

Thermal Destruction and Calorimetry of Ultradisperse Polytetrafluoroethylene

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Abstract

Ultradisperse tetrafluoroethylene powder obtained by thermo-gas-dynamic method (FORUMTM material) was studied by derivatography, mass spectrometry, and differential scanning microcalorimetry. Thermal decomposition of FORUM and its thermophysical properties differ significantly from those of commercial PTFE. The temperature range of decomposition increased more than fourfold: 465–595 °C for PTFE, and 70–550 °C for FORUM. Thermal decomposition of FORUM gave a wide spectrum of molecular fragments with atomic weights from 31 up to 881. In the crystalline phase, there are no phase transitions characteristic of commercial PTFE samples; at the same time, the melting and transformation points in the amorphous part of the polymer are shifted.

INTRODUCTION

Polytetrafluoroethylene (PTFE) possesses a number of unique properties responsible for its wide practical applications. The use of the polymer, however, is restricted because of its weak adhesion to solid surfaces and cold flow. For this reason, researchers are now seeking methods of modifying PTFE, including morphological modification into ultradisperse powders. The thermo-gas-dynamic method [1] affords powder with particles sized less than 1 μm , which is useful as antifrictional, protective, and wear-preventive additives to engine oils [2]. The product is an ultradisperse material whose registered trademark is FORUMTM (FluoroORGanic Ultradisperse Material). Tunnel microscopy [3], laser dispersion [4], and IR and NMR spectroscopy [5] studies suggested that FORUM possesses microscopic and morphological structures different from those of commer-

cial teflon powders. Therefore, it was interesting to study the calorimetric properties and thermal decomposition of FORUM powder and to compare them with those of commercial PTFE samples.

The present contribution deals with the results of our experimental investigations of FORUM by derivatography, mass spectrometry, and differential scanning microcalorimetry.

SYNTHESIS AND EXPERIMENTAL PROCEDURES

FORUM samples were obtained at the Fluoride Materials Laboratory (Institute of Chemistry, Far East Branch, Russian Academy of Sciences). The samples are white powders with an average size of monoparticles of 0.55 μm . Monoparticles are prone to formation of conglomerates 1.5–2.0 μm in size and of larger associates more than 30 μm in size, which are

loosely bonded and can easily be destroyed by air current [4]. The chain macromolecules of the polymer are composed of CF_2 groups with few percent of CF_3 - and other groups (NMR and IR spectral data) [5].

Derivatography measurements were conducted in an air-helium atmosphere with a Q-1500D derivatograph. For measurements, we used a platinum crucible. The heating rate was $5^\circ\text{C}/\text{min}$ in the temperature range 25 – 1000°C ; Al_2O_3 reference; 50 mg samples.

Mass spectra were registered with an MI-1201 mass spectrometer at temperatures of 357 – 410°C for PTFE and 140°C for FORUM using Knudsen's effusion method. A 1 or 2 mg sample of teflon powder was placed in a molybdenum effusion chamber with an inner volume of 0.4 cm^3 , effusion aperture of 0.3 mm in diameter, and channel length of 0.2 mm. The chamber temperature was set in arbitrary steps using a PIT-3 high-precision heat regulator. The temperature of the effusion chamber was measured with a Pt/PtRh thermocouple. The current values of chamber temperature and peak intensity of ion current were recorded concurrently throughout the whole experiment.

Calorimetry measurements were conducted by differential scanning microcalorimetry (DSC) with a modified DSM-2M calorimeter. An approximately 130 mg ultradisperse PTFE (UPTFE) sample was packed into an aluminum container, which was then put in the calorimeter cell. Measurements were conducted at temperatures from -100 to $+500^\circ\text{C}$ with a gradient of $8^\circ\text{C}/\text{min}$. Low-temperature measurements were conducted in gaseous helium. Repeated measurements were in the low-temperature field were carried out to see if the results were reproducible.

