFE has been stimulated for three reasons. Compared with other polymers, there is a dearth of knowledge regarding the effects of oxidative plasmas (from oxygen and air) on PTFE surfaces. Also, we have recently found plasmas from water vapour to be very useful for production of oxygen-containing surface groups on several polymers[15], but the chemical effects of a water vapour plasma on PTFE have not been studied. Furthermore, early work on plasma surface modification often used treatment times of 1 min or more. Recent reports, however, have indicated that times of much less than 1 min are sufficient[14–16]; such short treatment times open up the feasibility of commercially acceptable plasma surface modification of moving substrate. This report on plasma surface treatments of PTFE in several gas atmospheres demonstrates that for PTFE likewise short treatment times are sufficient and presents X.p.s. data on the chemical changes induced by the various plasmas.

EXPERIMENTAL

A custom built reactor with capacitively coupled, parallel plane electrodes was used for plasma treatment experiments. The spacing of the rectangular (18 x 90 mm) electrodes was 16 mm. The plasma apparatus has been described earlier[7]. Its facility for continuous coating by transportation of substrates was not used in the present work. Even with stationary substrates, however, the controlled, steady gas flow past the substrates during treatment in our reactor provides a more realistic simulation of continuous web plasma treatment than

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does the conventional plasma treatment in a bell jar reactor with stationary substrates and filled with gas that is not flowing, thus possibly changing in composition with time. Electrical power was supplied by a custom built radio-frequency oscillator operating at 700 kHz with a power input into the oscillator of 12.5 W.

Polytetrafluoroethylene sheet material (Teflon, DuPont) was washed by soaking in ethanol with sonication, cut into strips of 80 x 12 mm, and the strips attached to the electrodes by double-sided sticky tape. The gases used for plasma treatment were argon, oxygen, air, and water vapour. Oxygen and argon were supplied from cylinders. The air used was conditioned, low humidity ambient air. Water vapour was obtained from the boil off under vacuum from water stored in a round bottom flask kept at ambient temperature. In all cases the gas stream was regulated by a manual flow control valve located upstream of the reactor, to a flow rate of ~10–15 sccm min^{-1}. Continuous flow of gas through the reactor was maintained throughout the duration of the plasma treatment. By appropriate adjustments of both the gas flow and the throttle valve to the pump, the pressure in the reactor was set to 0.6 Torr prior to plasma ignition. Treatment times ranged from 15 to 120 s. Subsequent to treatment the gas flow was stopped, the residual gas pumped off, the reactor vented and the samples exposed to air.

The wettability of samples was assessed using a modified Kernco model G-II contact angle meter. The samples were kept flat on the stage by means of small holes in the stage that allowed gentle vacuum suction to be applied to the sample. The syringe associated with the instrument was mounted on a goniometric stage. The plunger of the syringe was coupled to a micrometre drive mechanism for accurate dispensing. Sessile contact angles were measured on both sides of five drops for each sample and test liquid and the average value calculated. Test liquids were distilled water, H_2O, and methylene iodide, CH_2I_2 (Ajax Chemicals).

X-ray photoelectron spectroscopy was performed on an apparatus previously described[17] using Al $K\alpha$ excitation. The PTFE film samples were mounted on copper holders using double-sided sticky tape. The Cu $2p_{3/2}$ peak (binding energy 932.7 eV) was used for energy referencing.

RESULTS AND DISCUSSION

Surface energy. The change in surface energy with plasma treatment was assessed by measurement of the sessile contact angles. Untreated PTFE showed contact angles of 112° (±3°) to H_2O and 84° to CH_2I_2. Plasma treatment with all the gases used produced substantial changes in the contact angles. In all cases the contact angle was reduced for both liquids; the data obtained for samples treated for 60 s are listed in *Table 1*. The magnitude of the decrease depended on the treatment duration. *Figure 1* illustrates the contact angles as a function of treatment duration in a plasma of water vapour; for the other gases the results were analogous. It is apparent that 15-s-treatment duration was sufficient to cause substantial modification of the surface, and that by further treatment a smaller additional degree of modification was obtained. Extended treatment, i.e. for several minutes as has been used in some of the earlier work, appears unnecessary and instead is likely to cause some ablation and ultimately surface roughening. Gerenser has recently described similarly short plasma treatment times for surface oxidation[16], and Clark and Hutton found the interaction of PTFE with hydrogen plasma to proceed within less than a minute[14]. In addition, recent work of ours has documented that fluorinated ethylene propylene (FEP) likewise could be plasma surface modified with similarly short treatment duration[18].

