Decomposition of Burning Polytetrafluoroethylene

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Synopsis

PTFE rods, 0.6–3.8 cm diameter, were burnt from the top downwards in a gently rising atmosphere of oxygen. The burning was only possible in concentrated oxygen, or at elevated temperature or pressure. At its surface temperature of 920 $\pm$ 25°K, the polymer evolved monomeric C_2F_4 which oxidized in a surrounding gas flame; 15–35% of all the carbon in the gas was found present as monomer just above the larger rods. Depolymerization of the solid was not its only mode of decomposition, however. The heat radiated and conducted from the flame into the condensed phase was too little to depolymerize it completely, and heterogeneous reactions with species from the gas phase must also have contributed to the decomposition. Overall, the polymer burnt in O_2, but the gaseous reactant which attacked the surface need not have been O_2 or O in all cases, for these rare species just above the larger rods. Elemental fluorine was present in the gas even when elemental oxygen was absent, and calculations indicate that F atoms would be a major flame species at equilibrium. It is possible that heterogeneous attack by flame generated F atoms consumed part of the polymer and also supplied energy to help depolymerize the rest.

Introduction

The literature on the pyrolysis of polytetrafluoroethylene (PTFE) suggests that a heat shield in hypersonic flow gasifies in large part by depolymerization. Combustion of the polymer or of the fuel gas derived from it evidently contributes to the decomposition, because PTFE ablates more easily in air than in inert nitrogen.[1] The processes occurring under such extreme conditions might also occur when the polymer burns in a very gently moving atmosphere, and we have studied the decomposition under the milder conditions. The main difference is that all the heat must come from combustion rather than only a part of it as in ablation in air.

There are two different ways in which PTFE might decompose when it burns in a gently moving atmosphere. It might pyrolyze in the heat of a surrounding diffusion flame and continually feed the flame with fresh fuel. Or it might react heterogenously with species from the gas. For brevity, we call a pure thermal pyrolysis candle burning, and call a surface reaction with species from the gas heterogenous burning.

For the distinction to make sense, we must agree that heat flow from the flame does not include the heat evolved in heterogenous chemical reactions. In this paper heat flow is meant to include radiation and the sensible energy carried in internal and translational degrees of freedom of the molecules, as

long as the molecules do not react chemically at the surface. The flame might generate species which diffuse to the surface and react exothermally, and this process might be an effective way of heating the condensed phase. But we call such a process heterogenous burning and do not include its energy in heat flow from the flame.

Burning Experiments

PTFE rods, 0.63–3.8 cm diameter, were burnt from the top downwards. The rods were mounted vertically on a shaft driven by a gear train, so that the distance from the tip to a sampling probe could be held constant by racking up the specimen as it burnt. The rod, the probe, and the ignition system were all enclosed in a bell jar, 13 cm in internal diameter, which was jacketed and heated to a constant temperature. Metered flows of oxygen and inert gas were mixed, preheated to the vessel temperature, and distributed so that the oxidant streamed up the jar with a velocity of 2 cm/sec (calculated at room temperature, atmospheric pressure, and with the flow unperturbed by the burning).

After ignition, by a manipulable hydrogen flame which was then extinguished, the rod either continued burning or went out, depending on several variables. PTFE is difficult to burn when it is initially at room temperature. It burned more readily when all reactants were preheated, as is shown in the upper part of Figure 1. In this figure, the vertical axis gives the minimum mole fraction of oxygen required in the gas for the polymer to continue burning. The fraction is called the critical oxygen index n and is
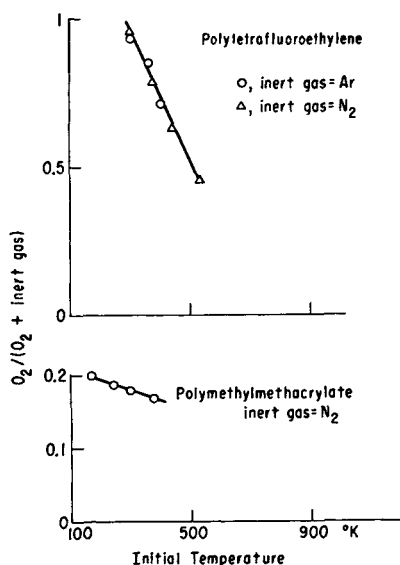

