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PTFE and FEP Thermal Stability

Abstract

The thermal stability of PTFE and FEP have been evaluated under a number of conditions: aerobic and anaerobic atmospheres, two temperatures (360C and 500C), and under varying levels of fuel load. The last variable has evidently been scantily appreciated by the larger analytical community, which makes most, if not all, of the previous literature virtually meaningless. Product yield and distribution can easily vary by 10X when the polymer/oxygen mass ratio is changed by a factor of two or three. Nevertheless, these data demonstrate that the data reported by Mabury (1) were an over estimate by approximately a factor of 10,000 for the amount of HFP and TFA produced by the pyrolysis of PTFE at 500C.

Need

So long as we are in the business of manufacturing fluorocarbons, it is likely that periodically we will have a need to be able to respond to internal or external requests for information dealing with PTFE and FEP thermal stability under a variety of conditions. We need to have a body of data that can be evaluated in the context of previous data in the literature and it also needs to be reproducible. At your request, we undertook this work to supply us with the needed information.

Results and Discussion

The latest motivation for these types of studies was provided by the publication of an article in *Nature* (1), which purported to have detected very large amounts of TFA from the thermo-oxidative degradation of PTFE. There exist in the literature many reports of the study of the pyrolysis of PTFE and FEP, some of which are referenced here (2-7).

The Table (electronic attachment) contains the findings of the gaseous degradation products from the pyrolysis of PTFE and FEP using two different detection methods: 1) infrared spectroscopy and 2) gas chromatograph with mass selective detection coupled with a parallel ion chromatography effort for fluoride ion. Because of the differences in what was measured, these two efforts should be viewed as being complementary in many respects. There was no effort to capture or quantitate the amount of resin that remained as a solid (likely condensed ultra-fine particles) in some part of the apparatus, other than in the sample boat.

Experimental variables included either 50% relative humidity air or nitrogen, a temperature of either 500C or 360C, and the fuel load (ratio of mass of oxygen to that of the polymer) was varied from 0.3 to 10.5. Inspection of the table reveals:

- Anaerobic degradation produces substantially more monomer and substantially less oxidized products as compared to an aerobic degradation of both PTFE and FEP. Surprisingly, the largest amount of PFIB is produced in an oxygen starved, but not absent, condition.
- As expected, the amount of degradation products observed at 360C as compared to that observed at 500C is reduced by orders of magnitude for both PTFE and FEP.
- At 500C, the variable that has the most pronounced affect on the product amount and distribution is the fuel load.
- Note that some of the data for PTFE was obtained under conditions similar to those employed by Mabury (1) and indicate that his estimate of the amount of HFP is too high by a factor of 10,000 and for TFA his over-estimate is also near a factor of 10,000. However, note that the data for FEP under these conditions indicate it would be possible to find about 5% TFA produced compared to Mabury's finding of 7.8% for PTFE (which is clearly incorrect).

This work characterizes the types and amounts of degradation products for FEP and PTFE over a variety of conditions and should be of some utility in the future for dealing with future needs. However, it needs to be recognized that not only the amounts, but the types of degradation products are a function not only of the atmospheric composition, the temperature, the polymer type, the fuel load, and the amount of water available, but also of the type of mixing that takes places in the gas phase as well as heat transfer profiles. In other words, it would appear that it will be very difficult to replicate this type of work unless great care is taken to describe the



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experimental apparatus in excruciating detail. This recognition does not appear in any of the analytical reports that we are aware of in the literature. It is likely that it will be very difficult, if not impossible, to reproduce these literature works and hence their utility is greatly limited.

Furthermore, the central issue in the Mabury (1) article was the production of TFA; he argues that there is no natural source and that there is too much in the environment to be accounted for by decomposition of HCFCs and HFCs. Others (8) have argued that TFA is not an environmental risk. Recently a paper by Frank (9) has reported that TFA is a naturally occurring chemical, homogeneously distributed in ocean waters of all ages with a concentration of about 200 ng/L. Hence, TFA from degradation of fluoropolymers would not appear to be an issue at this time.

Lastly, we also attempted to quantify the amount of perfluorocarboxylic acids that were produced in the thermal degradation of PTFE and FEP. No detectable amount of PFOA or C6 perfluorocarboxylic acid were observed in the degradation of PTFE; approximately 50 ppm PFOA and C6 perfluorocarboxylic acid each were detected from the thermal degradation of FEP at 500C.

Experimental Procedures

Tube Furnace Experiments:

Infrared Spectroscopy

The heat source used was a Lindberg/Blue M Model 55035 "Mini-mite" 800-watt tube furnace with 12" heating zone. Quartz tubes of 1" I.D. and 24" length were used to contain quartz sample boats (approx. 3/8" deep x 3.5" long) into which polymers were placed in the center of the furnace. The sample boat was positioned in the center of the furnace where temperature regulation should be optimal. The temperature gradient within this area of the furnace is reported by the manufacturer to be small.

In a typical run, the tube furnace was preheated to a selected temperature of 500C or 360C. Sample was placed in a quartz boat, with the weight (0.1 to 1g) predetermined on an analytical balance. The boat was slid into a quartz tube and the tube sealed with rubber stoppers with transfer lines attached. Gas flow (50% RH air) was established at 40 or 80 ml/minute with a calibrated rotameter.

Air of 50% RH was created by 1:1 combination, by flow rate, of a dry stream of air with a water-saturated stream of air. Dry air was obtained directly from the cylinder. Cylinder air was passed through a 250-ml gas-washing bottle, with glass-fritted stem, ~2/3 filled with deionized water to produce water-saturated air.