Table 1 Sessile contact angles (in degrees) of PTFE surfaces modified by plasma treatment for 60 s in different gas atmospheres

	Plasma atmosphere			
Test liquid	Ar	O_2	H_2O	Air
H_2O	79	91	74	86
CH_2I_2	66	72	71	76

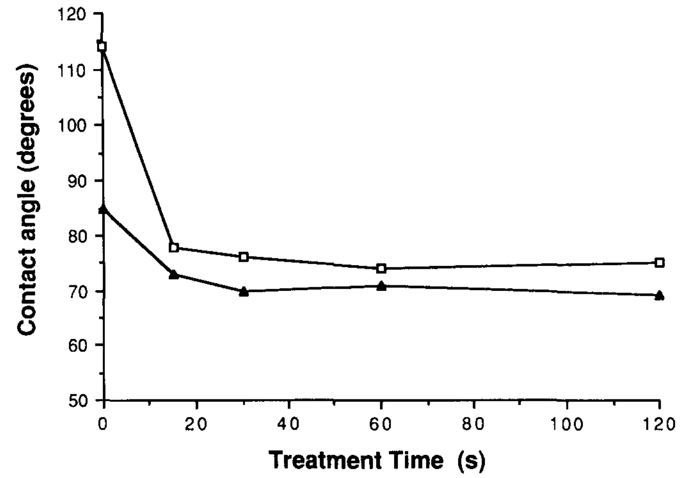

Figure 1 Sessile contact angles of PTFE surfaces modified by treatment in a water vapour plasma, as a function of treatment duration. Distilled water (□) and methylene iodide (▲)

For industrial applications short plasma treatment times are required for commercial viability, and it is desirable to perform plasma treatment on extended lengths of plastic substrate which is transported as a continuous web through the plasma zone, analogous to large scale corona treatment which requires only very short resident time of plastic substrates in the discharge. In our equipment the plasma takes of the order of 10 s to stabilize after ignition; thus the smallest time used in this study (15 s) represents probably only a few seconds of 'steady-state' plasma treatment. Such startup and shutdown effects can be avoided in plasma treatment using a moving substrate; when passing the substrate through a stable plasma glow region, the treatment begins immediately on entering the plasma region. We did not have available any suitable PTFE extended ribbon samples of dimensional stability adequate for transport in order to test the viability of very short treatment times on moving PTFE. Experiments using moving FEP substrate web, however, have investigated the effects of transport of tape samples of extended length through a stable, equilibrated plasma in our reactor, and the results will be presented elsewhere[18]. In summary, even shorter treatment times are adequate. We conclude that it is feasible to surface modify fluoropolymers in a transport system at reasonable speeds. Probably polymer surfaces are often overtreated, and the minimum times

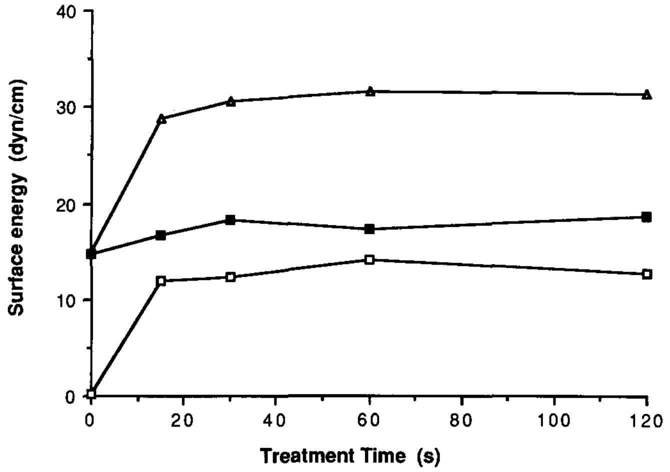

Figure 2 Surface energy (Δ), and its polar (□) and dispersion (■) components, of PTFE samples treated in an argon plasma

required for adequate plasma treatment, while dependent on equipment geometry, appear viable.

From the contact angles, the values of the surface energy of the untreated surface and the treated surfaces were determined by Kaelble's method[19] and their polar and dispersion components calculated. The values of 21.8 and 51.0 dyn cm^{-1} for H_2O, and 49.5 and 1.3 dyn cm^{-1} for CH_2I_2 were used for the dispersion and polar components, respectively, of the surface energy of the test liquids. *Figure 2* reproduces a typical set of values obtained for a modified PTFE surface, with argon plasma in this instance, as a function of treatment duration. Results were very similar for all the different gases. The PTFE surfaces treated by the different gases appeared not to be greatly different; the chemical groups implanted may be similar as they achieved very similar effects to the surface free energy. It is apparent that within 15 s all the plasma treatments provided a substantial increase in the polar component of the surface energy.

