

Degradation of Thin Films of a Fluoropolymer

HARLAND G. TOMPKINS, *Bell Laboratories, Columbus, Ohio 43213*

Synopsis

1H-1H-Pentadecafluorooctyl methacrylate, a fluoropolymer, is used as a barrier coating to control spreading of thin liquid films, notably silicone oil. Using infrared spectroscopy and thermogravimetric analysis, this work describes the thermal degradation of thin films of this fluoropolymer. The conclusions are that the degradation is a two-stage, thermal bond-breaking phenomenon which does not require an additional reactant such as oxygen or water vapor. Rate constant data are presented for both stages of the degradation.

INTRODUCTION

The control of spreading liquids is important in the areas of lubrication and electrical contacts, among others. In the area of lubrication, it is necessary to prevent the lubricating oils from creeping away from the surface of interest; whereas in the area of electrical contacts, it is necessary to keep a contaminant liquid from creeping to the contact surface.

The approach used to prevent the creeping is similar in both areas. A liquid will creep only if the resulting surface has a lower free energy than the original surface (because spontaneous processes involve lowering of free energy). In order to prevent creeping, it is necessary to make the free energy of the solid surface lower than that of a surface of the creeping liquid. Under these conditions, the liquid will not creep since creeping would cause the free energy to increase. We are assuming here that the creeping liquid does not alter the surface by reaction or solubility.

Silicone oil, one of the primary creeping liquids, has a surface free energy¹ of the order of 20 ergs/cm². Any protected solid surfaces must have a free energy that is significantly less than this.

One approach taken in the area of lubrication is to coat the surface with a fluorocarbon polymer.² The repeat unit for one such polymer (the one investigated in this work) is shown in Figure 1. The molecular weight of the polymer is between 300,000 and 1,000,000 atomic mass units.³ The polymer, 1H-1H-pentadecafluorooctyl methacrylate (PFOM), investigated in this work was purchased from the 3M Company. The repeat unit of the polymer orients itself in such a way that the exposed surface consists primarily of CF₃ groups. The surface free energy of the composite surface in this configuration⁴ is approximately 10 ergs/cm²; thus it acts as a barrier to creeping silicone oil.

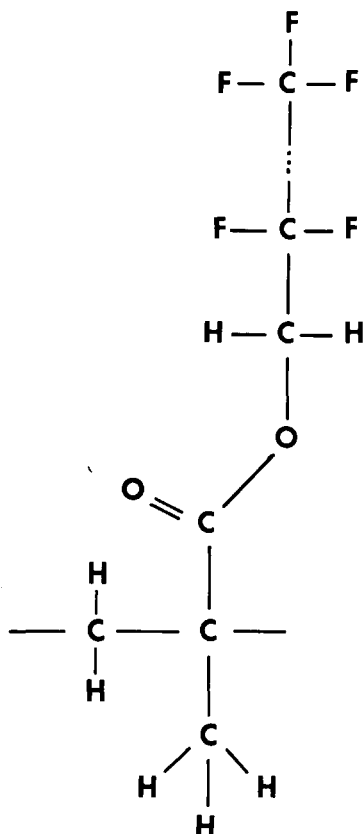


Fig. 1. Repeat unit for 1H-1H-pentadecafluorooctyl methacrylate (PFOM).

For lubrication retention, the coating is applied in thicknesses of the order of 1 micron, or 10,000 Å. For application in the area of electrical contacts, it is sometimes necessary to use coatings as thin as 200 Å. Considerable work has been done in the areas of properties and applications of the thicker films,^{2,4} but very little has been published concerning the degradation of thin films of this material. The primary purpose of this paper is to study the mechanisms of degradation of thin films of PFOM (1H-1H-pentadecafluorooctyl methacrylate).

