This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Surface Property Characterization of Plasma-Polymerized Tetraf luoroethylene Deposits

Basil D. Washo[a]
[a] IBM Corporation, Poughkeepsie, New York

To cite this Article Washo, Basil D.(1976) 'Surface Property Characterization of Plasma-Polymerized Tetraf luoroethylene Deposits', Journal of Macromolecular Science, Part A, 10: 3, 559 — 566
To link to this Article: DOI: 10.1080/00222337608061199
URL: http://dx.doi.org/10.1080/00222337608061199

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. MACROMOL. SCI.—CHEM., A10(3), pp. 559-566 (1976)

Surface Property Characterization of Plasma-Polymerized Tetrafluoroethylene Deposits

BASIL D. WASHO

IBM Corporation
Poughkeepsie, New York 12602

Downloaded At: 09:32 25 January 2011

ABSTRACT

Plasma-polymerized tetrafluoroethylene (PPTFE) deposits were characterized by contact angle measurements and critical surface tension γ_C measurements. The measurements showed surface property changes of the deposits as a function of time and treatments: helium and nitrogen in the feed gas, plasma degradation of the films, and of vacuum/temperature posttreatments. The process was a flow rf plasma vapor deposition process, inductively-coupled, using tetrafluoroethylene as the monomer gas. The study aimed toward effecting variable surface properties of the film deposits via plasma process parameters and gas feed admixtures. In addition, the nature and structure of the fluorocarbon deposits were elucidated using surface property characterization and ESCA techniques.

INTRODUCTION

The word adhesion means to adhere; and the word abhesion means nonadherence or to release. For the polymer system

Copyright © 1976 by Marcel Dekker, Inc. All Rights Reserved. Neither this work nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

poly(tetrafluoroethylene) (Teflon) these two properties appear to be mutually exclusive, but in fact are needed in order to use the material as a film. This is true because the functionality of a film depends in many respects on its ability to adhere to a substrate. Poly(tetrafluoroethylene) uniquely presents a dilemma here since we are asking an antistick material to stick. This problem for the case of the bulk polymer has been addressed previously [1] (e.g., chromic-sulfuric acid etch, sodium metal chemical attack). Here we are concerned with the problem of fluorocarbon thin films, their adhesion, their properties, and their structures—in particular, those films made via the rf plasma vapor deposition technique, specifically using tetrafluoroethylene as the monomer gas. The technique allows the development of thin films grown conformally and precisely on arbitrary substrates. The deposits studied were of the order of magnitude ~1000 Å.

Consider first the distinction made between the bulk Teflon (TFE) polymer and plasma-polymerized tetrafluoroethylene (PPTFE) deposits. The bulk polymer can be generally characterized as being a linear, thermoplastic high polymer with high crystallinity. On the other hand, the plasma deposit is generally characterized as a network and highly branched polymer, of low or nonexistent crystallinity, low density, and having a "contaminated" repeat unit in the chain molecule. This "contamination" results from the plasma process which creates fragmented monomers that incorporate themselves into the polymer in an irregular fashion. Although both types of polymers are fluorocarbon polymers, it is clear that properties of the two types will differ in many areas, such as electrical properties and moduli, due to these differences in structure and morphology. On the other hand, surface properties such as surface free energy and coefficient of friction may be expected to be similar.

Downloaded At: 09:32 25 January 2011

EXPERIMENTAL

The plasma vapor deposition process has been described elsewhere [2]. Essentially, it uses an electrical discharge in a rarefied stream of monomer feed gas to activate polymerization and film formation reactions. The principle mechanism for polymerization appears to occur via free radicals [3]. Accordingly, the plasma deposit has been shown to be "alive" with free radicals, which decay with time and/or posttreatment, such as vacuum/temperature posttreatment [4].

The basic plasma vapor deposition process used here is actually a sequential process, starting out with a degas period, followed by a He/O_2 pretreat cleaning [5], an inert gas purge, plasma strike and deposition, a CASING (Cross-linking via Activated Species

of INert Gas) posttreatment [6], and a vacuum/temperature posttreatment.

