



## Effect of supercritical carbon dioxide on ultradispersed polytetrafluoroethylene

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### ABSTRACT

The morphology and structure of ultradispersed polytetrafluoroethylene (UPTFE, FORUM trademark) samples after treatment with supercritical carbon dioxide (sc-CO<sub>2</sub>) were studied by physicochemical methods. It was shown that, in sc-CO<sub>2</sub>, low-molecular-weight fractions are dissolved and removed from pristine UPTFE. The structures of separated fractions were studied. With an increase in the dissolving power of sc-CO<sub>2</sub> (by increasing pressure and varying temperature), the fractionation process gradually involves oligomers with higher molecular weights.

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### 1. Introduction

Polytetrafluoroethylene (PTFE) holds a special position among polymeric materials actively used in industry since it has a combination of valuable properties persistent in a wide temperature range. At the same time, these properties are responsible for the difficulty of processing PTFE since it is soluble in almost none of the known solvents. This causes the search for PTFE modification and processing methods. At the Institute of Chemistry, Far East Division, Russian Academy of Sciences, a method was suggested for processing fluoroplast-4 (F-4) waste into an ultradispersed polytetrafluoroethylene (UPTFE) powder (FORUM trademark, abbreviated from Fluoro**OR**ganic **U**ltradispersed **M**aterial). This material is characterized by a wide molecular weight distribution. Its low-molecular-weight fraction, being insoluble in common organic solvents, is dissolved in supercritical carbon dioxide (sc-CO<sub>2</sub>) [1]. A practical use of the dissolution process requires an understanding of mechanisms of action of a supercritical solvent on UPTFE and knowledge of solubility parameters as a function of pressure and temperature, as well as the structure and properties of the products. In the present work, we experimentally studied mechanisms of action of sc-CO<sub>2</sub> on UPTFE, as well as physicochemical characteristics of low-molecular-weight (LMW) and high-molecular-weight (HMW) UPTFE fractions constituting

the initial material. The main difference between PTFE and UPTFE is possibility of LMW fractions of UPTFE to dissolve in scCO<sub>2</sub>.