DEPOSITING THE FILM

The polymer is received from the manufacturer as a 2% solution in xylene hexafluoride. The material can be applied to the surface of interest in two different ways. If a known amount of solution is applied to a horizontal surface and the solvent allowed to evaporate, a film of any given thickness can be obtained. The limiting factor is that when the film is too thick, some of the solvent will be retained. Generally, however, films can be deposited in this way with thicknesses greater than several microns. Using this deposition technique, selected areas may be coated while leaving

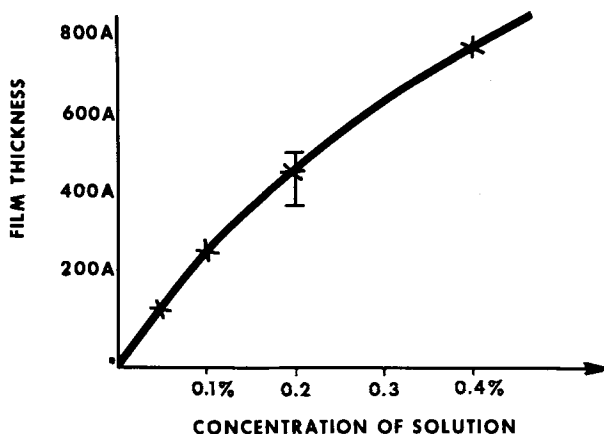


Fig. 2. Film thickness as a function of solution concentration.

other areas uncoated. The coating may be applied conveniently with a small brush. A second method is to dip the surface to be coated in a solution of the barrier coat material. When the surface is retracted, the surface is coated with the barrier coat material.

This second method is inviting from two points of view. From the point of view of manufacturability, dipping offers many advantages since many parts can be dipped at once. For electrical contacts it is sometimes necessary to make electrical connection through the barrier coat material; hence a thin film is desirable. Dipping in dilute solutions, as will be shown below, allows reasonably thin films to be deposited.

It is not clear at this point in the paper which factors determine the thickness of a dipped film. The following work describes the determining factors.

Experimentally, a solid copper substrate was used. The surface was given an optical polish and allowed to stand in air for about a day. This time was needed to allow the oxide growth to stabilize to the point that it did not influence the measurement of the barrier coat thickness. The surface was dipped in a solution having a given concentration of PFOM. Measurements were made with an ellipsometer prior to dipping and after dipping to determine the thickness and index of refraction of the polymer film. Typically, the area measured was 0.2 in. by 0.2 in., so the value obtained is an average over this area. The film was allowed to dry for at least 15 min prior to measurement. Various concentrations of the solution were obtained by further diluting the 2% solution with Freon TF to the desired concentration. In the following comments, a 0.2% solution will mean a 2% solution in xylene hexafluoride which has been further diluted 10 to 1 with Freon TF.

Results of the study indicate that:

1. The primary determining factor is the concentration of the solution. Figure 2 shows film thickness as a function of concentration.

2. The variation in thickness at various locations of a single film was found to be of the order of 10% to 20% and randomly distributed. This was measured at 13 different locations using very small areas (spot diameter was 0.040 in.). The variation of the average thickness from sample to sample deposited from the same solution was also about 20%. The curve shown in Figure 2 must be considered as indicative rather than conclusive in light of this rather large variation.

3. The time which the sample is held in the solution has no effect on the thickness of the resulting film for times of 2 sec to 100 sec.

The conclusion is that when the substrate is withdrawn from the solution, some of the solution remains on the substrate due to surface tension. The solvent then evaporates leaving the barrier film. The determining factors are (1) how much solution adheres to the substrate, and (2) the concentration of polymer in the solution.

EXPERIMENTAL SETUP FOR DEGRADATION STUDIES

The primary tools used were infrared spectroscopy (IR) and thermogravimetric analysis (TGA).

For the IR studies, the sample was prepared by dipping a NaCl disc into a given solution. The sample was then placed in the infrared beam and a spectrum taken. The NaCl disc, of course, had a film on each side, so two films were involved. The thickness (or thinness) of the films caused the infrared absorption bands to be very small, so a scale expansion of 20X was used.

Thermogravimetric analysis consists essentially of a furnace and a balance. The TGA schematic setup is shown in Figure 3. A Sloan TGA