We have applied the CASING concept to plasma deposits, i.e., as a posttreatment to already formed plasma polymer deposits. Thus after the polymer deposit is formed via the deposition process, the deposit is exposed to a helium plasma for a period of time. We have found the enhancing attributes of CASING which apply to surface of bulk polymers also apply to the polymer deposit. For example, CASING was found to prevent a Freon TF "wash away" of PPTFE films on an evaporated metal substrate. Optical photograph (Fig. 1) shows a dissolution front of the film after a Freon TF spray. No dissolution front or border appeared if the films were first CASED.

Sample 13 highlights the results of this study. The sample was prepared under baseline conditions: 50/50 N_2/TFE feed ratio at 50 cc/min, chamber pressure of 0.15 Torr, and rf power of 250 W. Included in these conditions was a CASING posttreatment and vacuum/temperature (200°C/24 hr) posttreatment. Other samples were prepared under variations on these conditions according to a statistical experimental design. For example, sample 14 was prepared under baseline conditions, with the vacuum/temperature posttreatment being 100°C/24 hr, however.

Downloaded At: 09:32 25 January 2011

FIG. 1. Freon wash-off dissolution front of plasma fluorocarbon deposit.

RESULTS AND DISCUSSION

Contact angle measurements were chosen as a simple method that is application oriented to characterize the deposits. PPTFE films were plasma vapor deposited on sample substrates (evaporated proprietary metal films on an aluminum alloy substrate). Effects of time and the following treatments were studied by following contact angle changes with: time, He content in feed gas, CASING post-treatment, and vacuum/temperature posttreatment. In turn, critical surface tension measurements were derived to characterize the solid surface as an approximate of γ_S, the surface energy of the solid.

A semiempirical technique developed by Zisman was used to determine γ_C, the critical surface tension of the solid [7]. γ_C closely approximates γ_{SA} and is characteristic of the solid surface. A series of test liquids allows construction of a plot of cos θ vs γ_L, the latter being the surface tension of the test liquid in question. Extrapolation of cos θ = 1, or complete wettability of the surface, determines γ_C. Then all liquids with a γ_L below γ_C will spontaneously wet that surface.

Figure 2 shows a typical γ_C determination for sample 13, prepared under baseline conditions. In addition, sample 13 was

Downloaded At: 09:32 25 January 2011

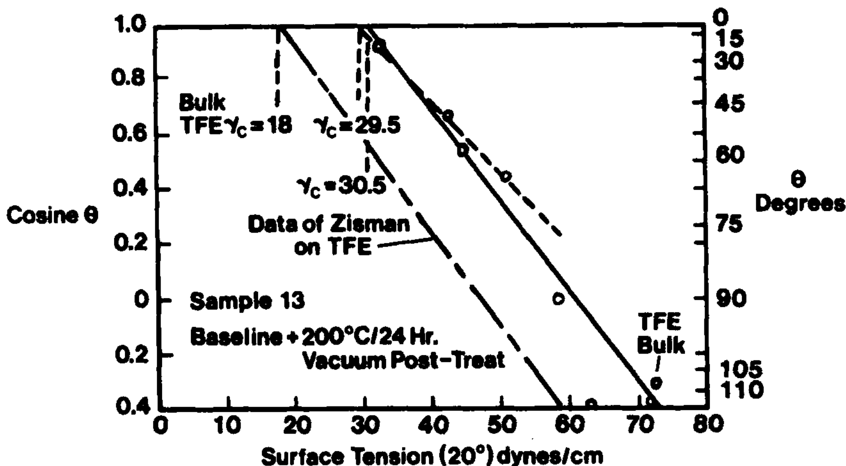

FIG. 2. γ_C Determination for sample 13; 200°C/24 hr. Posttreatment.

subjected to a vacuum/temperature posttreatment of 200°C/24 hr. A γ_C of 30 was determined. In particular, note that the slopes match between that of sample 13 and the data of Zisman on bulk TFE. All other γ_C plots on the samples prepared under a matrix of the aforementioned treatments showed smaller slopes. (For example, see Fig. 3.) With increasing vacuum/temperature posttreatment, the slopes approached and finally equalled that of the Zisman data. Moreover, and more importantly, samples receiving this particular posttreatment were found to attain their θ_{eq} (no transient behavior as typically exhibited in Fig. 4) instantaneously, and were found to be insoluble in and impervious to all common solvents. Part of this behavior is attributed to annealing of the films under this posttreatment.