Fig. 1. Critical oxygen index as a function of temperature at 1 atm pressure. The polymer samples were 0.63 cm diameter rods.

larger the less flammable the rod.[2]   The temperature dependence of PTFE is stronger than that observed for polyethylene or poly(methyl methacrylate), which are known to undergo candle burning.[3]   For comparison, the weaker dependence of poly(methyl methacrylate) is also shown in Figure 1.

PTFE burned more easily at higher pressures (Fig. 2).   Its oxygen index varied inversely with about the $1/2$ power of total pressure.   This is a much stronger dependence than is observed for polymers known to undergo candle burning such as polyoxymethylene,[2] polyethylene,[2] or poly(methyl methacrylate).   The weak dependence for poly(methyl methacrylate) is shown at the bottom of Figure 2.

Large rods burned with more difficulty than small ones.   In Ar–O₂ mixtures at 1 atm pressure and 400°K, the critical index was 0.72, 0.80, 0.88, 0.92 for rods of diameter 0.67, 1.27, 1.91, and 2.54 cm, respectively.   By contrast, polyethylene and poly(methyl methacrylate) showed a weaker dependence of the oxygen index on sample size.

Rods which continued to burn attained a constant regression velocity after a few minutes.   The burning surface possessed a small scale bubbling on it and a clear region of molten polymer in the condensed phase below it. PTFE remained rigid above its melting point, and the molten polymer did not drip.   The upper part of Figure 3 shows the appearance of a steadily burning 1.9 cm diameter rod as measured from a photograph.   The lower part of the same figure shows that at constant regression velocity, the height of the burning cone and the depth of clear melted polymer both increased with about the square of the rod diameter.   The flame surrounding the burning cone was blue, except that a trace of transient soot was seen by its yellow glow above 3.8 cm diameter rods at atmospheric pressure and above smaller rods too at higher pressures.

Temperatures were measured on a recording potentiometer connected to a thermocouple which was embedded in the polymer so that the heating
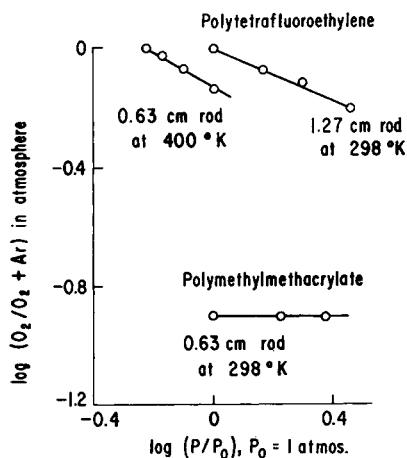

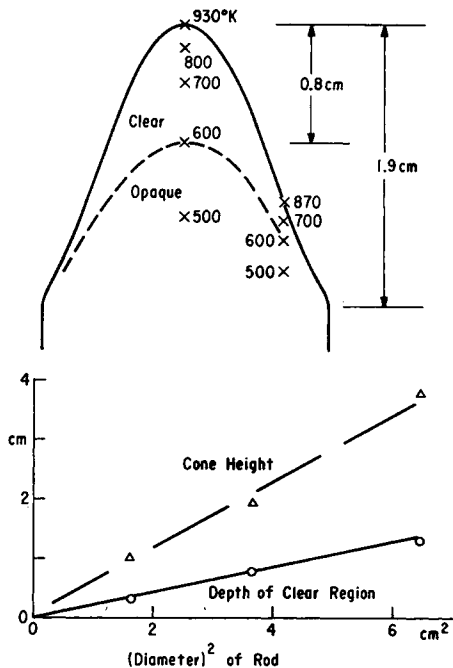Fig. 2. Critical oxygen index as a function of total pressure.