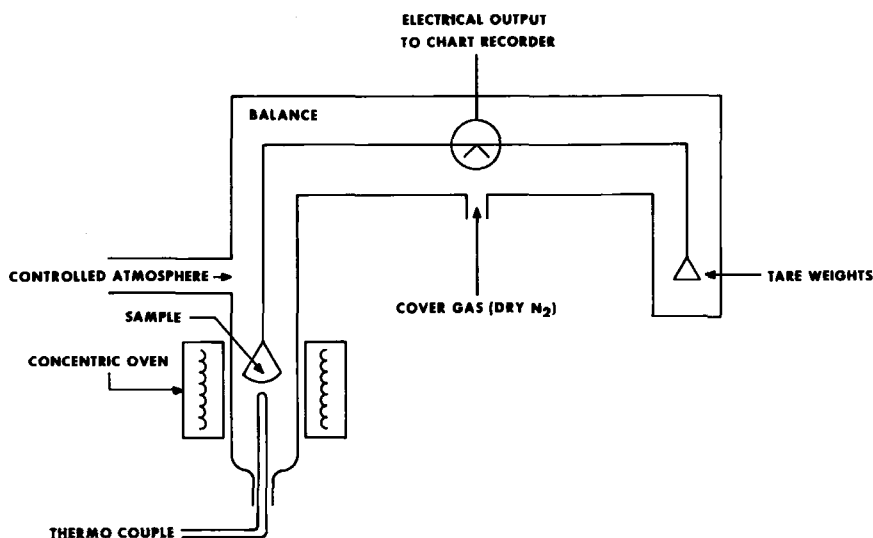


Fig. 3. TGA experimental setup shown schematically.

unit with a Cahn electrobalance was used. The solution of PFOM was placed in a hemispherical platinum balance pan and the solvent allowed to evaporate. Heating to 100°C aided the evaporation process. The pan had an area of approximately 1 cm², and a typical weight of the sample after evaporation of the solvent was 2 mg. Obviously, we are dealing with thick films or simply bulk polymer.

The TGA furnace was programmed to give a temperature increase of 10°C per minute. Weight and temperature are plotted on a strip chart recorder to give the TGA plot.

RESULTS AND DISCUSSION

Infrared Spectroscopic Studies of PFOM Films

A film was deposited on a NaCl disc by dipping the disc in a 0.1% solution of PFOM. After drying, an infrared spectrum was taken. Figure 4 is an example of the spectrum obtained. The bands at 1240, 1210, and 1150 cm⁻¹ are attributed to the fluorocarbon part of the polymer. By analogy with CH₂ and CH₃ bands,⁵ we assign the bands at 1240 cm⁻¹ and 1150 cm⁻¹ to the asymmetric and symmetric vibrations of the CF₂ group, respectively, and the band at 1210 cm⁻¹ to the asymmetric stretching of the CF₃ group. The band at 1760 cm⁻¹ is attributed to the C=O stretching vibration.

Because the films are thin, the absorption bands are quite small. A scale expansion of 20X was needed in most cases. The bands due to bond bending, C—C stretching, and the symmetric stretching of the CF₃ (expected at about 1166 cm⁻¹) cannot be distinguished from the noise. No bands attributable to CH₂ groups were observed. The Sadtler Standard Spectra⁶ for CF₃CH₂CF₃ indicates that the CH₂ band is much smaller than the CF₃ bands, and hence we would not expect to see the CH₂ bands in PFOM.

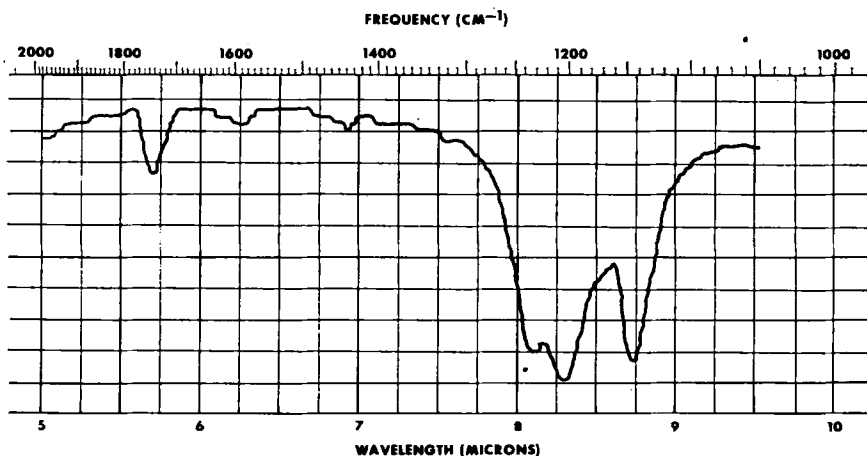


Fig. 4. Infrared spectrum of a thin film of PFOM prior to degradation.

