Chemically modified Teflon* as an effective humidity sensor

Sujata B. Dake and S. V. Bhoraskar
Department of Physics, University of Poona, Pune-411 007, India

and Prakash A. Patil and N. S. Narasimhan
Department of Chemistry, University of Poona, Pune-411 007, India
(Received 7 August 1985)

Humidity-sensing characteristics of Teflon® (PTFE) after etching its surface with sodium–naphthalene complex are reported. The change in impedance with relative humidity of the treated films is studied in various extremely dry gaseous atmospheres, viz. Ar, N_2, H_2 and O_2 and also in the presence of moist air. It was observed that the electrical conduction of the films increases by four orders of magnitude as the relative humidity varied from 20% to 80%. The results were analysed using X-ray photoelectron spectroscopy and infra-red techniques. Possible models of the reaction and the chemical behaviour of the sample in humid conditions are discussed.

(Keywords: humidity sensors; PTFE; Teflon)

INTRODUCTION

Polytetrafluoroethylene (PTFE) is highly stable and non-reactive to ordinary chemicals and solvents. Alkali metals, however, are reported to be effective in etching its surface[1,2]. These have the ability to break the very strong carbon–fluorine bonds and to make bonding with other metals easier[1].

This paper reports the application of the etching reaction to make PTFE useful as a humidity sensor. The method used depends on the change in impedance of the film with atmospheric humidity in different gaseous atmospheres, previously described as the simplest and most suitable property for use in electronic systems[3].

Teflon films were treated with sodium–naphthalene complex[1] to form conducting surfaces[4]. The effect of humidity on conductivity at different time intervals during the reaction and in various gaseous atmospheres was then investigated.

EXPERIMENTAL

Films of PTFE 250 μm thick (Du Pont de Nemours, USA) and dimensions 3 cm × 1 cm were cleaned by usual cleaning procedures, dried under an infra-red lamp and immersed in a solution of sodium–naphthalene complex in distilled tetrahydrofuran (THF). The films were removed after the required time of treatment, rinsed with distilled THF and dried under a vacuum of 10^{-3} Torr for an hour.

Infra-red spectra were recorded for identification of the reaction products by using a Perkin–Elmer 337 IR Spectrophotometer. X-ray photoelectron spectra were used for analysing the Na-doped PTFE by using a Vacuum Generators Model No. ESCA Mark III (AlKα target at 1486.6 eV).

Silver electrodes in planar geometry were then established by applying silver paint. The variations of electrical conduction in the reacted PTFE were measured in a vacuum and in the presence of dry and wet gases, viz. argon, nitrogen, hydrogen and oxygen. The pressure scale was calibrated in terms of relative humidity.

RESULTS

The originally white PTFE films change to black in colour with a velvety touch after reacting with the sodium–naphthalene complex, the dark colour indicating the presence of charge transfer complex[5] and the velvety nature showing that etching process was effective. A dramatic increase in the conductivity of the films by 6 to 7 orders of magnitude was observed when measured in air immediately after the reaction. The rate of the reaction was measured by the change in conductivity with time. The plot of conductivity against time of the reaction indicated that the reaction rate slowed down with time, ultimately resulting in saturation. *Figure 1* indicates that there are effectively three regions in each of which the conductivity can be expressed by a rate equation of the type

$$\sigma = \sigma_0 \exp(\lambda t)$$

where σ_0 is the initial conductivity in that region and λ is the rate constant. The reaction rate is highest in the first 24 h with a rate constant of 0.15 to 0.19, which subsequently decreased to 0.02 for the next four days and then reached a limiting value. The depth of the reaction from the surface for a fully reacted sample was detected to be $\sim 60\,\mu$m.

After measuring the conductivity in air the samples were exposed to vacuum. The conductivity in the evacuated atmosphere (10^{-1} Torr and below) resembled that of the virgin Teflon film (*Figure 2*). The samples under vacuum were then exposed to different gases (air, Ar, N_2, H_2 and O_2) at atmospheric pressures in extremely dry

---

* Du Pont's registered trademark

0032-3861/86/060910-03$03.00
© 1986 Butterworth & Co. (Publishers) Ltd.