Fig. 3. Appearance of 1.91 cm rod burning in 93% O_2 at $P = 1$ atm. Lower graphs show cone height and depth of clear region when rods of different diameter burn at 7 to 8 × 10^{-3} cm/sec. Polymer and O_2–Ar atmosphere preheated to 400°K.

and burning regions were traversed as the sample burnt. The uncoated thermocouple was either 0.013 cm diameter Pt–Pt, 10% Rh or chromel-alumel. Good thermal contact in the condensed phase was proved by the measurement of the correct melting temperature on the boundary between clear and opaque material, 600°K, and this measurement also showed that conduction of heat down the thermocouple wires was not a grave source of error. Radiation corrections were made in the gas following Kaskan,[4] and a not very critical assumption about the mass flow was needed to do this. Some internal temperatures are indicated in Figure 3, and complete traverses are shown in Figure 4. The curves could be repeated within ±10°K but, because of the difficulty of deciding where the surface was, the temperature is judged to be uncertain by ±25°K.

Gas samples were collected through a fine probe maintained at various distances above the burning tip. A quartz probe was attacked by the gas and had to be reworked each time it was used. An alumina probe was also eaten away by the flame and was more difficult to replace. The samples were analyzed mass spectrometrically for oxygen, argon, and carbon compounds. Fluorine was not determined, but proof of its presence is given later.

Some analyses above rods of various sizes are shown in Figure 5. No molecular oxygen was found just above rods of 1.91 cm diameter or larger,
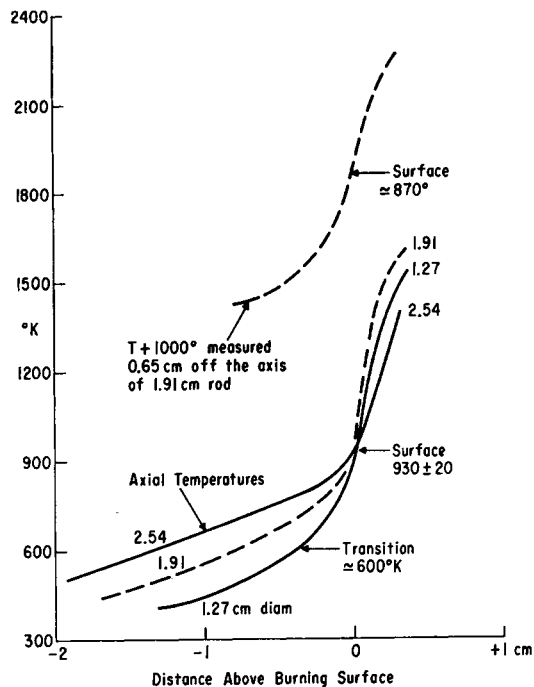
Fig. 4. Temperatures in and above PTFE rods burning at P = 1 atm. Regression rates were 8×10^{-3} cm/sec for 1.27 diameter rods burning in 88% O_2, 7×10^{-3} cm/sec for 1.91 and 2.54 cm diameter rods in 93% O_2.

but O_2 was present as close as we could sample to rods 1.27 cm or smaller. The material balances computed from the analyses are not very good; the overall ratios of F/C are a little greater than two, which is impossible, and we suspect that the O/C ratios at the top of the figure are a little smaller in general than the true ratio of O/C in the reactants. Perhaps CO, the chief carbon oxide, diffused faster from the flame than CF_4, for this might make F/C appear too large and O/C too small.