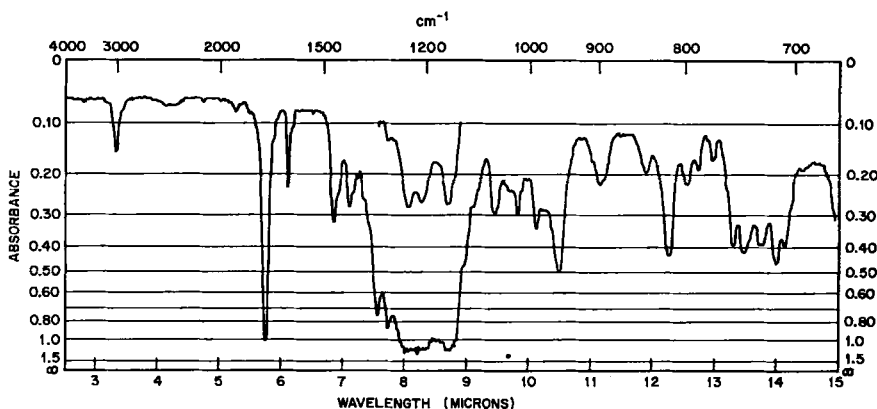


Fig. 5. IR spectrum of PFOM monomer in liquid phase.

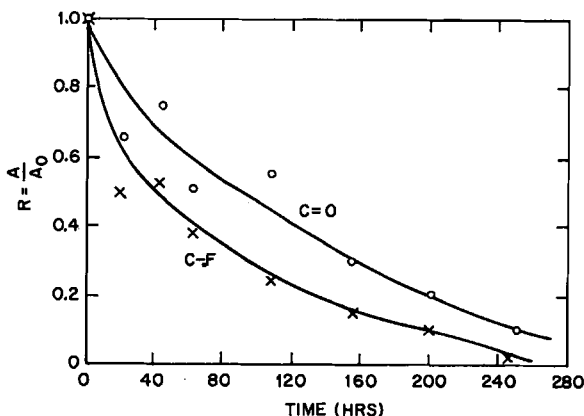


Fig. 6. Change in R with time for a thin film of PFOM at 140°C .

Figure 5 is an IR spectrum of the monomer in the liquid phase prior to polymerization (spectrum provided by the manufacturer). The absorption bands obtained with a thin film of the polymer correspond rather well to the larger bands for the monomer.

After taking a spectrum of the undegraded film, the sample was held at 140°C in room air for extended periods of time. The sample was removed from the oven periodically to obtain a spectrum. As the sample degrades, the bands gradually decrease in size. No shifting in wavenumber occurred.

To illustrate the decrease in band size, let us consider the absorbance $A = \log I'/I$, where I is the intensity at the peak of the band and I' is the background value of intensity. Let us denote the absorbance prior to any degradation as A_0 . We further define the ratio R such that $R = A/A_0$; R , then, is a measure of the remaining amount of the species which the band represents.

Figure 6 shows R as a function of degradation time. The experimental points for the C—F curve (lower) represent all three bands. Within

experimental error the ratio R for all three bands was identical. The curve for the C=O band generally has the same shape as the lower curve although it is consistently above the C—F curve. The C—F curve fits first-order reaction kinetics rather well after about 40 hr.

After each spectrum was taken, a hexadecane drop was placed on the edge of the sample and photographed. The contact angle was determined from the photograph. The drop was then removed by wiping with a cloth. Care was taken to ensure that the drop was not placed on an area which was sampled by the infrared beam.

The contact angle values were rather erratic but generally decreased until, at 340 hr, the contact angle was zero (i.e., the drop spread over the surface).

If we consider the exponential curve which approximates the points of the C—F curve in Figure 6, 340 hr corresponds to a value of $R = 0.03$. If the initial thickness were 250 Å as suggested in Figure 2, the film would act as a barrier coat down to an average thickness of 8 Å. We are making the simplifying assumption that R is proportional to thickness for illustration purposes. Since the monomer is considerably larger than 8 Å, the sample probably consists of areas where the substrate is exposed and areas which are covered with the polymer film, giving an average thickness of 8 Å. The amount of material required for the film to act as a barrier appears to be considerably less than a monolayer.

In general, the sizes of the C—F bands correlate rather well with the film's ability to act as a barrier as determined by contact angle measurement.