Chemical composition of the modified surfaces. The X.p.s. spectra of untreated PTFE samples showed peaks due to carbon, fluorine and oxygen (C, F and O). The F/C ratio was 1.52; the reason for the discrepancy to the expected value of 2 is not known, and reliable standards are not available. A small amount of adventitious hydrocarbon species was present as indicated by the shape of the C (1s) signal, which contained a small but clearly discernible, broad minor peak at ~285.0 eV, assigned to a 'neutral' contribution. The contamination could not be eliminated by ultrasonic washing whereas on FEP all hydrocarbon surface contamination was eliminated. This suggests that for PTFE the hydrocarbon species were not simply adsorbed on the surface but were strongly incorporated, probably from the manufacturing process. However, the amount of contaminant was small as assessed by the intensity of the 285.0 eV peak relative to the CF_2 signal, and insufficient to account for the discrepancy between the theoretical and the measured values for the F/C ratio. This unsolved calibration problem was not, however, a major problem as we were interested in *changes* to the ratio as a function of plasma exposure; the relative ratios between samples could be obtained with sufficient accuracy.

With all the process gases used, a decrease in the F/C ratio resulted following plasma treatment (*Figure 3*), in agreement with all the previous literature reports[1,10,11,14]. The effects of all the plasma atmospheres were qualitatively identical. As in the contact angle data, the full effect was almost reached after 15 s of treatment, with little further change with longer plasma exposure times.

The oxygen content was very low in the untreated PTFE (<3%) and did not increase markedly as a result of any of the plasma treatments. For instance, after 120 s in an oxygen plasma an oxygen content of 4% was determined. This observation is in marked contrast to the strong oxygen uptake with plasma treatment of hydrocarbon polymers[16].

Detailed analysis of the C (1s) peak shape of treated PTFE surfaces was in agreement with the marked loss of fluorine without substantial oxygen addition. The C (1s) peaks again consisted of a dominant component due to C–F_x and a smaller, lower energy peak assigned to a combination of neutral carbon and carbon bound to oxygen, with the neutral carbon contribution the stronger. The neutral carbon contribution increased relative to that found on the untreated surface.

The decrease in the F/C ratio, the increase in the neutral carbon signal, and the absence of significant oxygen attachment indicate a specific pathway for the plasma modification of the PTFE surface, and this pathway appears, surprisingly, to be virtually independent of the process gas. The first step probably involves the breakage of C–F bonds which occurs by electron impact dissociation, resulting in the abstraction of fluorine atoms from the surface. The backbone –$\dot{C}$F– radicals thus created can then undergo chain scission, react with other radicals on the polymer surface, or react with oxygen-containing species impinging on the surface from the gas phase (during plasma exposure or on subsequent venting to air). A likely reaction is the combination of carbon-centred radicals. If the radicals are located on adjacent chains, crosslinking of the polymer surface is obtained; if they are neighbours on the same chain, C=C bonds result. Evidence exists to support the formation of C=C bonds on plasma treatment of PTFE surfaces from previous X.p.s.[12] and attenuated total reflection–infra-red[13] studies. Previous workers have also found that on prolonged exposure to

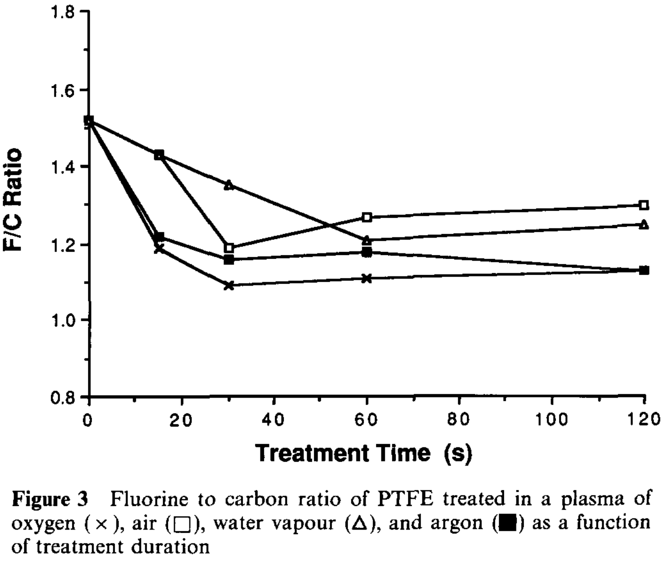

Figure 3 Fluorine to carbon ratio of PTFE treated in a plasma of oxygen (×), air (□), water vapour (Δ), and argon (■) as a function of treatment duration

plasma, the surface became yellowish, probably due to conjugated unsaturation[13]; under our milder conditions, no such discoloration was observed. Another possibility is the disproportionation:

$$-CF_2-\dot{C}F-CF_2- + -CF_2-\dot{C}F-CF_2- \rightarrow$$
$$-CF_2-CF{=}CF- + -CF_2-CF_2-CF_2-$$

which, however, appears less likely due to the stability of the C–F bond. Finally, chain breakage could also occur, via $\alpha\beta$ cleavage:

$$-CF_2-CF_2-\dot{C}F-CF_2- \rightarrow -\dot{C}F_2 + CF_2{=}CF-CF_2-$$

However, the insolubility of PTFE prevented study of changes in the mean and distribution of molecular weights that should result from chain cleavage reactions and crosslinking. Thus, the relative importance of crosslinking, chain breakage and C=C bond formation could not be assessed.

