

## Thermal Degradation of Polytetrafluoroethylene in Tube Reactors

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We have studied the thermal degradation of polytetrafluoroethylene (PTFE) in wet air, dry air and nitrogen gas at temperatures ranging from 310°C to 520°C. The principal gas product was tetrafluoroethylene (TFE). The nitrogen experiments yielded only TFE, but experiments in dry and wet air also produced several other minor gas products. The dry air experiments produced the most smoke and the least gas products, with the nitrogen experiments giving no smoke and the highest amounts of gas products. Wet air experiments gave intermediate results for smoke and gas formation. The rate of degradation in wet air showed an apparent activation energy of 103 kcal/mol. We also performed FTIR analyses of the smoke particulate, determining that the particulate formed in dry air is different than that formed in wet air.

Polytetrafluoroethylene (PTFE) is widely used by industry in such applications as electric insulation and coatings. The chemical and thermal stability of PTFE is the primary reason for its widespread use. However, once the PTFE starts to decompose at high temperatures, the gas products and the smoke particulate formed in the degradation are known to be very toxic [1], causing symptoms known as "fume fever" [2-4]. It is believed that much of the toxicity is due to ultrafine particles ( $d < 100$  nm) from the degradation process. This problem becomes particularly serious on space craft where no venting is possible [5]. In this paper we present the results of the first part of our ongoing efforts to obtain an understanding of the effect of gravity on the toxicity of ultrafine particles and gas phase materials produced when fluorocarbon polymers are thermally degraded or burned. The motivation for the project is to provide a basic technical foundation on which policies for space craft health and safety with regard to fire and polymers can be formulated.

Figure 1 illustrates the experimental apparatus we constructed to study the pyrolysis and burning of PTFE. Nitrogen, dry air, or wet air flowed into the steel tube of 2.5 cm inner diameter and 80 cm long. The furnace and the Monel tube were preheated to a desired temperature before a glass boat containing 1 gram PTFE powers (Aldrich cat. No. 18,247-8) was put into the center of the furnace. The smoke produced in the reaction was collected by adsorption onto densely-packed glass wool. The gas products were directed to either a cryogenic trap, a mass spectrometer (MS) or a gas chromatograph (GC). The gas flow was ~90 ml/min. In the dry and wet air reaction atmospheres, there was sufficient oxygen in the reactor for the complete oxidation of PTFE.

The experimental temperatures ranged from 310°C to 520°C. Gas products were separated by a 30 meter HP-1 capillary column before entering the flame ionization detector. Figures 2a and 2b show the typical GC results for the gas products. There were major peaks at retention time 0.93 minutes. For reactions in the air atmospheres, several

small peaks were also observed at longer retention times.

Figure 3 shows the major peaks (peaks with retention time 0.93 minutes) for reactions at different temperatures. The areas of the peaks are listed in Table 1. For temperatures lower than 370°C, peak areas are negligible. At temperatures higher than about 370°C, the peak start to be evident. Figure 4a shows the peak area A as a function of the temperature. In figure 4b, a plot of  $\log A$  vs.  $1000/T$ , the data points form a straight line. The slope of the line corresponds to an apparent activation energy of 103 kcal/mol. The value is close, perhaps merely coincidentally, to the bond dissociation energy of a C-F bond.

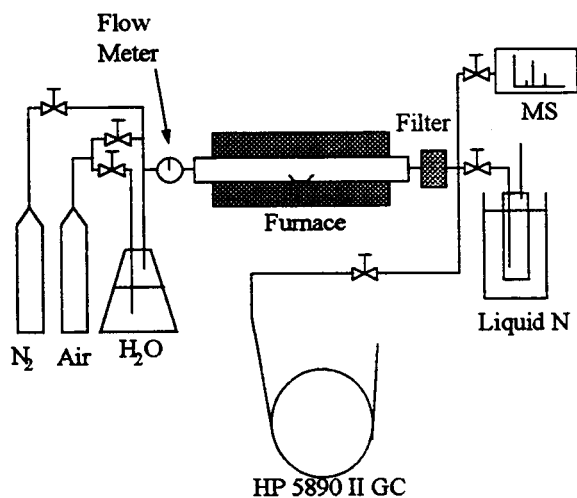


Figure 1: Experimental set up.