Freshly deposited samples not undergoing this vacuum/temperature posttreatment showed no particular susceptibility to organic solvent attack but did show water penetration and subsequent rupture of the films. At long times (~48 hr), however, this susceptibility to water became significantly less.

Table 1 summarizes the γ_C data for deposits produced using pure TFE monomer and 50% He. γ_C was found to equal the γ_C for bulk TFE polymer. A slight increase was observed when we used He in the feed gas. However, the γ_C of samples purposely degraded

Downloaded At: 09:32 25 January 2011

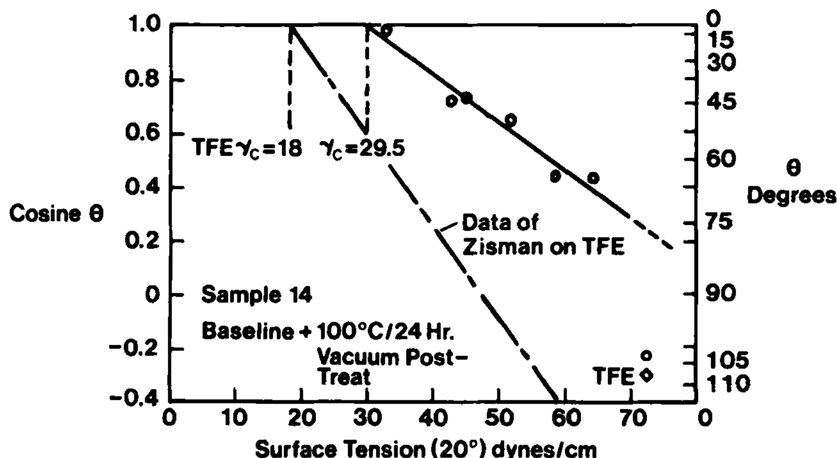

FIG. 3. γ_C Determination for sample 14; 100°C/24 hr. Posttreatment.

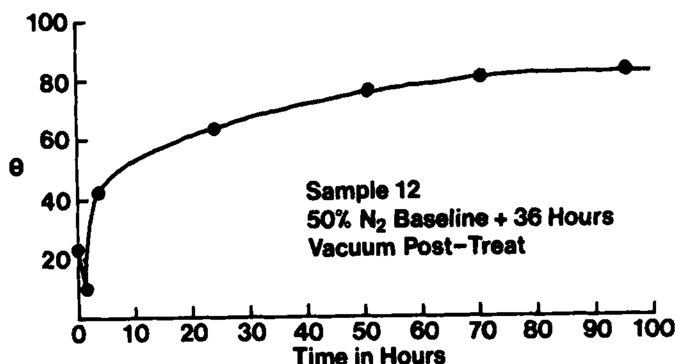

FIG. 4. Contact angle transient behavior with time.

TABLE 1. Summary of γ_C Data of Plasma-Polymerized TFE

	γ_C
50% He	19.5
Pure TFE monomer	17.0
Degraded TFE (1)	25.0
Degraded TFE (2)	26.5
Degraded TFE (3)	31.5
Bulk TFE	18.0

under high rf power conditions was found to increase significantly. A highly charred sample (3) yielded a relatively high γ_C of 31.5.

Figure 5 shows the wetting effect of CASING posttreatment on water contact angle measurements of PPTFE deposits. A CASING treatment effect on γ_C yielded +6 units of γ_C surface change under baseline conditions.