Derivatography measurements

Derivatography measurements of PTFE were performed by several research groups. Thus one of the most recent works [6] reported on thermal decomposition of the polymer in air. Polytetrafluoroethylene is a heat-resistant polymer: weight loss starts above 465°C and ends at 595°C . Decomposition was observed [6] as four stages according to changes in the character of

weight loss owing to destruction in different temperature ranges: 465 – 495 , 495 – 540 , 540 – 580 , and 580 – 595°C . Unfortunately, DTG data are lacking [6], which hinders detailed analysis of thermal weight loss. Three exothermic peaks (495 , 540 , and 580°C) were noted on the differential thermal analysis (DTA) curve; these peaks were correlated [6] with oxidation of polymer decomposition products. This is most likely to be due to processes in the block polymer, or more specifically, in its melt, as suggested by the good fit among the characteristic points of the TG and especially DTG curves (Fig. 1, *a*) obtained in our studies of the test samples of commercial PTFE ("Fluoroplast-4"). Note that our measurements of the test sample of PTFE differ from the data of [6] only in the absence of a weak peak at 495°C for the test sample. The discrepancy may be associated with differences in instrument sensitivity; the properties of fluoropolymers, including thermophysical properties, are strongly dependent on the technologies and history of thermal treatment of the sample. The DTG curves (see Fig. 1, *a*) show distinct features suggestive of three-stage thermal decomposition. The DTA curves show two exothermic peaks at 545 and 575°C , which coincide with the features on the DTG patterns.

Derivatography data of FORUM differ strongly from those of commercial PTFE (see Fig. 1, *b*). An appreciable weight loss occurs above 70°C , *i. e.*, at a temperature almost 400°C below the weight loss temperature of commercial PTFE; complete decomposition takes place around 550°C . In other words, the temperature range of decomposition for FORUM is four times wider than for commercial samples. The TG curve shows a change in the decomposition rate in the range 260 – 290°C , which coincides with the anomaly observed in the microcalorimetry study described below.

The DTA curves of FORUM (see Fig. 1, *b*) contain no distinct features typical of commercial PTFE samples (see Fig. 1, *a*), although weak exothermic and endothermic effects are observed at 490 and 530°C respectively.

Mass spectrometry

According to a widespread belief [1, 2], around 500°C in vacuum PTFE preferably dis-

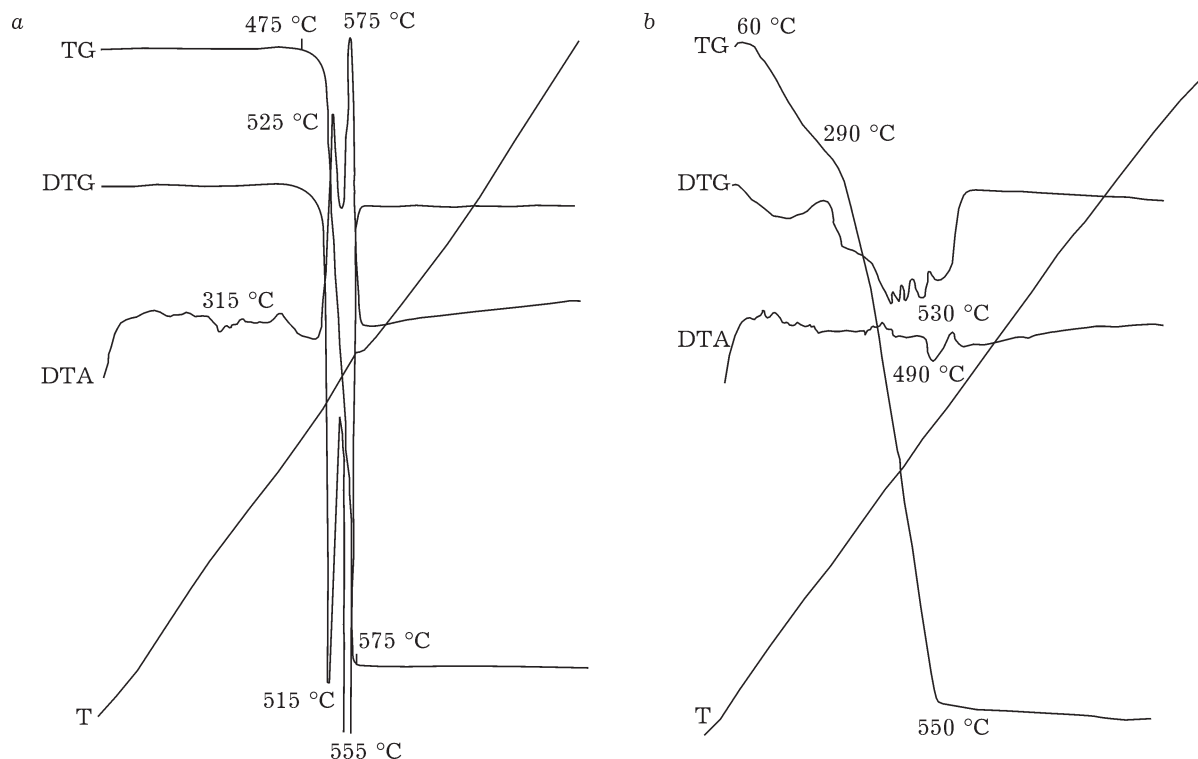


Fig. 1. Thermal analysis data for PTFE (a) and FORUM (b) samples. The figures at the curves refer to decomposition points.