Depolymerization of Burning PTFE

The presence of monomeric C_2F_4 in the gas (Fig. 5) indicates at least a partial depolymerization, and this is consistent with the literature. Madorsky[5] found that the vacuum pyrolysis at 700 to 786°K gave mainly monomer. His initial rates can be expressed

$$\log \left(\frac{\text{per cent depolymerization}}{\text{sec}} \right) = 20.5 - (80,500/4.57T) \qquad (1)$$

which also agrees with experiments by Siegle et al.[6]. Extrapolated to our surface temperatures, eq. (1) predicts 6–80% depolymerization per second at 895–945°K. The temperature in the condensed phase was within 10°K of the surface temperature to a depth equal to the regression
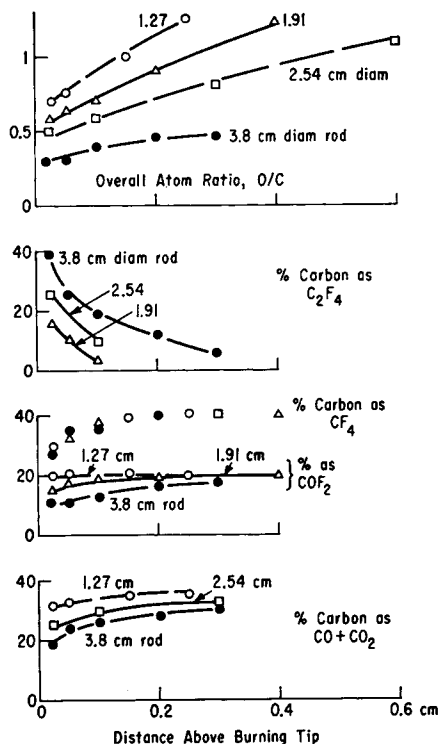
Fig. 5. Gas composition along the axis above PTFE rods burning at 1 atm pressure. Polymer and oxidant preheated to 400°K. Regression rates and gaseous oxidants the same as for Fig. 4. The 3.8 cm diameter rod (not included in Fig. 4) burnt in pure O_2 with a regression rate $\simeq 5 \times 10^{-3}$ cm/sec.

rate per second, so it seems reasonable that the rate of depolymerization should have been an appreciable fraction of the rate of regression.

We do not believe that the decomposition of the condensed phase occurred entirely by depolymerization, however, because this would require an improbably large flow of heat from the flame back into the polymer. Taking the heat of depolymerization from Table I and adding the heat to warm to 920°K, we get

$$\frac{1}{m} (C_2F_4)_m \longrightarrow C_2F_4 \quad \Delta H \simeq 50 \text{ kcal} \qquad (2)$$
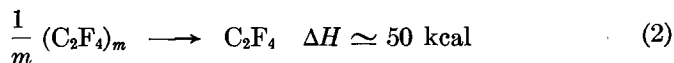
Polymer at 400°K   Gas at 920°K

The 50 kcal required is about $^1/_2$ of the entire heat of combustion of the polymer, an improbably large fraction when compared with previous estimates[3] of the heat flow from the flame into other burning polymers. The flow into poly(methyl methacrylate) was estimated to be about 5% of the entire heat of combustion, into polyoxymethylene about 14%, and into polyethylene about 7%.

TABLE I
Heats of Formation at Room Temperature[a]

	$-\Delta H$, kcal/mole
COF_2	150.4
CF_4	217.2
C_2F_4, gas	151.7
$1/m(C_2F_4)_m$, polymer	192.8

[a] First two entries from McBride and co-workers.[7] C_2F_4 monomer from Neugebauer and Margrave,[8] and polymer from Siegel et al.[6]

Another way of stating the heat requirement is to note that a rod regressing at 7×10^{-3} cm/sec would need a heat flow into it of 7.5 cal/sec per square centimeter of cross-sectional area. The rod in Figure 3 with a burning surface 2.9 times its cross-sectional area would need an average flux of $7.5/2.9 = 2.6$ cal/cm²-sec.