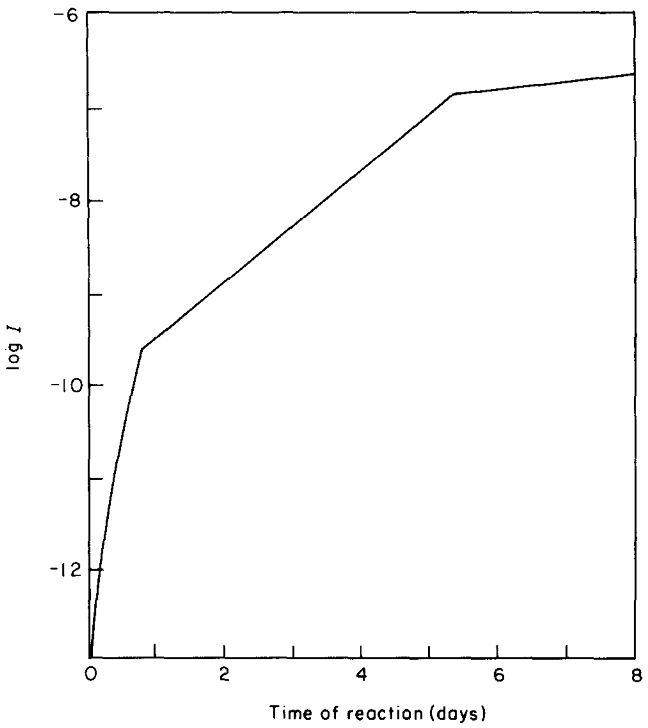


Figure 1 Increase in surface conductivity with time of treatment. The plot shows the logarithm of current (at 1 V) measured in air with the time of reaction

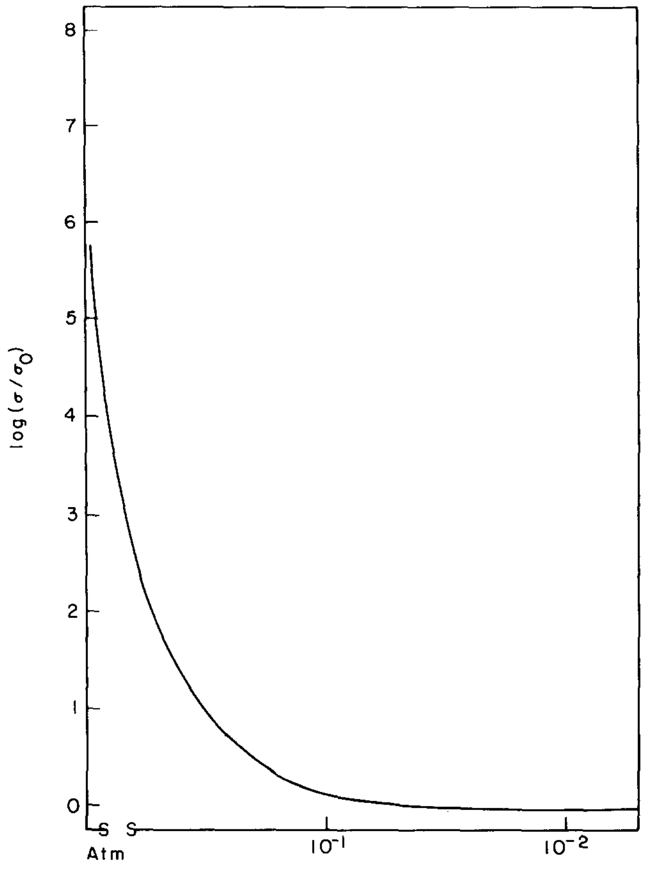


Figure 2 Measurements of conductivity in vacuum ranging from 1 atm to 10^{-2} Torr. At lower pressures, the conductivity decreases from the original value and approaches that of virgin PTFE

conditions. The conductivity, measured *in situ*, showed no variation and remained at its lowest value (*Figure 3*). However, when moist air was passed into the vacuum chamber the conductivity started increasing at about 2 Torr. The experiments were repeated with moist gases (Ar, N_2, H_2, O_2) and it was confirmed that the only cause of the change was the moisture.

To have an exact scale of humidity the water vapour pressure in the vacuum chamber was calibrated in terms of relative humidity as reported by Seiyama *et al.*[3] It was observed that the conductivity increased by four orders of magnitude for the variation in relative humidity from 20% to 80%. The conductivity variation on a linear plot of relative humidity is shown in *Figure 3*. This indicates that the present polymeric system can be used as potential humidity sensor and is comparable to other reported ceramic sensors[5].

In an attempt to understand the nature of chemical changes occurring the films were examined by XPS and i.r. spectra measurements.