tegrates into monomers, namely, into tetrafluoroethylene C_2F_4 molecules. In the hot reaction zone, the gaseous products of disintegration interact, dimerizing into perfluoropropylene and perfluoroisobutylene. On the cold details of apparatuses, powder is generally formed in small amounts. This powder was thought to be the product of monomer repolymerization because it formed after the traps and filters. Moreover, non-destructive decomposition (without disintegration into monomers) of the polymers was suggested [3], with large particles and oligomers escaping from the polymer block.

Decomposition of PTFE by high-temperature radiolysis [7] (gamma radiation dosage rate $7.66 \cdot 10^6$ R/h; temperature 360, 407, 462 °C) gave a wide spectrum of decomposition products (Table 1). In addition to the above fragments, C_3F_6 (atomic mass 150) and C_4F_8 (200) have been observed. The intensity ratio of the fundamental components varied depending on the temperature, the proportion of low-molecular fragments increasing with temperature. This may be due to disintegration of large

fragments into smaller ones; the process is promoted at elevated temperatures.

High-temperature thermal decomposition of PTFE in various gases [8] confirmed that the mixture of decomposition products contained 15 fragments with weights of up to 131 units (C_3F_5). Pyrolysis in an oxygen-containing atmosphere gave carbon oxyfluoride compounds among other decomposition products.

The range of thermal decomposition products of UPTFE was much wider than for commercial samples (see Table 1); it included fragments with weights from 31 (CF) to 881 ($C_{18}F_{35}$) (data obtained at 140 °C are given). The basic components were C_3F_5 (131), CF_3 (69), C_3F_7 (169), C_2F_5 (119), C_4F_7 (181), and C_4F_9 (219). The amount of the lightest fragment (CF) was low compared with the data of [7]. Note that the amount of tetrafluoroethylene C_2F_4 was also insignificant, although this is the major product of pyrolysis of commercial PTFE.

The chemical composition of the title powder is close to that of PTFE. The crystal structure of UPTFE is the high-temperature (above

TABLE 1

Gas-phase mass spectra of FORUM powder at 140 °C (substance temperature)

Fragmentation ion	<i>m/Z</i>	Relative intensity, %	Fragmentation ion	<i>m/Z</i>	Relative intensity, %
[C ₁₉ F ₃₄] ⁺	874	0.2	[C ₆ F ₁₁] ⁺	281	10.5
[C ₁₈ F ₃₅] ⁺	881	0.4	[C ₆ F ₉] ⁺	243	1.3
[C ₁₇ F ₃₅] ⁺	869	0.45	[C ₅ F ₁₁] ⁺	269	17.1
[C ₁₆ F ₃₁] ⁺	781	0.52	[C ₅ F ₉] ⁺	231	21
[C ₁₅ F ₃₁] ⁺	769	0.08	[C ₅ F ₇] ⁺	193	2.1
[C ₁₅ F ₂₉] ⁺	731	0.66	[C ₄ F ₉] ⁺	219	30.0
[C ₁₄ F ₂₉] ⁺	719	0.13	[C ₄ F ₇] ⁺ *	181	36.8
[C ₁₄ F ₂₇] ⁺	681	0.76	[C ₄ F ₅] ⁺	143	1.3
[C ₁₃ F ₂₇] ⁺	669	0.16	[C ₃ F ₇] ⁺	169	42
[C ₁₃ F ₂₅] ⁺	631	0.79	[C ₃ F ₅] ⁺ *	131	100
[C ₁₂ F ₂₅] ⁺	619	0.2	[C ₃ F ₃] ⁺ *	93	2.6
[C ₁₂ F ₂₃] ⁺	581	1.05	[C ₂ F ₅] ⁺ *	119	34
[C ₁₁ F ₂₃] ⁺	569	0.4	[C ₂ F ₄] ⁺ *	100	30
[C ₁₁ F ₂₁] ⁺	531	1.32	[C ₂ F ₃] ⁺ *	81	1.6
[C ₁₀ F ₂₁] ⁺	519	0.5	[CF ₃] ⁺ *	69	97.4
[C ₁₀ F ₁₉] ⁺	481	1.58	[CF ₂] ⁺ *	50	1.8
[C ₉ F ₁₉] ⁺	469	1.0	[CF] ⁺ *	31	2.6
[C ₉ F ₁₇] ⁺	431	1.71	[COCF ₃] ⁺	97	4.2
[C ₈ F ₁₇] ⁺	419	1.8	[C ₂ H ₂ CF ₃] ⁺	95	0.8
[C ₈ F ₁₅] ⁺	381	2.37	[OCF ₃] ⁺	85	1.0
[C ₇ F ₁₅] ⁺	369	3.7	[HCF ₂] ⁺	51	2.1
[C ₇ F ₁₃] ⁺	331	4.2	[OCF] ⁺	47	0.5
[C ₇ F ₁₁] ⁺	293	0.5	[HF]	20	4.0
[C ₆ F ₁₃] ⁺	319	8.9			