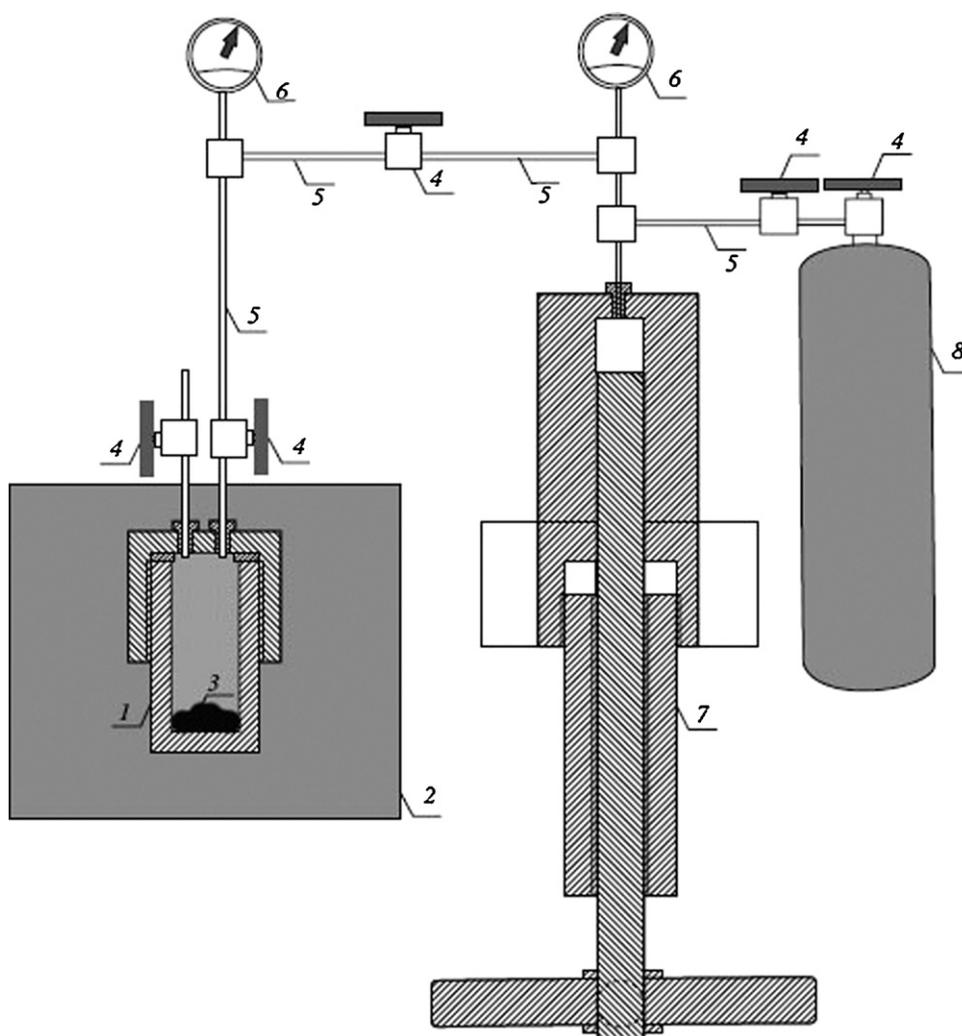
### 2. Experimental

The initial material was FORUM UPTFE produced by pyrolytic treatment of F-4 block polymer (thermogas-dynamic method) [2]. The method consists in generation of gaseous pyrolysis products including fluorocarbon molecules and active radicals. Under definite thermodynamic conditions, this gaseous medium produces nanoaerosols with a typical particle size on the order of a few tens of nanometers, and their coagulation yields block particles 0.3–2.0 μm in size [3,4]. Varying thermodynamic parameters can lead to coarsening of agglomerates to 2–5 μm and formation of bulky associates (10–50 μm), which are destroyed with a change in external conditions. According to [5], powder grains contain low- and high-molecular-weight UPTFE fractions. Chain macromolecules of fractions differ in length, supramolecular structure, and morphology. IR and <sup>19</sup>F NMR studies have shown that molecules of the LMW component have terminal fluoroolefin groups with double bonds (–CF=CF<sub>2</sub>) and pendant trifluoromethyl groups (–CF<sub>3</sub>) [6–10]. Ultradispersed PTFE is insoluble in common organic solvents (acetone, toluene, ethanol, methanol, chloroform, etc.). However, fractions can be separated by repeated pyrolysis at different temperatures.

UPTFE was fractionated in sc-CO<sub>2</sub> under static conditions (i.e., without sc-CO<sub>2</sub> flow through an autoclave) on an experimental high-pressure setup schematically shown in Fig. 1. The setup consists of reaction cell 12 mL in volume 1 for exposure of sample

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**Fig. 1.** Schematic of the experimental setup: (1) a reaction autoclave (12 mL in volume), (2) a thermostat, (3) a sample, (4) a system of valves, (5) a system of capillary pipes, (6) pressure gauges, (7) a generator of pressure (High Pressure Equipment Co., United States), and (8) a CO<sub>2</sub> cylinder.

3; thermostat 2 for maintaining temperature; system of valves 4, capillary pipes 5, and pressure gauges 6 for recording the sc-CO<sub>2</sub> pressure in the cell; pressure generator (High Pressure Equipment Co., United States) 7; and CO<sub>2</sub> cylinder 8.