The same type of experiment was performed for much thicker films, with similar results.

Thermogravimetric Analysis (TGA)

A typical TGA plot is shown in Figure 7. The numbers along the curve are the temperatures in degrees centigrade. The atmosphere was nitrogen which had been passed through a drying agent.

Curves made in dry nitrogen, wet nitrogen, and dry oxygen are essentially identical when normalized. One sample had degraded in a vacuum of ~ 0.01 torr. Because of experimental difficulties, a TGA curve was not obtained, but the beginning weight and the weight of the sample after it reached 320°C were obtained. The latter value was zero, i.e., the sample had completely degraded. Figure 8 shows normalized curves for samples which were grossly different in initial weight (and, presumably, thickness). Again the curves are essentially identical.

These observations, taken together, indicate that the degradation mechanism is probably a thermal bond-breaking phenomenon and does not involve an additional reactant, i.e., it is not oxidation or hydrolysis. The fact that the infrared bands do not shift in wavenumber further substantiates this. Often, a changing chemical environment causes infrared bands to shift slightly. The fact that grossly different amounts give the

same normalized curve indicates that a bulk phenomenon rather than a surface phenomenon is involved.

Let us consider the typical TGA plot in Figure 7. It appears that the degradation is a two-stage process. One stage begins at about 140°C and

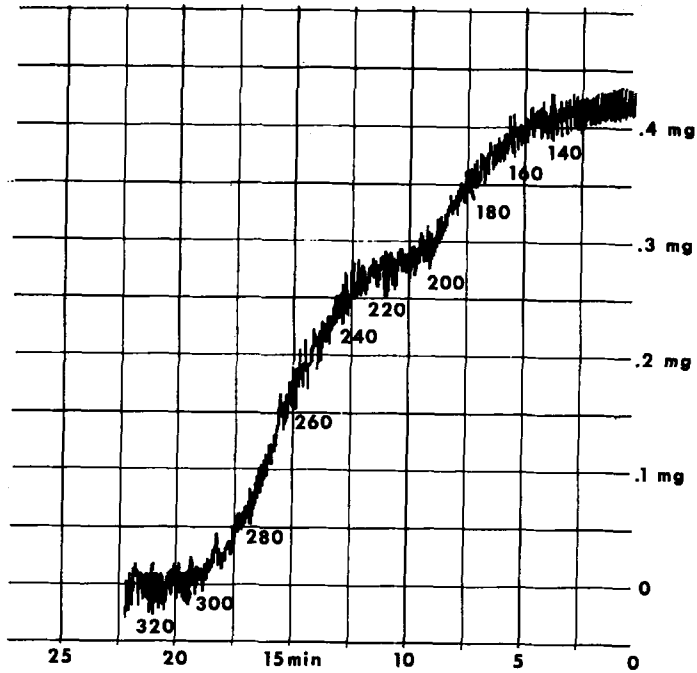


Fig. 7. Typical thermogravimetric analysis plot for PFOM.

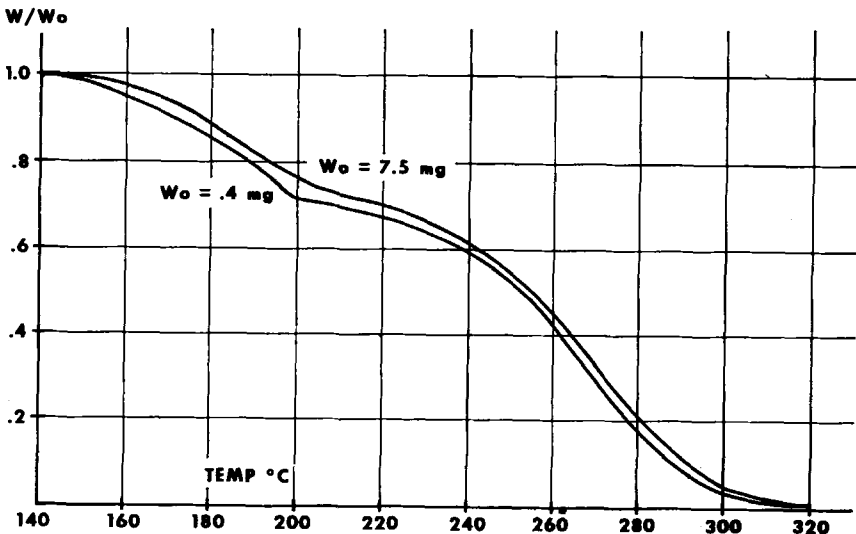


Fig. 8. Normalized TGA plot of PFOM samples having different initial weights.