Samples were purged with 50% RH air for at least 10 minutes. At the start of a run, a quartz tube containing sample was placed inside the furnace. An evacuated 8L "Tedlar®" gas bag was attached to the exit transfer line to collect gases. After 60 minutes of heating, the gas bag was detached, sealed, and analyzed in a 10 M IR gas cell.



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Gas bags were analyzed in a 10 meter IR gas cell with an MCT detector on a Nicolet Nexus 670 FTIR. The gas cell was evacuated and the contents of the gas bag were drawn into the cell under vacuum. All analyses were done at room temperature and ambient pressure. Any required dilutions, to bring component peaks on scale, were done *in situ* by withdrawal of some sample from the gas cell and replacement with nitrogen. Components were identified and measured based on established reference spectra of pure gases. Quantitative results are reported as mg of gaseous component per gram of sample heated, mg/g. At times, spectral overlap prevented positive identification or reliable measurement of certain components.

Sample weight loss was determined by difference, after heating, from the quartz boat with residue. When sample foamed out of the quartz boat, no weight loss could be determined.

Gas Chromatography with Mass Selective Detection

The thermal degradation experiments were conducted using the same type of furnace as used for the infrared spectroscopy results. The furnace was equipped with a stainless steel flow-through tube to house the sample holder and was preheated to a designated temperature with either nitrogen or air flowing through at a fixed flow rate. A weighed amount of fluoropolymer was placed inside a quartz boat and positioned inside the tube furnace. The resulting evolved gases were directly collected first through exposure to a 1/4" stainless steel sampling tube (20ml in volume, containing methylene chloride) in a dry ice trap and secondarily by a polyvinyl fluoride gas bag.

The gas bag was analyzed for any volatiles by gas chromatography equipped with a mass selective detector (Hewlett Packard 6890 Gas Chromatograph equipped with an HP5873 Mass Selective Detector). The GC/MSD separation was performed with a rtx-1 105m GC column (Restek). Approximately 10 ml methylene chloride solvent was used for the dry ice sample. The resulting methylene chloride solution was analyzed by GC/MSD. To analyze for acids, the methylene chloride solution was derivatized with methanolic HCl so that the acids were converted to the corresponding esters and extracted into a hexane solvent prior to GC/MS analysis. The fluoride content of the evolved gases was determined by first collecting the evolved gases, in separate thermal degradation experiments, into a 20% caustic (NaOH) solution, which was then analyzed by ion chromatography.

Different concentrations of calibration standards for various components were prepared in air and methylene chloride. Trifluoroacetic acid, C6 and C8 perfluorocarboxylic acids, were prepared as methanol solutions, then derivatized with methanolic HCl solution, and finally extracted into hexane as the solvent.



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Control Terms to be included

FEP
PFTE
Thermal Degradation



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Environmental Impact of the Degradation of Materials

Degradation of all materials, whether naturally occurring or man-made, necessarily produces chemicals as a result of the process. The degradation of polyethylene and candle wax can produce a variety of chemicals including formaldehyde (a key ingredient in embalming fluid), acrolein (a quite toxic chemical), along with hundreds of other chemicals.¹ Recently, Ellis *et. al.*² have claimed that the high temperature aerobic degradation of poly(tetrafluoroethylene) (PTFE) and other partially fluorinated polymers produces very large amounts of trifluoroacetic acid. The experimental approach employed by these authors did not allow for them to capture, let alone identify, the vast majority of the degradation products; furthermore, their proposed findings are at odds with the wealth³ of literature that has dealt with this subject for more than half a century.⁴

The major thermo-oxidative degradation product of PTFE is carbonyl fluoride.^{5,6} Carbonyl fluoride was not detected by Ellis *et. al.*² and only small amounts of tetrafluoroethene were detected due to the use of a thermal trapping methodology that was too warm (-78°C) relative to the boiling points of carbonyl fluoride (-85°C) and tetrafluoroethene (-76°C). This flaw in the experimental procedure raises serious questions as to the accuracy of the analysis of the evolved gasses and the ability to characterize either the types or amounts of degradation products.

While it has long been known that the thermal degradation of PTFE can produce trifluoroacetic acid (TFA), production of this chemical depends critically upon the details of the degradation variables. This is reflected by the fact that while some public health laboratories have reported detection of TFA⁵, others have not.⁶ Previous reports of the degradation of fluoropolymers in air indicates that the amounts of TFA produced from copolymers of tetrafluoroethene, which are known to be less stable than polytetrafluoroethylene, were less than 0.2%.⁷ These amounts when compared to the 7.8% reported by Ellis *et. al.*² again point to their inability to produce an accurate measure of the degradation products due to likely difficulties with the analytical procedures.

Release into the environment of chemical species that are long lived is an issue that is worthy of responsible discussion. In the case of TFA, there is evidence of substantial concentrations in the oceans and other bodies of water⁸ that seem to indicate accumulation over a period of several hundred years.^{9,10} The amount of TFA being produced from the thermolysis of PTFE and related polymers, while unknown, is undoubtedly a very small amount compared to that currently present in the environment and to that present in the pre-industrial environment.¹⁰ Apparently, there are natural sources of TFA which have not yet been identified.¹⁰ Furthermore, the environmental risk of TFA in rain water at the concentration (100 ng/l) suggested has been evaluated and concluded to not be an issue at this time.⁹ The detection of other fluorinated acids by Ellis *et. al.*² is also brought into question by the lack of attention to detail evident in their experimental design and execution.

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