Fractionation of UPTFE was carried out as follows. Before the experiment, a container made of filters (Nucleopore Corp., United States) with 200-nm pores was prepared. The UPTFE powder to be studied was placed into the container. Our experiments showed that UPTFE in sc-CO<sub>2</sub> first considerably swelled and then dissolved. The dissolved LMW polymer, along with CO<sub>2</sub> molecules, penetrated the filter, which ensured the separation of fractions. For deposition of the dissolved polymer, the quality of the solvent was deteriorated in the course of the experiment by decreasing pressure and/or temperature in the autoclave. The resulting LMW fractions were deposited outside the container as flakes in the bulk or on the autoclave walls. When CO<sub>2</sub> was input into the cell and when it was output after the experiment was finished, the direct escape of the initial powder from the container was excluded. The cell was sealed, and then the required pressure at specified temperature was created in the autoclave placed into thermostat 2 by means of pressure generator 7 through capillary pipe system 5 equipped with valves 4 and pressure gauges 6. The sc-CO<sub>2</sub> density at selected pressure and temperature was calculated with the Nist software (National Institute of Standards and Technology, Gaithersburg, United States). The

sample was exposed in the autoclave and then decompressed. Since preliminary experiments showed that, after 2 h of treatment no appreciable changes in the weight of the UPTFE sample occurred, most experiments were performed at this duration of treatment in scCO<sub>2</sub>. Depending on pressure and temperature maintained in the experiment, the weight of the dissolved LMW fractions was typically 5–20% of the initial sample. UPTFE fractionation was carried out at pressures of 10–70 MPa and temperatures of 45–110 °C. The analysis results are provided only for a few conditions, showing the most dramatic difference. The dissolved LMW fractions were collected for physicochemical studies.

Physicochemical properties of the pristine UPTFE, dissolved LMW fractions, and insoluble HMW fraction were studied by scanning electron microscopy (SEM), IR spectroscopy, X-ray diffraction, and thermogravimetric analysis (TGA).

The morphology of the samples was studied on a JEOL JSM-6380LA scanning electron microscope at an accelerating voltage of 80 kV. The IR spectra of fluoropolymers were recorded on a Thermo Nicolet NEXUS spectrophotometer in the range 400–4000 cm<sup>-1</sup>. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 449C instrument in the temperature range 20–600 °C in a nitrogen atmosphere at a heating rate of 5 K/min. All samples had nearly the same weights of 0.6 ± 0.1 mg. X-ray diffraction studies were carried out on a Shimadzu XRD-6000 diffractometer at