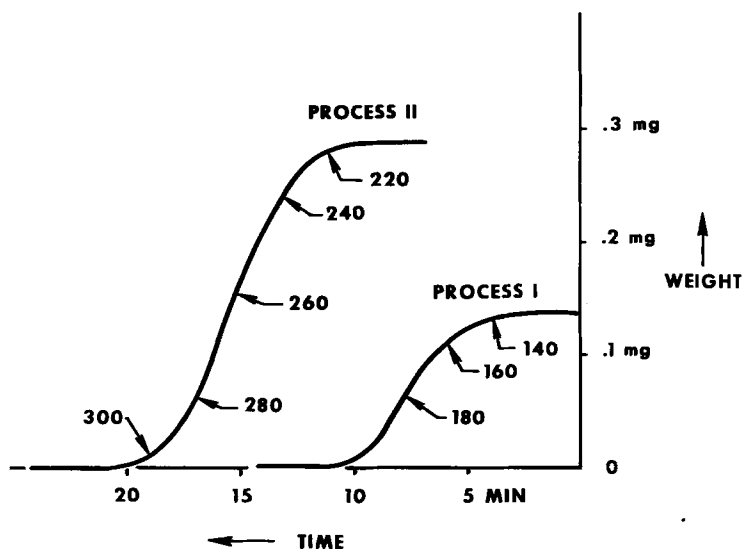


Fig. 9. TGA plot (Fig. 7) separated into two processes.

is almost complete at 200°C, and the other begins at about 220°C and is complete at 320°C. If we separate the two processes, we get the two curves shown in Figure 9.

If the reactions are first order, then the equation which describes each process is

$$\frac{dc}{dt} = -kc \quad (1)$$

where c is the amount of the reacting species and k is the rate constant. Generally, k has the form

$$k = Ae^{-E/RT} \quad (2)$$

where E is the energy of activation, T is the temperature in degrees Kelvin, R is the gas constant, and A is the preexponential factor (this A is a constant and should not be confused with absorbance which we also denote as A). For constant temperature, eq. (1) can be integrated to give the usual exponential decrease. In TGA, however, the temperature is not constant. If we rearrange eq. (1) to

$$-\frac{1}{c} \frac{dc}{dt} = k \quad (3)$$

we can obtain the value of k at any point on the TGA curve from the value of c and the slope of the curve and hence obtain k as a function of temperature. The value of the energy of activation E can be obtained from an Arrhenius plot of $\ln k$ versus $1/T$, where the slope gives E/R and the intercept gives the preexponential factor A . Figure 10 is such a plot