* Radiopyrolysis products of PTFE according to [7].

30 °C) pseudohexagonal phase of PTFE. Hence, the strong difference between the thermal decomposition processes is due to the peculiarities of the morphological structure of the ultradisperse powder.

Due to the large quantity of components in the mass spectrum of UPTFE, the latter can serve as a better reference for mass spectrometer scale calibration compared to the standards now in use.

Calorimetry measurements

DSC measurements showed a specific heat (c_m) anomaly at $T_1 = (-21.5 \pm 1.0)$ °C in the UPTFE sample, which was confirmed by repeated measurements (Fig. 2, *a*). The enthalpy

of the anomaly was determined by integrating the function $\Delta C_p(T)$: $\Delta H_1 = (17 \pm 2)$ J/g. The anomaly is observed over a wide temperature range (80 °C) and has no sharp peaks. In the high-temperature range, an asymmetric anomaly with a maximum of heat capacity is observed at $T_2 = (267.0 \pm 1.5)$ °C (see Fig. 2, *b*). The enthalpy difference is $\Delta H_2 = (34 \pm 5)$ J/g.

At temperatures above 310 °C, excess heat capacity increases abruptly, which is attributed to active decomposition of UPTFE. This is supported by the TG curves (see Fig. 1, *b*) where the slope of the curve increases in the above temperature range. Opening of the microcalorimeter chamber after experiment confirmed that the sample had decomposed.