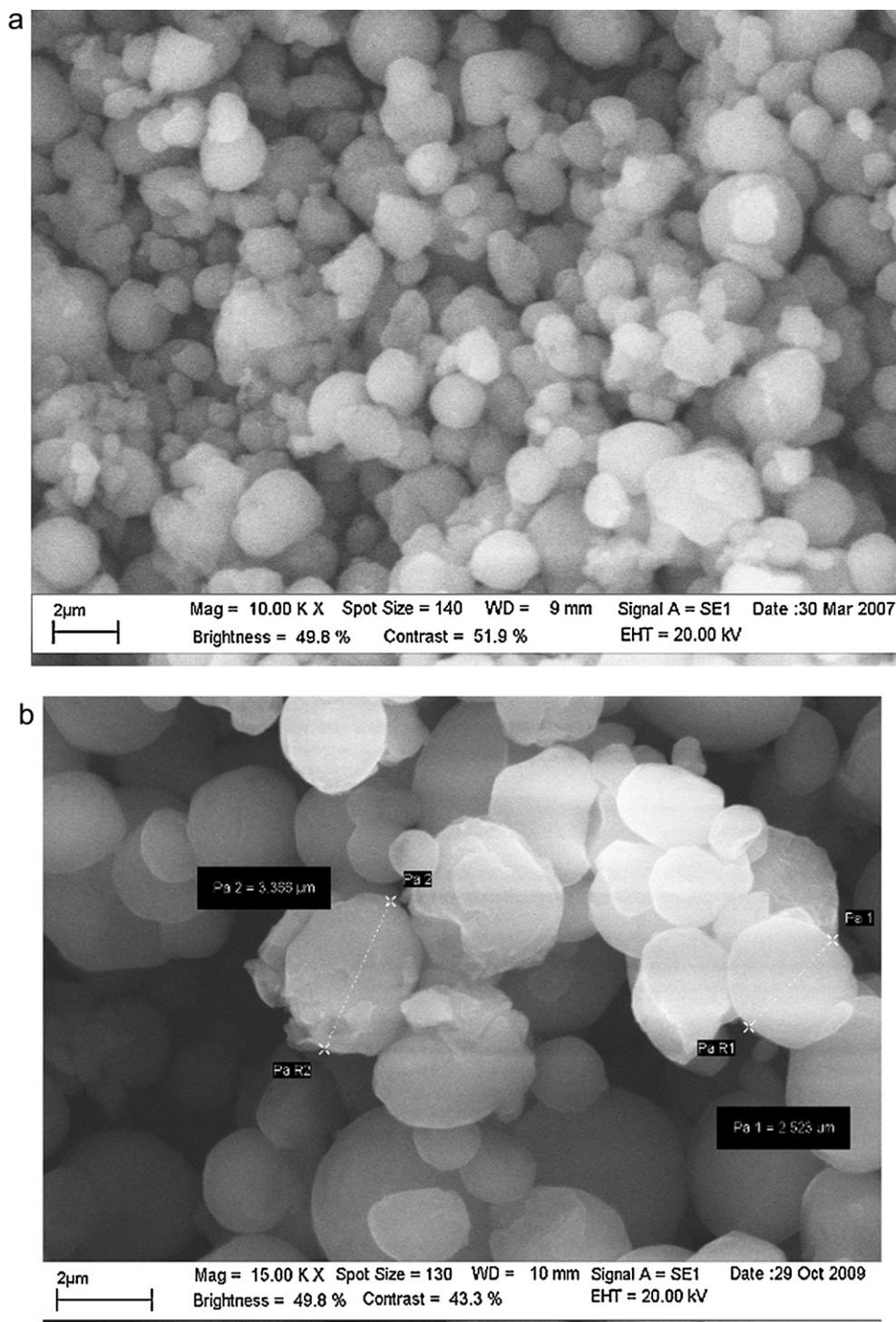


Fig. 2. (a) Initial FORUM UPTFE and (b) the insoluble fraction.

room temperature in the  $2\theta$  range of 2–70° with an increment of 0.02° ( $2\theta$ ).

The degree of crystallinity was estimated from the ratio of the areas under the reflection contours and halo corresponding to the crystalline and amorphous regions of the corresponding X-ray powder diffraction patterns. Profile analysis was performed with the Origin 7.0 program. The diffraction peak shape was approximated by a combination of Gaussian functions. The strongest peaks were used for determining the degree of crystallinity.

### 3. Results and discussion

Fig. 2 shows the SEM images of the pristine FORUM UPTFE (Fig. 2a) and the insoluble fraction obtained after treatment of UPTFE with sc-CO<sub>2</sub> at 60 °C and 60 MPa (Fig. 2b).

Fig. 2 shows that treatment with sc-CO<sub>2</sub> leads to a change in the UPTFE morphology. The particles of the initial sample have a characteristic size on the order of 1  $\mu$ m, whereas the microparticles of the insoluble fraction have a more regular spherical shape as a result of removal of soluble LMW fractions. At the same time, the