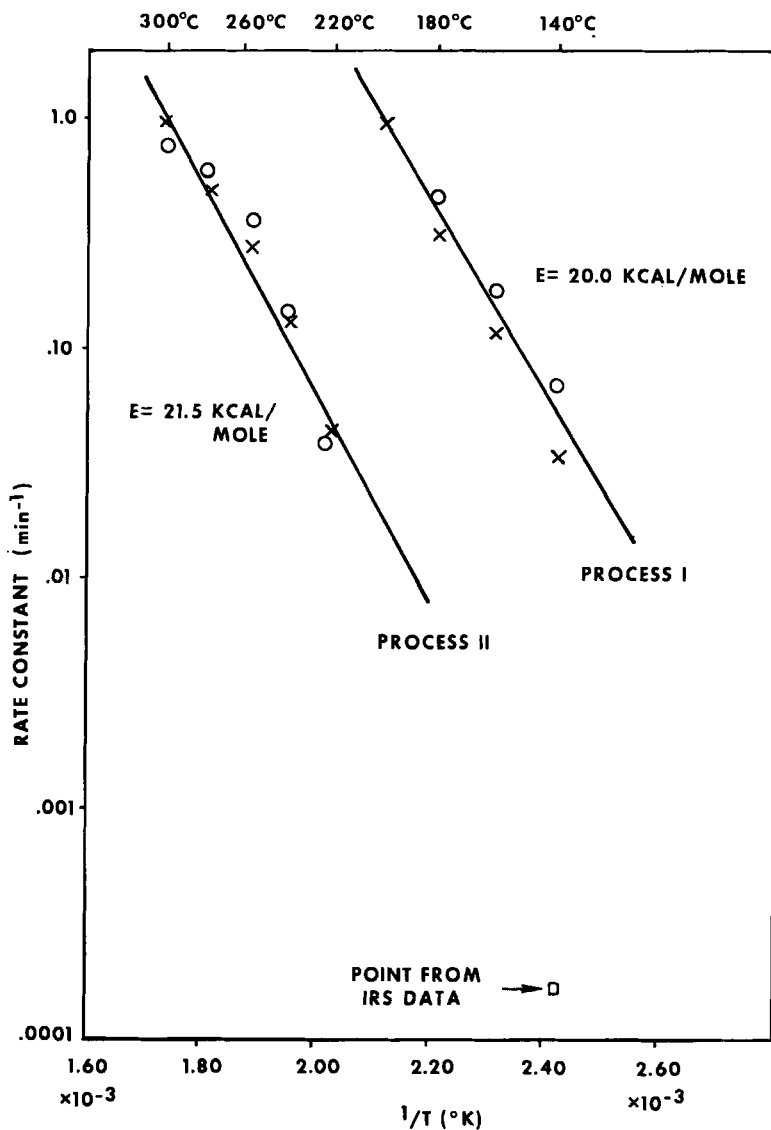


Fig. 10. Arrhenius plot for the two processes shown in Fig. 9.

for two TGA curves. The circles are the values computed from Figure 9. Straight lines have been drawn through the points. The crosses are the values computed from another TGA curve.

If we consider the average values of the activation energy E , i.e., the value obtained from the straight lines in Figure 10, we find that the values of E for the two processes are very close to each other. If the value of the rate constant obtained from the IR data shown in Figure 6 is plotted on Figure 10 (the point represented as a square), we see that it would fall on the average value line for process II rather well, and it is not particularly

close to process I. The degradation described in Figure 6 probably proceeds through process I rather quickly, and most of what we see involves process II.

Infrared Spectroscopy of the TGA Degradation Product

Samples were degraded at temperatures appropriate to process I in a mild vacuum and the degradation products collected in an infrared gas cell. An infrared spectrum was then obtained and the gas pumped out of the cell. The sample was then heated at such a temperature as to ensure that process I was completed and process II was underway. A second gas sample was then collected which consisted of the degradation products of process II and an infrared spectrum obtained. Except for intensity (indicating amount), the two spectra were identical to each other but slightly different from the spectra of the film itself prior to degradation. Figure 11 is an example of the spectra of the degradation products. The bands have all increased in wavenumber by 10 cm^{-1} . The most noticeable difference, however, is the fact that the relative heights of the peaks are quite different from the relative heights in Figure 4. The increased size of the band at 1240 cm^{-1} relative to the others is consistent with the increased size of this band in the monomer (Fig. 5). The reason for the differences in relative height and wavenumber of the peaks is not understood but probably involves the fact that the environment in the gas state is quite different from that in the solid state. A significant point, however, is that the detectable degradation products from process I and from process II have essentially the same infrared spectrum. It is possible, of course, that all degradation products may not have been collected.

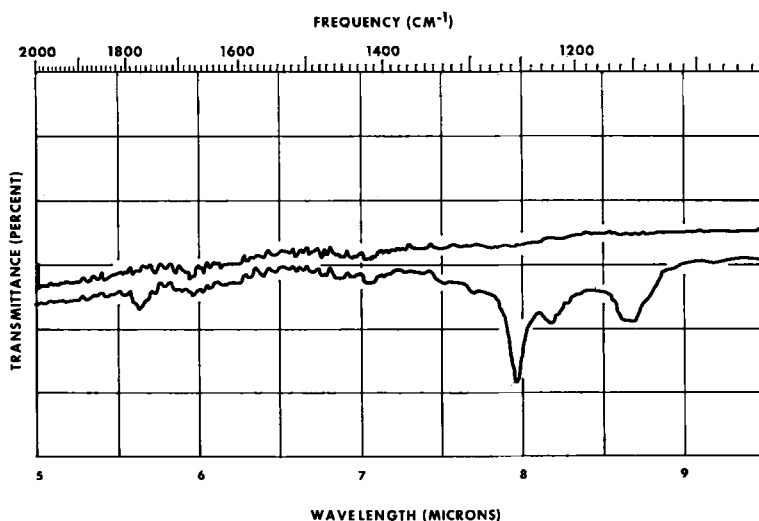


Fig. 11. Infrared spectrum of the gaseous degradation products of PFOM (upper line is background).