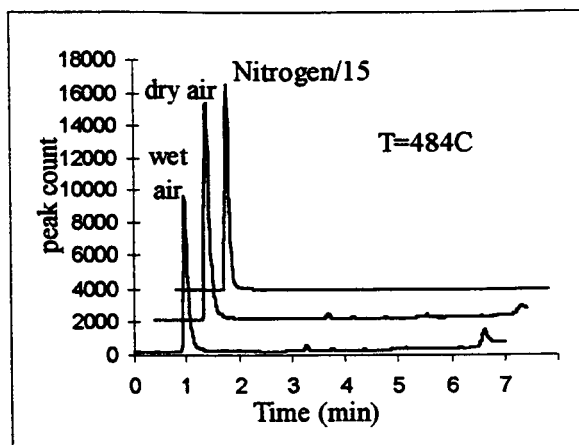


Figure 2a: Gas chromatograms of the gas products. Samples were taken 40 minutes after the PTFE powders were put into the reactor.

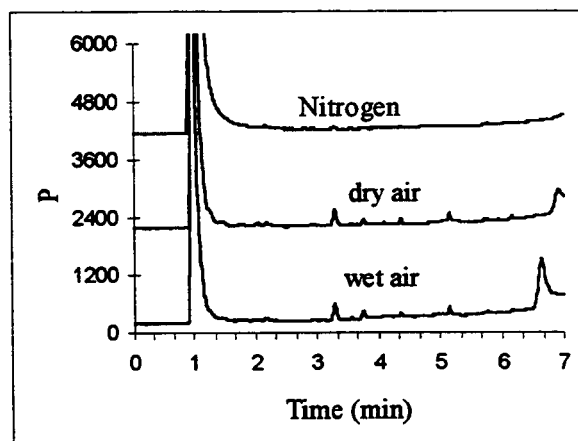


Figure 2b: Peaks other than the major peak are very small. T=484°C.

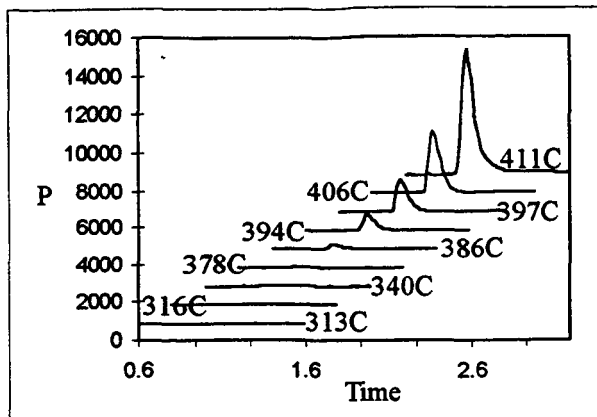


Figure 3: Temperature dependency of the major peaks.

T(°C)	313	316	340	378
Area	trace	trace	trace	497
<hr/>				
	386	394	397	406
	1308	4418	8945	16863
				36503

Table 1: Areas of the major peak at various temperatures.

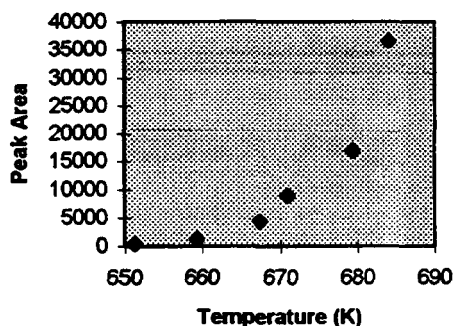


Figure 4a: Temperature dependency of the peak areas.

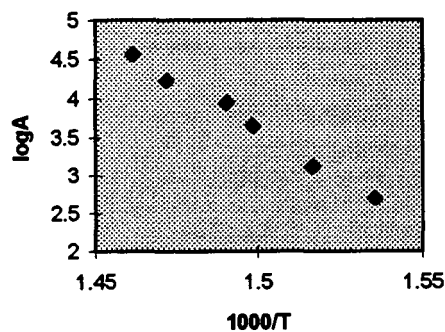


Figure 4b: The data point follows Arrhenius relation with  $E_a=103\text{kcal/mol}$ .

