

NOTE

Partial Reduction of Polytetrafluoroethylene Polymer Sheet by Metals (Cr and Mn) in Pyridinium Poly(hydrogen fluoride) at Room Temperature*

INTRODUCTION

Polytetrafluoroethylene (PTFE) has the distinction of being chemically very stable and, consequently, has found varied industrial uses.^{1,2} A DSC study of the reaction of PTFE with metals/metal oxide mixtures showed the formation of metal fluorides,³ and with atomic hydrogen at low temperatures, no reaction was observed.⁴ However, PTFE is known to react with alkali metals, chlorine trifluoride, and fluorine at high temperatures, but in no case has formation of C—H bonds in PTFE been reported.⁵ In recent years, we demonstrated the use of pyridinium poly(hydrogen fluoride) (PPHF) as a versatile and efficient fluorinating reagent at room temperature for the synthesis of inorganic fluorinated compounds,⁶⁻⁹ the latest being the action of PPHF on metals,¹⁰ which indicated the fluorination of the metals and a concomitant amount of hydrogen being liberated. During this reaction, we observed that the PTFE-coated magnetic follower was attacked. Therefore, a detailed study was undertaken on a PTFE sheet. The investigation indicated that the surface of the PTFE sheet was attacked. The released off-white powder was found to be partially reduced PTFE. Details of this interesting reaction are given below.

EXPERIMENTAL

Materials and Methods

- (a) All reagents used were A.R. grade.
- (b) Pyridinium poly(hydrogen fluoride) (PPHF) (70 : 30) was prepared by the method of Olah by reacting pyridine and anhydrous hydrogen fluoride at low temperature.^{11,12} The resulting light pink liquid (bp temp 55°C) was stored in polyethylene bottles at -20°C.

- (c) The reactions were carried out in a polyethylene Erlenmeyer flask fitted with a Teflon stopper through which an outlet tube passes. This was attached to a tower of NaF (to strip off vapors of anhydrous hydrogen fluoride (HF)).
- (d) The processing of the products was done with standard polyethylene ware (separating funnel, beakers, Petri dish, filtering funnel, desiccator, etc.).
- (e) All operations were done in a fume cupboard with standard safety norms for working with anhydrous HF.
- (f) The IR spectrum was recorded on a Hitachi Model 270-50 spectrometer (KBr pellet, 10 ton pressure); XRD, on a Philips 1050/70 X-ray diffractograms; SEM, on a JSM 840 A scanning electron microscope; and NMR, on a Bruker 270 MHz instrument.
- (g) Synthesis procedure: A PTFE sheet (2 mm thick) (commercial product [imported] from Khushaldas, Bangalore) was cut into tiny bits ($\frac{1}{2} \times 1$ in.). The bits were well washed with acetone and cleaned well with a brush. Then, they were washed with running water followed by distilled water. The adherent water was blotted out with a clean tissue paper and dried in the oven at 100°C for 10 h. A known weight of the bits (11.4115 and 2.6081 g) were separately taken in two Erlenmeyer flasks. About 1 g of metal powder, chromium, was introduced, followed by 25 mL of PPHF at room temperature. The contents were vigorously shaken/stirred continuously for 10 days. At the end of this period, a white powder was seen floating. The solution was filtered and the remaining PTFE bits as well as the powder was well washed with copious amounts of water to remove all the adhering PPHF. The PTFE bits and the powder were then taken and stirred with water in a beaker. The bits were removed singly, and the adhering powder was washed off into the same beaker. The separated bits and also the powder after filtering and washing, were dried in the oven overnight at 100°C. The results indicate that the yield was around 12%. In a typical case, 11.4115 g of the PTFE sheet gave rise to 1.3023 g of the off-white powder, indicating a yield of 11.4%.

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In the above case with chromium, the main reaction of metal with PPHF is the formation of pyridinium hexa-

fluorochromate, $(C_5H_5NH)_3CrF_6$. This is soluble in PPHF and thus washes out with PPHF. However, with manganese, the reaction product with PPHF is MnF_2 . This remains insoluble in PPHF and therefore precipitates along with the powder. In this case, it is necessary to boil the powder containing MnF_2 (white), with a hydrochloric acid solution (1 : 1), when MnF_2 dissolves. The powder is filtered, washed free of acid, and dried. This acid washing is necessary even when the powder is contaminated with unreacted metal powder.

RESULTS AND DISCUSSION

Characterization

The powder is insoluble in most organic solvents and its density was 1.77, whereas that of the PTFE taken for reaction was 2.24. The reported density for PTFE is 2.26–2.27.¹³ This indicates that it is lighter than PTFE.