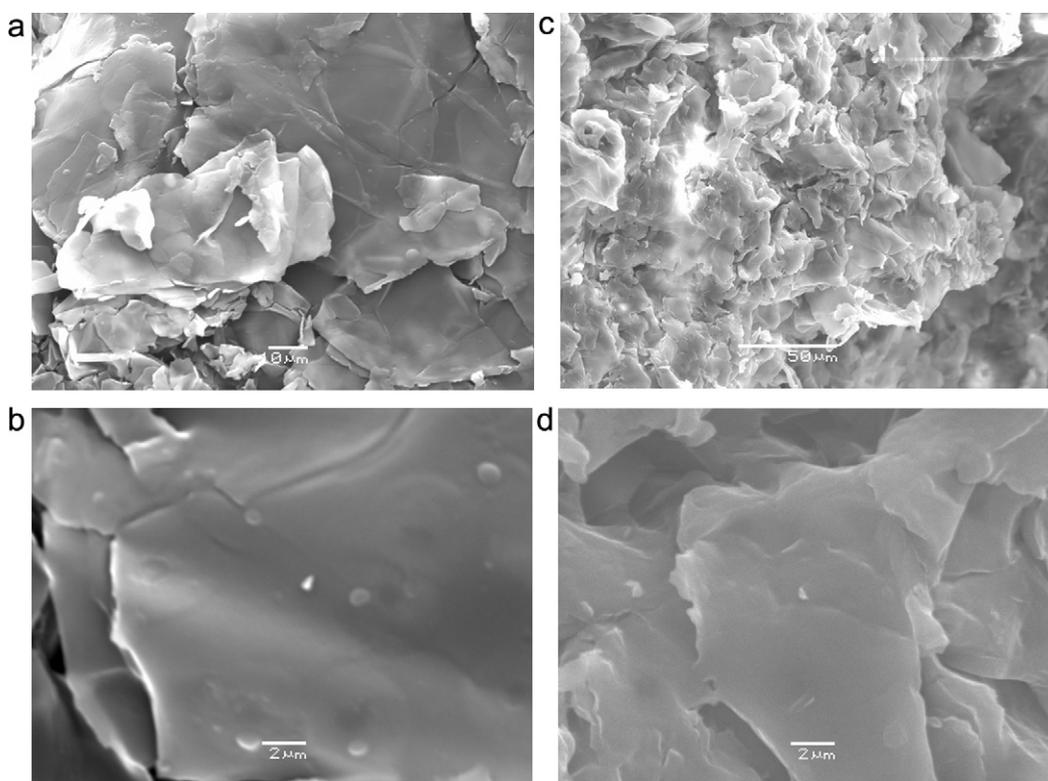


Fig. 3. SEM images of the FORUM fractions dissolved at (a, b) 60 °C and 20 MPa and (c, d) 60 °C and 60 MPa.

LMW fractions extracted from the initial sample (Fig. 3a–d) form lamellar structures of nanometer thickness with characteristic lateral size significantly exceeding the size of initial particles. This can be explained by the possibility that similar films of LMW fractions exist in the initial sample and form multilayer coatings on almost spherical particles. Thus, the exposure to sc-CO<sub>2</sub> changes the morphology of both the soluble and insoluble fractions.

As is known, the weight loss onset temperature measured in TGA experiments depends on the PTFE macrochain length so that the increase in the chain length even by a few units leads to a noticeable increase in the weight loss onset temperature [5]. To verify the validity of this rule for UPTFE fractionation products, two groups of samples of various polymer fractions were prepared. The first group (Fig. 4a) involves the fractions separated at fixed temperature 90 °C and various pressures: curve-1 – 15 MPa, curve-2 – 30 MPa, curve-3 – 70 MPa, as well as curve-4 – the initial sample and curve-5 the insoluble HMW fraction. The second group (Fig. 4b) involves the UPTFE fractions that remained insoluble after treatment with sc-CO<sub>2</sub> at a pressure of 15 MPa and temperature of 65 °C (curve-2, Fig. 4b) and 125 °C (curve-3, Fig. 4b), as well as (curve-1, Fig. 4b) the initial sample. Such an approach allowed us to monitor the effect of thermodynamic parameters of a medium (pressure and temperature) on the properties of the LMW fractions.

Curve 4 in Fig. 4a shows that initial UPTFE starts losing weight at about 100 °C. This process has several steps (100–150, 150–300, 300–500 °C), which is evidence that UPTFE contains LMW fractions with different molecular weights [12].