Gas products from reactions in wet air were analyzed by mass spectrometry. Figure 5 shows one of the spectra. There is no peak above 100 amu, the mass of  $\text{C}_2\text{F}_4$  molecule. So the concentrations of chemicals having fragments heavier than 100 amu (such as  $\text{C}_3\text{F}_4$ ,  $\text{C}_2\text{F}_6$ ,...) are negligible. Table 2 lists the mass peaks (less those peaks contributed by air). All fragments in Table 2 correspond to fragments of  $\text{C}_2\text{F}_4$ . We therefore believe that the gas appearing at 0.93 minutes in the gas chromatograms is  $\text{C}_2\text{F}_4$ .

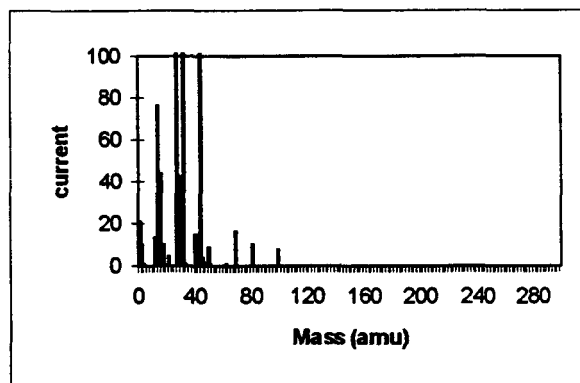
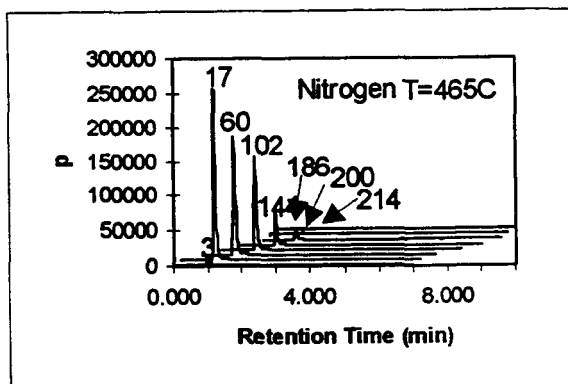


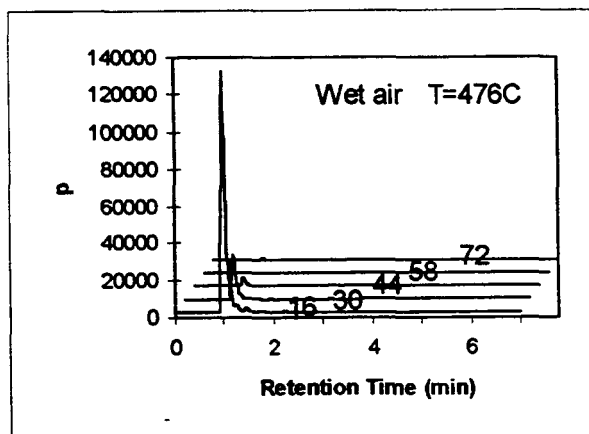
Figure 5: MS of the gas products. No mass heavier than 100 amu was seen ( $T=510^\circ\text{C}$ ).

fragment	C	CF	CF <sub>2</sub>	CF <sub>3</sub>	C <sub>2</sub> F <sub>3</sub>	C <sub>2</sub> F <sub>4</sub>
mass	12	31	50	69	81	100
1000*I/I(31)	325	1000	205	405	250	195

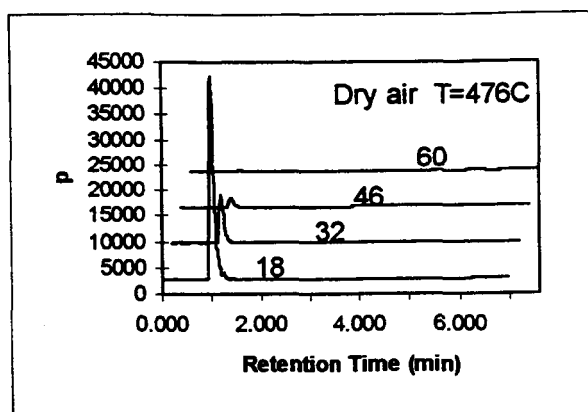
Table 2: The fragments of the gas products.



**Figure 6a:** Chromatogram of the emission from reaction of 1 gram PTFE powder in pure nitrogen. The numbers denote the minutes after the sample was put into the reactor.