The XRD pattern for the powder shows totally different "C"-axis values for the (001) reflections, whereas the treated PTFE sheet shows a marginal change when compared to the original PTFE sheet taken ([no. in parentheses is the intensity] powder [4.8840(100), 4.1079(30), 3.7095(16)]; treated sheet [4.8900(100), 2.8234(15.4), 2.4447(24), 2.1817(23)]; untreated PTFE [4.9293(100), 2.8318(6.7), 2.4661(6.9), 2.1874(6.2)]). This indicates a changed conformation for the product powder and a marginal change for the PTFE sheet after reaction. This is reflected in the analysis[†] of the reactants and products. The analysis gives the mol ratio of C : H : F as 3.05 : 3.36 : 3.25, indicating the presence of hydrogen in a 1 : 1 : 1 mol ratio along with carbon and fluorine, which, in turn, will lead to entirely different cell parameters compared to the treated and untreated PTFE whose analysis shows a marginal increase of fluoride content in treated PTFE, perhaps due to surface fluorination after cleavage of the reacting layers of PTFE. The treated PTFE sheet did not show the presence of any hydrogen. (PTFE [treated] C, 23.66%; F, 78.4%. PTFE [untreated] C, 23.72%; F, 74.0%.)

The INFRARED SPECTRUM (KBr pellet) of the sheet samples of treated and untreated PTFE are similar (2500 cm^{-1} [m], $1100\text{--}1400\text{ cm}^{-1}$ [broad, band, strong]), along with a few weak bands as reported in literature^{14,15}). The powder shows, in addition, four new absorption bands of medium intensity around $2800\text{--}3100\text{ cm}^{-1}$ due to ν_{C-H} vibrations and the disappearance of the 2500 cm^{-1} absorption band and the broad band around $1100\text{--}1400\text{ cm}^{-1}$ due to that the ν_{C-F} is split into two bands in the same region. These results indicate the presence of both C—H and C—F bonds in the molecule.

When pressed with KBr, the product powder sometimes was found to form fibers. This is known to occur with PTFE,¹⁶ but this occurrence in the powder is of impor-

tance, as this shows its polymeric nature of being capable of fiber formation.

The powder is found to be insoluble in most common organic solvents. However, very dilute solutions were obtained by refluxing in toluene and acetonitrile for 6 h. The NMR study on these samples shows a 1H signal (solvent = toluene, T.M.S std, $CDCl_3$ lock) at 3.64 ppm and ^{19}F signal (solvent CH_3CN ; C_6F_6 std; $CDCl_3$ lock) at -223.67 and -186.18 ppm. This indicates the presence of both proton and fluorine in the product powder. Blank experiments on the solvents were done to rule out the possibility of any contamination.

As a metal was employed for reaction, it was necessary to look for its presence in the product. The treated PTFE sheet was subjected to EDAX (SEM-360 Cambridge Instruments). EDAX indicated the absence of chromium and showed the fluorine edge. This indicates that metal fluoride formation on the PTFE is not a reaction and metal hydride adsorption on PTFE is also not present.

SEM

The SEM photographs are shown in Figure 1. Photographs 1346 and 1352 show the surface of the untreated and treated PTFE sheet and 1589 shows the surface of the product powder.

The untreated sheet shows large holes with microporosity and unbonded regions and distribution is not very uniform. In the treated sheet, the distribution is more uniform, has unlaminated growth with the size of holes small, and shows better bonding. This may be due to fluorination on the surface, as the analysis shows a higher percentage of fluorine in the treated sample. The powder, on the other hand, shows agglomeration of fine particles that are compact and globular.

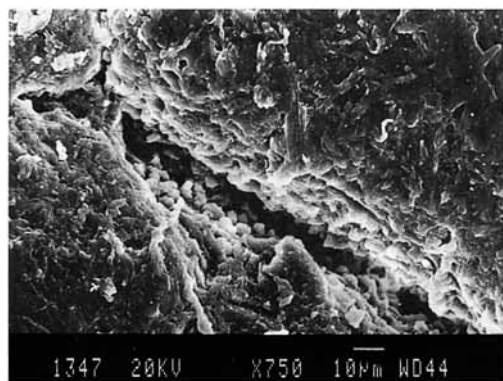
CONCLUSIONS

These data clearly indicate that the PTFE surface is attacked in the presence of PPHF and metals (Cr and Mn) under vigorous stirring conditions and that the cleaved particles undergo hydrogenation.