The ESCA results (*Figure 4*) showed that on the surface of the film the (C(1s)) signal was intense with a peak position at 287.5 eV tailing towards higher binding energy up to 291 eV. This indicated a possible presence of –C–OH, C=O, CHF (288 eV)[8], CF (289.5 eV)[7] and CF_2 (291 eV)[7] groups. According to Dwight and Riggs[2] the high-energy peaks between 291 and 292 eV usually correspond to highly oxidized states like CF_2. The low intensity on the high energy side (291 eV), which arises from the CF_2 group, probably indicated the masking of this by metallic sodium. This may also be an effect of fluorine etching. It is also observed that the (C(1s)) peak

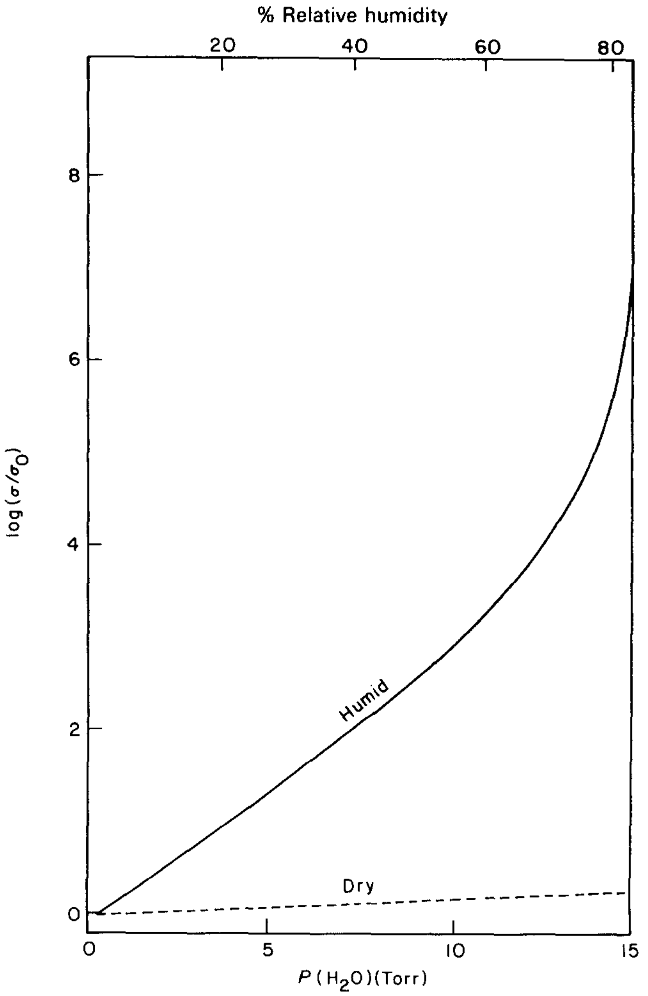


Figure 3 The conductivity variations in presence of dry and wet gases of Ar, O_2, N_2, H_2 and air. The relative humidity is calibrated against pressure

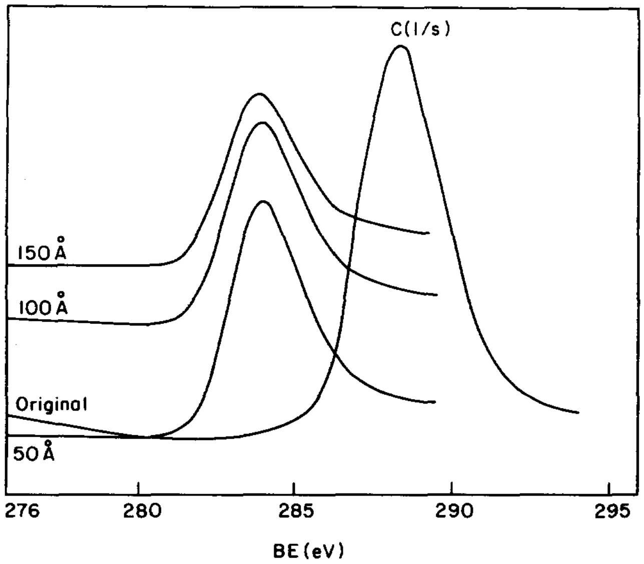


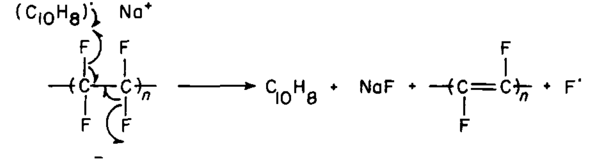
Figure 4 XPS spectra indicating the variations in peak heights and binding energy shifts for depth profiling of the reacted surfaces to the different depths marked

on the surface is at a higher energy than that below the surface and this may be due to surface contamination. After depth profiling up to 50, 100 and 150 Å, it was confirmed that fluorine was still present in the sample, either in the free state or bonded with sodium.