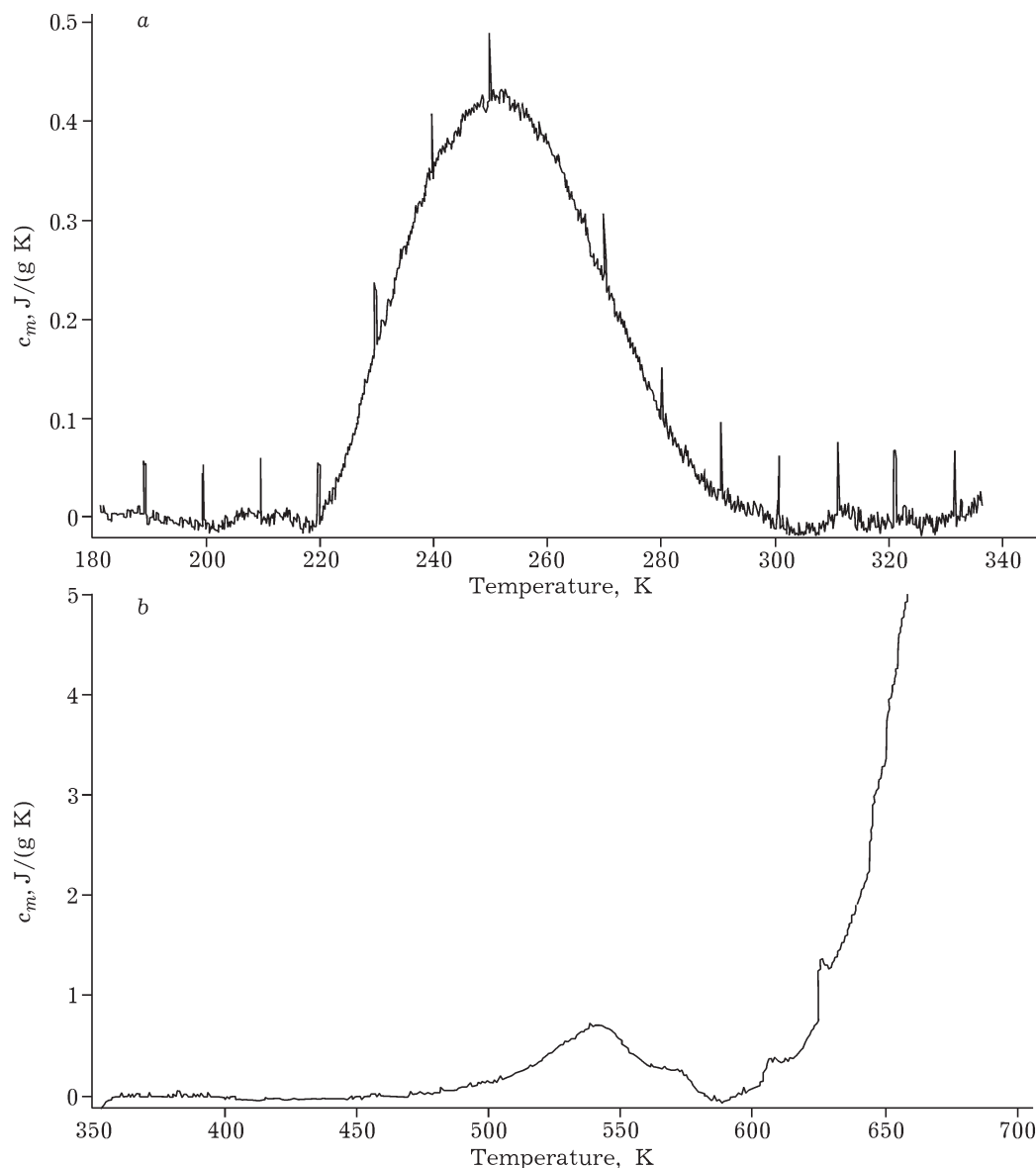


Fig. 2. Low-temperature (a) and high-temperature (b) anomalies of specific heat (c_m) in the FORUM sample from microcalorimetry data.

Numerous data on phase transitions available for commercial PTFE samples and obtained by different physical methods show inconsistencies in both quantitative characteristics and interpretation [9]. However, one can distinguish four regions with specific features of polymer behaviour, °C: $-70 \dots -115$, $20-47$, $115-140$, and $310-344$. The wide temperature ranges may be due to differences in the experimental procedures and in the production process and temperature history for the samples. The second temperature region corresponds to two structural phase transitions in the crystalline part of the polymer associated with changes in pack-

ing of macromolecules in the unit cell and with orientation disordering of CF_2 groups around the axis of the macromolecule. The features in the first and the third region are attributed to processes that occur in the amorphous part of the polymer. The fourth region corresponds to polymer melting.

It is reasonable to give a similar interpretation of data for FORUM. Thus the high-temperature anomaly may be associated with polymer melting; this parameter obviously decreases compared to the similar parameters of commercial PTFE samples. No anomalies can be observed for phase transitions in the crystal-

line part. The low-temperature anomaly lies at least 50 °C higher than for commercial samples and may be interpreted as transformations in the amorphous component of the polymer.

CONCLUSIONS

Our studies showed that thermal decomposition of ultradisperse tetrafluoroethylene powder FORUM obtained by the thermo-gas-dynamic method and its thermophysical properties differ significantly from the properties of commercial PTFE. The temperature range of decomposition increased more than fourfold, which may be indicative of the strong heterogeneity of the FORUM components regarding thermal decomposition. The latter may be attributed to the wide scatter of molecular weight of the ultradisperse powder macromolecules. Thermal decomposition of FORUM yields molecular fragments with atomic weights ranging from 31 to 881. No phase transitions characteristic of commercial samples of PTFE occur in the crystalline phase. At the same time, the melting and transformation points of the amor-

phous part of the polymer are shifted. Since FORUM has virtually the same microscopic structure as commercial PTFE, its thermal behaviour is probably associated with the supramolecular state and morphology of powder particles.

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