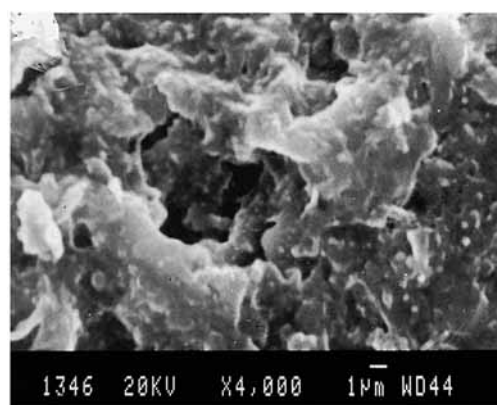
The mol ratio of carbon to hydrogen to fluorine in the PTFE (H) powder has been found to be nearly 1 : 1 : 1 by analysis. However, the physical studies show that the present product is different from poly(vinylidene fluoride), perhaps due to the ordering not being uniform. The hydrogenated powder does not contain any metal incorporation. The IR and NMR data show the presence of both C—H and C—F bonds being present in the molecule. The XRD patterns and SEM photographs indicate the formation of a new structured polymer molecule out of PTFE, which is fine, globular, and less dense than that of PTFE.

With the present data, it is very difficult to say exactly how hydrogenation occurs, since this is a slow reaction

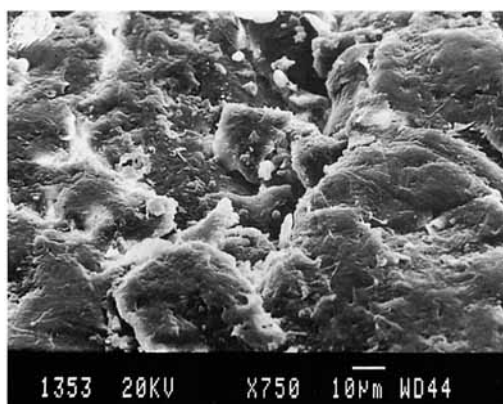
[†] Analysis done at Prof. Peter Sartori's Chemical Laboratory, University of Duisburg, G. H. Duisburg, Germany.



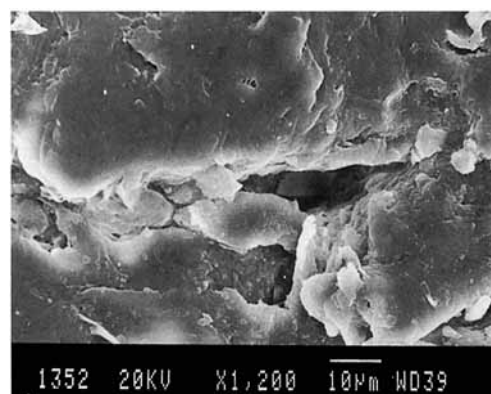
a



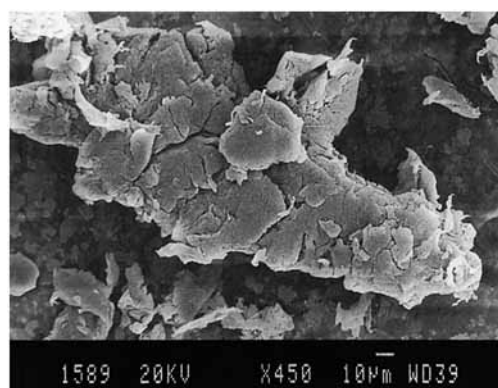
a



b



b



c

Figure 1 SEM photographs of the treated untreated and the powder samples of Teflon: (a) 1347, SEM photograph of untreated Teflon sheet; 1346, SEM photograph of untreated Teflon sheet. (b) 1353, SEM photograph of treated Teflon sheet; 1352, SEM photograph of treated Teflon sheet. (c) 1589, SEM photograph of powder (reaction product) from the Teflon sheet.

requiring intimate contact mixing conditions with metal powder and PPHF. As pointed out in the Introduction, the reaction of metal with PPHF yields either the metal fluoride or the pyridinium salt of the metal fluoride with hydrogen evolution. This nascent hydrogen or the hydrogen adsorbed on the metal (metal hydride) could be the reducing agent in this highly acidic medium. A blank experiment in the absence of the metal powder has been carried out with PTFE and PPHF. The results indicate that PTFE is stable in PPHF solutions under vigorous stirring conditions. Another blank experiment set consisted of vigorously stirring PTFE in a water solution in the presence of a metal powder. Though there was wearing out of the PTFE sheet in both cases and formation of a powder, no reaction occurred, as the PTFE powder thus obtained showed similar XRD patterns as those of the original PTFE taken.

Further investigations are necessary to ascertain the mechanism of hydrogenation and the structure of the hydrofluoro polymer formed.

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