The results obtained showed an unsaturation and presence of double bonds on the surface giving active sites for bonding. The presence of graphitization, conjugation and attachment of polar side groups have been reported by Kaeble and Cirlin[9].

The i.r. spectrum indicated the presence of the hydroxyl group, showing a broad signal at 3200 cm^{-1}. The absorption in the frequency range 1550 to 1800 cm^{-1} was also observed to be increased and modified after treatment. This showed the presence of the –C=C– group leading towards unsaturation. The presence of C–OH was also detected previously in sodium-etched PTFE.

The etching of the surface by the charge transfer complex produces conjugated double bonds as in polyacetylene[4] and a simple picture of the chemical reaction can be represented as

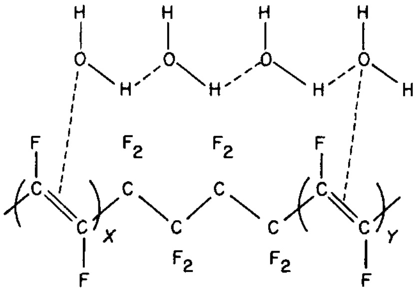


$$(C_{10}H_8)^{-} Na^{+} + -(CF_2-CF_2)_n- \longrightarrow C_{10}H_8 + NaF + -(C{=}CF)_n- + F^{\cdot}$$

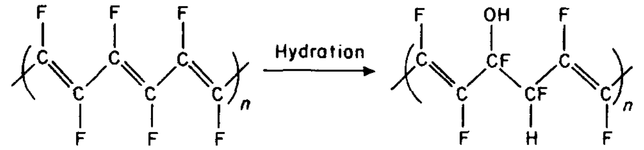
$$(C_{10}H_8)^{-} Na^{+} + F^{\cdot} \longrightarrow C_{10}H_8 + NaF$$

The extreme sensitivity of the treated films towards moisture requires some additional explanation and although it is not possible to make a conclusive statement, a few possibilities are as follows.

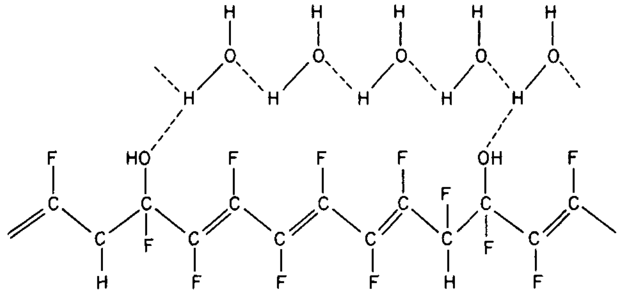
(1) Patches of conjugated structure may be bridged by the moisture by physical adsorption to complete the electrical circuit.



(2) Reaction of sodium naphthalide with PTFE under atmospheric conditions might have actually incorporated hydroxyl groups at several places in the structure



and these hydroxyl groups could further adsorb moisture, to establish continuity for electrical conduction.



(3) NaF formed in the reaction might not have been removed completely from the surface of the reacted film and in presence of moisture, Na$^+$ (aq) and F$^-$ (aq) system may behave similarly to NaCl (aq), giving rise to ionic conduction.

Whatever the explanation, the treated PTFE films can be used as an effective humidity sensor and function effectively over a very small effective area.

ACKNOWLEDGEMENT

The authors wish to thank the Department of Atomic Energy and U.G.C. for financial support.

REFERENCES

1 Benderley, A. A. *J. Appl. Polym. Sci.* 1962, **6**, 221
2 Dwight, D. W. and Riggs, W. M. *J. Colloid Interface Sci.* 1974, **47**, 650
3 Seiyama, T., Yamazoe, N. and Arai, H. *Sensors and Actuators* 1983, **4**, 85
4 Yashino, K., Yanagida, S., Sakai, T., Azumu, J. and Inuishi, Y. *Jpn. J. Appl. Phys.* 1982, **21**, L301
5 Rubner, M. and Deits, W. *J. Polym. Sci., Polym. Chem. Edn.* 1982, **20**, 2043
6 Nitta, T., Terada, Z. and Hayakawa, S. *J. Am. Cer. Soc.* 1980, **63**, 259
7 Tompkins, H. G. and Sharma, S. P. *J. Appl. Polym. Sci.* 1980, **25**, 211
8 Czanderna, A. W. 'Methods of Surface Analysis', Vol. 1 (Ed. A. N. Czanderna), Oxford University Press, 1975, p. 142
9 Kaeble, D. H. and Cirlin, E. H. *J. Polym. Sci. A-2* 1971, **9**, 363