**Figure 6b:** Chromatogram of the emission from reaction of 1 gram PTFE powder in wet air. The numbers denote the minutes after the sample was put into the reactor



**Figure 6c:** Chromatogram of the emission from reaction of 1 gram PTFE powder in dry air. The numbers denote the minutes after the sample was put into the reactor

The formation of  $C_2F_4$  was very sensitive to the reaction atmosphere. In pure nitrogen gas, no smoke was formed and  $C_2F_4$  was the only degradation product. The reaction lasted longer and the concentration of  $C_2F_4$  gas in the emission was higher for the nitrogen environment than for the wet air or dry air environments (see figures 6a, 6b, and 6c). Degradation in dry air yielded the least  $C_2F_4$  gas, but the most smoke. Visual observations indicated that the amount of smoke formed by reactions in dry air was much higher than that formed in wet air.

Figures 7a, 7b, and 7c show the results of FTIR analyses of pure PTFE and the smoke powders formed by reactions in wet and dry air atmospheres. The three IR spectra are clearly different. Pure PTFE powder has two relatively sharp peaks around  $1212\text{ cm}^{-1}$  and  $1156\text{ cm}^{-1}$ . The IR spectrum for powder formed by reaction in wet air has a major peak at about  $1101\text{ cm}^{-1}$ , with several smaller peaks located at  $1637\text{ cm}^{-1}$ ,  $1421\text{ cm}^{-1}$ ,  $934\text{ cm}^{-1}$ , and  $805\text{ cm}^{-1}$ . The IR spectrum for the powder formed by reaction in dry air has very large peaks at  $1101\text{ cm}^{-1}$  and  $768\text{ cm}^{-1}$ . These results show that the chemical formula of the powder formed by

reaction in wet air is different from that of the powder formed by reaction in dry air.

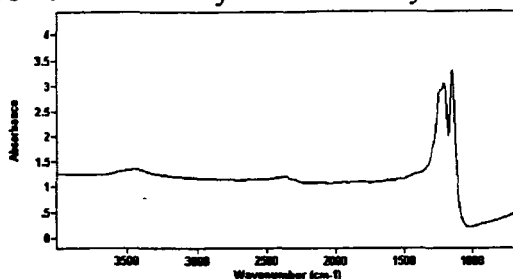


Figure 7a: IR spectrum of pure PTFE powder.

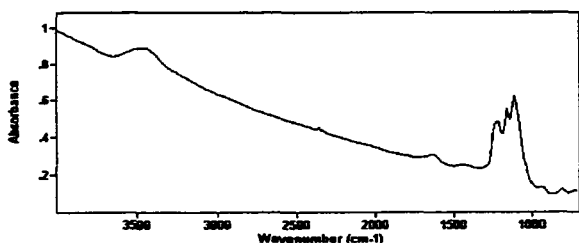


Figure 7b: IR spectrum of powder formed by PTFE reaction in wet air.

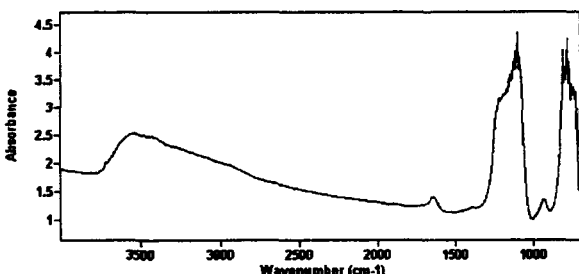


Figure 7c: IR spectrum of powder formed by PTFE reaction in dry air.

In summary, we have studied the thermal degradation of PTFE in pure nitrogen gas, wet air, and dry air at temperatures ranging from 310°C to 510°C. The primary gas product is  $C_2F_4$ . The reaction rate follows the Arrhenius formula  $r = Ae^{-E_a/kT}$ , with  $E_a \sim 103$  kcal/mol. The nitrogen experiments yielded the highest  $C_2F_4$  concentrations, the longest reaction times, and no observable smoke. The dry air experiments gave the

lowest  $C_2F_4$  concentrations, the shortest reaction times, and large amounts of smoke. Wet air experiments gave results intermediate to the nitrogen and dry air experiments. IR spectra indicate differences between smoke formed in wet air and dry air environments.

We are in the process of obtaining more information on the mechanisms of the formation of smoke. Various experiments, including measurements of smoke concentration, reaction at higher temperature, TEM and SEM experiments,  $C_nF_{2n+2}$  ( $n=6, 7,$  and 8) thermal degradation and computer simulations will take place in the near future.

We thank NASA for supporting this research under contract number NAG3-1628.

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