Surface radicals can be expected to react rapidly with oxygen molecules and oxygen-containing species impinging from the plasma atmosphere. However, such oxygen attachment was not observed in our X.p.s. spectra, in marked contrast to plasma treatment of hydrocarbon polymers[16]. Furthermore, the similarity of data on treatment in air compared with argon indicates that reactive, oxygen-derived plasma species did not react efficiently with the surface radicals. One possibility is rapid dissipation of the surface radicals so that they did not survive long enough for an activated molecule from the plasma gas phase to reach them. Thus, the interesting comparison arises in that on plasma treatment of hydrocarbon polymers the reactions of radicals on the polymer surface with approaching molecules, atoms, radicals and ions from the plasma gas phase are competitive with the formation of double bonds and crosslinks and are dependent on the process gas, whereas for plasma treatment of PTFE this is not the case. Polytetrafluoroethylene is quite unique in this respect because not only hydrocarbons, but also other polymers can be extensively surface oxidized in plasmas. The uniqueness of PTFE is not due to its perfluorinated nature because FEP can be surface oxidized under the same plasma conditions[18].

Another possibility is that the reaction between oxygen-containing species and $-\dot{C}F-$ radicals in the PTFE chain is inefficient due to low reactivity whereas FEP might be more reactive. This cannot be clarified prior to detailed understanding of the plasma effects on FEP, which is the subject of current studies[18], and analysis of the species present in the plasma gas phase.

Evidence to support rapid radical dissipation on the treated surfaces derived from the argon plasma treatment. For other polymers one observes oxygen incorporation in the treated surface, thought to be due to the combination of surviving surface radicals with atmospheric oxygen on venting the reactor. Our observations suggest that, unlike for other polymers we have treated under similar conditions, the radicals on the PTFE surface were dissipated by the time of venting.

Our observations contrast with those of earlier studies that had reported substantial oxygen incorporation on oxygen plasma treatment of PTFE[1,11], but agree with the observations by Golub *et al.*[20] published while this work was in progress, that Teflon was scarcely oxidized in an oxygen plasma. Our results extend this conclusion to other oxidative plasmas. The effects of plasma treatments are known to be highly dependent on the reactor systems and the plasma conditions used, and the relative importance of the various possible plasma reactions may differ considerably between systems. As in our treatments the reactions between two $\dot{C}F$ radicals appear more favoured than reaction between a $\dot{C}F$ radical and a gaseous oxygen-containing species, we suggest the possibility that the density of radicals produced on the PTFE surface was rather high in our experiments to give crosslinks and double bonds efficiently.

The end result of the processes initiated by exposure of PTFE to a plasma appears to be surface toughening by crosslinks rather than oxidation of the surface, and this occurs independent of the gas used. We believe this to be due to the low efficiency of reaction between surface radicals and oxygen-containing species, and that the radicals preferably form crosslinks. Etching due to liberated fluorine atoms may play a role also, as earlier work on plasma-treated PTFE reported marked changes to the surface topography[10,12]; however, we found no change observable by scanning electron microscopy. Experimental conditions and reactor design differ; in addition, it is possible that the present plasma treatments produced an etch depth too small for detection, in particular at the relatively short treatment times used.

CONCLUSIONS

Plasma treatments of PTFE with air, oxygen, argon, and water vapour process gases created modified surfaces that were more polar and had a higher surface energy. A plasma treatment duration of 15 s was sufficient; this is considerably shorter than the treatment times usually reported. It thus appears feasible to plasma surface modify PTFE with times short enough for industrial applications. X-ray photoelectron spectroscopy data indicated that the plasmas from all these process gases mainly led to the loss of a considerable fraction of the fluorine atoms. In all cases the amount of oxygen uptake was much less than the amount of fluorine loss, indicating that the radicals generated by fluorine abstraction reacted with other radicals rather than oxygen-containing species from the plasma. The absence of an optically measurable level of conjugated double bonds suggested that double bond formation was less important than crosslinking of the surface for radical dissipation. The main effect of plasma treatments of PTFE is not oxidative as is the case for most other polymers, and depends little on the plasma process gas used.

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