DISCUSSION OF THE MECHANISM

We have included some of the discussion in the section on results. In this section, let us put the results together to suggest a mechanism of degradation. The IR data and the TGA data indicate that the degradation process is the same for thin and thick films. The key results are:

1. The TGA work indicates that the degradation is a bulk phenomena rather than a surface phenomena and that degradation does not require an additional reactant.

2. The TGA work indicates that degradation occurs in two stages, with the energy of activation being about 20 kcal/mole for each process.

3. From the IR work, the degradation products from both processes appear to be the same.

Because of the similarities of PFOM with poly(methyl methacrylate), PMMA, some comparisons are in order. Degradation of PMMA has been studied extensively by Grassie and Melville⁸ and recently by McNeill.⁹ McNeill⁹ finds that for PMMA prepared by free-radical mechanism, degradation occurs in two stages. The accepted explanation is that the polymerization terminates by disproportionation, leaving one chain end unsaturated and the other saturated. The first stage of degradation consists of an unzipping initiated at the less stable unsaturated ends. The second process is a reaction initiated by random scission⁹ on the more stable species with the saturated chain end. In both processes, monomer is the sole product of degradation. Polymers prepared by an anionic process when there are no unsaturated chain ends exhibit only one degradation process.

In comparing PFOM with PMMA, we see that in both cases the reaction proceeds without an additional reactant and that both are two-stage processes. We also see that the degradation products of the two stages are the same for PFOM and that monomer is the sole product for both processes for PMMA. Accordingly, it seems reasonable to postulate that the degradation mechanism is the same for PFOM and for free-radically polymerized PMMA. The low energy of activation is not understood at this time, and more experimental work is required to better understand the lack of thermal stability.

SUMMARY

We have discussed the deposition and degradation of thin films of a fluoropolymer, 1H-1H-pentadecafluorooctyl methacrylate (PFOM) on solid surfaces.

Studies of the degradation of the polymer using infrared spectroscopy and thermogravimetric analysis are presented. The conclusions are that degradation is a two-stage process which does not involve additional reactants. The degradation products are the same for both processes, and in all probability the product is monomer. Analogously to PMMA, we postulate that the two processes involve species with unsaturated and

saturated chain ends, respectively. The lack of thermal stability is not understood at this time.

The author would like to acknowledge the help of M. H. Drozdowicz for taking the infrared spectra and making the ellipsometry measurements; and D. L. Allara, M. G. Chan, H. Schonhorn, and D. Schuele for helpful discussions.

References

1. W. D. Bascom, R. L. Cottingham, and C. R. Singleterry, *Dynamic Surface Phenomena in the Spontaneous Spreading of Oils on Solids*, Advances in Chemistry Series, No. 43, American Chemical Society, Washington, D.C., 1964, p 355.
2. V. G. FitzSimmons, C. M. Murphy, J. B. Romans, and C. R. Singleterry, *A New Approach to Lubricating Ball Bearings*, Naval Research Laboratory Report 6356, 1965.
3. J. D. LaZerte, 3M Company, private communication.
4. M. K. Bennett and W. A. Zisman, *Hydrophobic and Oleophobic Fluoropolymer Coatings of Extremely Low Surface Energy*, Naval Research Laboratory Report 6039, 1964.
5. R. N. Jones and C. Sandorfy, *Chemical Applications of Spectroscopy*, ed. by W. West, Interscience, New York, 1956, p. 338.
6. *Sadtler Standard Spectra*, Midget Edition Infrared Spectrogram No. 650, 1959.
7. R. N. Jones and C. Sandorfy, *op. cit.*, p. 335.
8. N. Grassie and H. W. Melville, *Proc. Roy. Soc. (London)*, **A199**, 1, 14, 24, 39 (1949).
9. I. C. McNeill, *Eur. Polym. J.*, **4**, 21 (1968).

Received April 2, 1973

Revised June 4, 1973