Weight loss for the LMW fraction obtained at 90 °C and 15 MPa (Fig. 4a, curve 1) begins at the same temperature as for the initial sample (~100 °C) but occurs in one step and ends at a considerably lower temperature of ~200 °C. At the same time, the LMW fraction obtained at 90 °C and 30 MPa (Fig. 4a, curve 2) contains, in addition to the component with the weight loss onset at 100 °C, an extra component for which the decomposition begins at 150 °C and finishes at 250 °C. The weight ratio of these components is ~1:2. The

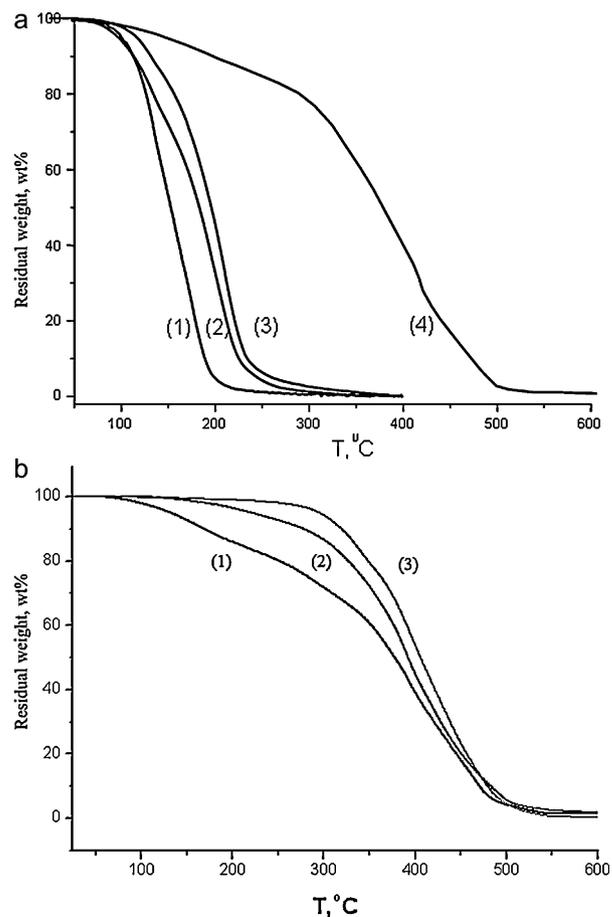


Fig. 4. TG curves for different UPTFE fractions extracted at (a) constant temperature and (b) constant pressure.