We see no evidence for so large a flow of heat. The temperature gradient normal to the burning surface is not more than $3500°$K/cm either at the tip (Fig. 4) or at a point on the burning cone 0.65 cm off the axis (topmost curve in Fig. 4 and shape in Fig. 3). These are upper limits because any surface reactions on the thermocouple ought to make the observed gradient too large. If the thermal conductivity of the gas is $\simeq 2 \times 10^{-4}$, the heat flux is not more than $3500 \times 2 \times 10^{-4} = 0.7$ cal/cm²-sec, which is only 1/4 of the average flux required. It is about 12% of the entire heat of combustion of the polymer, however, and thus comparable to those values just quoted for other polymers.

Radiation from the flame is a less important source of heat than conduction. If one supposes the flame emission is equivalent to that from a 1-cm thick layer of gas at $1900°$K which contains 0.6 atm pressure of CO_2, the emissivity is[9] ~ 0.016. The heat transferred by radiation is then

$$\sim 0.016 \times 1.38 \left\{ \left(\frac{1900}{1000} \right)^4 - \left(\frac{900}{1000} \right)^4 \right\} = 0.27 \text{ cal/cm}^2 \text{ sec}$$

which is about 1/10 of the flux required.

One might try to save the hypotheses of candle burning by supposing that the polymer vaporized as dimer, trimer, etc., and that a heat supply insufficient to give monomer could gasify the condensed phase as a mixture of heavier species. However, the only heavier species found in our analyses was a little C_2F_6 and C_3F_6 suggested by mass numbers 119, 131, and 150. It has been suggested[10] that PTFE pyrolyzes to give CF_2; if so, the heat required at the surface would be increased, and the difficulty of candle burning compounded.

If pure candle burning does not occur, heterogenous burning must. We suggest that PTFE does burn heterogenously, that it may exhibit a more marked dependence of oxygen index on temperature, pressure (Figs. 1 and 2) and on sample size than poly(methyl methacrylate) or polyethylene because PTFE burns differently.

Possible Importance of Elemental Fluorine

Granted that heterogenous burning occurs, it is not always obvious what species react at the surface.   Oxygen was present as close as we could sample to the tips of the smaller rods, and elemental oxygen may have consumed part of the polymer and also supplied energy to help depolymerize the rest. However, O_2 and O atoms were rare species at the tips of the larger rods, and in these cases at least the surface reactions must not have involved elemental oxygen.   We ask what other species might attack the surface.

Table II gives the equilibrium flame products for various mixture ratios as calculated from Table I and from other data.[7]   It shows that gas, containing neither O_2 nor O, and possessing our observed distribution of carbon among carbon oxides, COF_2, and CF_4, would also contain 6–10% of F atoms.   If a concentration of this order existed in the flame and if F reacted rapidly at the surface, F atoms might be a more important oxidant than elemental oxygen.

TABLE II

Adiabatic Equilibrium Products of Polytetrafluoroethylene

Burning in O_2 (Initial Temperature = 400°K), Partial Pressure in Atmospheres

O/C	T, °K	P_{CO}	P_{CO_2}	P_{O_2}	P_{COF_2}	P_{CF_4}	P_F
1.5	2080	—	0.23	0.06	0.31	0.06	0.34
1.0	2350	0.12	0.14	—	0.35	0.14	0.25
0.75	2200	0.27	0.05	—	0.30	0.27	0.10
0.65	2170	0.36	0.02	—	0.21	0.35	0.06
0.5	1940	0.49	—	—	0.01	0.49	—[a]

[a] Trace of CF_3, which becomes the chief radical species in sufficiently rich gases.

An indication for the presence of fluorine was obtained by packing small axial holes in 1.27 or 2.54 cm rods with ground mixtures of PTFE and potassium iodide.   These rods burnt with a green flame.   Examined spectroscopically, with a 1 m grating spectrograph, a slit width of 0.5 mm, and 10 minute exposure on Kodak Tri-X film, the flame was found to be colored by the IF bands observed by Durie on burning iodine in F_2.[10]   Our intensity distribution was similar to his for the 34 bands he listed between 4358 and 6250 Å.   Since he observed the bands when iodine or its compounds reacted with fluorine or chlorine trifluoride, we consider them specific for elemental fluorine.   The flame above 2.54 cm rods was brightly colored right down to the decomposing surface where elemental oxygen was absent.