Table 2 shows an estimation of the structure and nature of the fluorocarbon surface via the principle of γ_C group additivity [7]. If one F— is stripped from the polymer, leaving a branched or network polymer with a C/F ratio equal to 1, then γ_C is predicted to be 34. Highly degraded TFE films yielded 30 for γ_C. The γ_C

Downloaded At: 09:32 25 January 2011

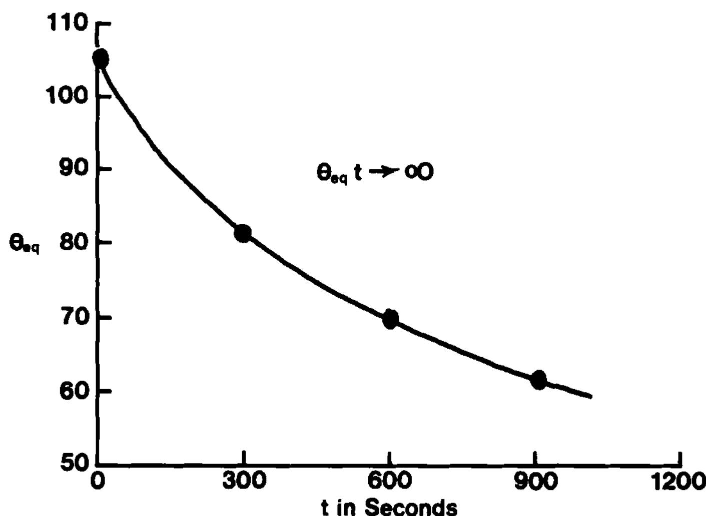

FIG. 5. Water contact angle vs helium CASING exposure.

Downloaded At: 09:32 25 January 2011

TABLE 2. Estimation of Critical Surface Tensions via Principle of Group Additivity [7]

Surface constitution	γ_C	Observed
$-CF_2-$	18	18
$>C-$ F	34	30 ave, degraded TFE
$>C<$	50	46[a]
$-CF_2$ + $(-C(NO_2)_3)$ 65%[b] 35%	27	30 for N_2/TFE films
$>CF-$ + $(-C(NO_2)_3)$ 65%[b] 35%	32	30

[a]Estimated via H_2O^{θ} graphite = 85.7° and Zisman slope $\left(\frac{\Delta \cos \theta}{\Delta \gamma_C}\right)_{TFE} = -0.0341$.

[b]ESCA analysis data.

predicted for a completely F— stripped fluorocarbon (a hypothetical amorphous networked carbon) is 50. The γ_C estimated using the contact angle of water on graphite together with extrapolation using the Zisman slope

$$\left(\frac{\Delta \cos \theta}{\Delta \gamma_C}\right)_{TFE} = -0.0341$$

for TFE yields 46; a crude, approximate but illustrative calculation. ESCA analysis on the nitrided films at baseline conditions indicated a content of 35% $-NO_2$ groups and allowed critical surface tension estimates. These estimates agreed well with measured values on the samples ($\gamma_C \sim 30$).

REFERENCES

[1] G. E. P. Elliott and A. C. Reddiford, Recent Prog. Surf. Sci., 2, 111 (1964).
[2] F. K. McTaggart, Plasma Chemistry in Electrical Discharges, Elsevier, New York, 1967.
[3] A. F. Denaro, P. A. Owens, and A. Crowshaw, Eur. Polym. J., 4, 93 (1968).
[4] M. M. Millard, J. J. Windle, and A. E. Pavlath, J. Appl. Polym. Sci., 17, 2501 (1973).
[5] D. F. O'Kane and K. L. Mittal, J. Vac. Sci. Technol., 11, 567 (1974).
[6] H. Schoenhorn and R. H. Hansen, J. Polym. Sci., B, 4, 203 (1966).
[7] W. A. Zisman, Rec. Chem. Prog., 26, 13 (1965).

Downloaded At: 09:32 25 January 2011