We had no hope of measuring the concentration of elemental fluorine in the flame by sucking samples through corroding probes.   We tried to find some of it after the hot gas had cooled by mixing with the surrounding atmosphere, even though neither F nor F_2 would survive if equilibrium was maintained as the gas cooled to room temperature.   On burning 1.27 or 2.54 cm rods at 2 atm pressure, and bubbling the cooled output of the bell jar through dilute aqueous HI, we found iodine liberated equivalent to

1.0 ± 0.1% of all the fluorine in the polymer.   Then 10 mole-% of F atoms in the flame described in Table II corresponds to 5.6% of all the fluorine. Pure O_2 did not liberate iodine in the times used, and a stronger oxidant must have been present; we think F_2 was formed from part of the F as the gas cooled.

These tests, particularly the emission of IF, suggest the presence of elementary fluorine.   They do not prove that F atoms attain or are limited to the equilibrium concentration, but we think it worthwhile to consider whether the equilibrium concentration could supply energy of the order required at the surface, about 2.6 cal/cm²sec in the example in the last section.   F atoms could supply as much as 79 kcal/mole [the heat of reaction of F + $(1/4m)(C_2F_4)_m$ polymer → $^1/_2$ CF_4] and therefore we seek a reaction rate of about

$$\frac{2.6}{79 \times 10^3} \simeq 3 \times 10^{-5} \text{ moles/cm}^2 \text{ sec}$$

Kinetic theory says that at atmospheric pressure a gas containing 10% F atoms makes collisions at the surface corresponding to 0.03 mole of F/cm²-sec, so a collision efficiency of 10^{-3} would suffice.

If F atoms were this reactive, however, the process might be limited by diffusion; the relevant question might be whether a diffusive flux of order

$$Dd[F]/dx \simeq 3 \times 10^{-5} \text{ moles/cm}^2 \text{ sec}$$

was possible. D is the diffusion coefficient and $d[F]/dx$ the concentration gradient of F atoms.   Ten per cent of F atoms is a concentration of $[F] = 6 \times 10^{-7}$ mole/cm³, and presumably this value might occur about 0.1 cm from the surface where C_2F_4 becomes small for 1.9-cm rods.   If F atoms react rapidly enough at the surface, the gradient could be of order $6 \times 10^{-7}/0.1 = 6 \times 10^{-6}$, and a reasonable $D \simeq 3$ cm²/sec could give a flux of the right order, $\simeq 2 \times 10^{-5}$, versus 3×10^{-5} required.

Remembering that conduction and radiation together could supply about 18 of the 50 kcal required per monomer unit to gasify PTFE, we estimate that the heat provided by one F atom might help gasify around 2.5 monomer units.

Summary

Polytetrafluoroethylene burns in atmospheres containing a high content of oxygen or at elevated temperatures or pressures.

The gas evolved at the decomposing surface contains monomeric C_2F_4, but the heat required to gasify the polymer completely at the rate observed seems more than can be provided by radiation and thermal conduction from the flame.

It is suggested that heterogenous oxidation reactions also occur at the decomposing surface to consume part of the polymer and help supply energy to gasify the rest of it.   These reactions might involve elementary oxygen

in some cases, but not in all because oxygen does not penetrate to the burning surface in all cases.

Even when oxygen is absent, elementary fluorine is present in the gas near the decomposing surface. If fluorine atoms attain a concentration of the order of the equilibrium value, the diffusive flux of F atoms could provide more energy by reacting at the polymer surface than could be supplied by thermal conduction or radiation from the flame.

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