**Table 1**  
Results of determination of the solubility of UPTFE in sc-CO<sub>2</sub>.

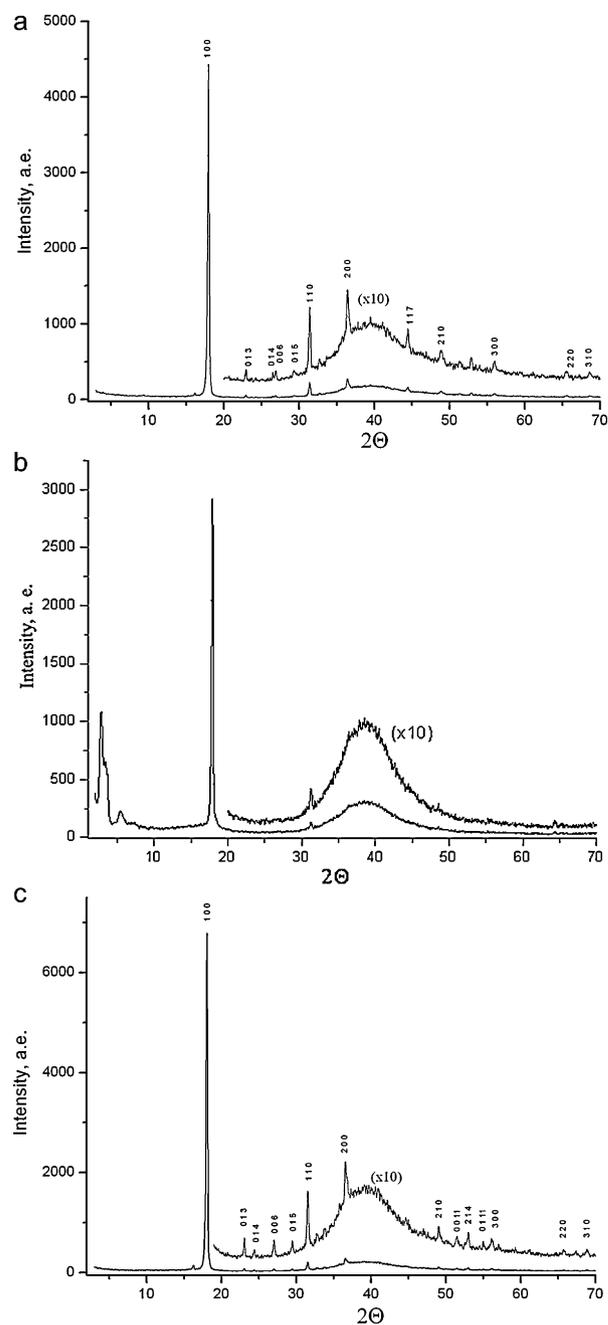
<i>P</i> (MPa)	Solubility <i>S</i> , kg/m <sup>3</sup>	Density scCO <sub>2</sub> , kg/m <sup>3</sup>
<i>T</i> = 318 K		
10	3.09	515.2
15	5.01	747.3
20	5.20	816.3
25	4.79	860.2
30	5.04	893.2
60	4.34	1009.0
<i>T</i> = 333 K		
10	2.41	297.5
15	5.14	613.6
20	6.09	729.4
25	5.68	790.5
30	6.13	832.9
40	5.67	895.7
50	5.99	936.2
70	5.46	999.3
<i>T</i> = 348 K		
10	3.21	237.8
15	5.29	472.9
20	7.37	634.4
25	6.82	706.5
30	7.51	770.9
40	9.87	845.4
50	7.11	888.4
60	7.17	934.8
70	7.09	963.0
<i>T</i> = 363 K		
10	3.79	206.5
15	6.28	378.6
20	8.00	541.7
25	7.91	643.2
30	8.86	708.5
40	8.93	793.0
50	8.50	851.9
60	8.17	893.0
70	9.08	928.9
<i>T</i> = 383 K		
15	6.46	308.1
20	8.54	443.9
25	11.03	552.0
30	10.74	628.7
50	12.11	790.5
60	11.61	836.0
70	11.89	882.4

decomposition temperature of the fraction obtained at 90 °C and 60 MPa (Fig. 4a, curve 3) is higher than those of fractions 1 and 2 but significantly lower than that of the initial UPTFE. At the same time, with increasing sc-CO<sub>2</sub> treatment temperature the thermal stability of the insoluble polymer fraction increases (Fig. 4b). Thus, in the course of dissolution, LMW fractions with different molecular weights are removed from the initial UPTFE. As the pressure increases, higher-molecular-weight fractions of UPTFE start dissolving, which is explained by the enhancement of the dissolving power of sc-CO<sub>2</sub>.

The results on the solubility and separation of low Molecular weight fractions are summarized in Table 1. As can be seen, with increasing pressure and temperature, the concentrations of these fractions in sc-CO<sub>2</sub> increase.

The initial UPTFE, the soluble UPTFE fraction separated at 60 °C and 60 MPa, and the fraction insoluble under the same conditions were studied by X-ray diffraction. The corresponding X-ray powder diffraction patterns are shown in Fig. 5a–c. All patterns contain the strong reflection peak at  $d/n = 4.90 \text{ \AA}$  (18.01°) and the amorphous halo at 38.80° characteristic of UPTFE (Table 2).

Indexing the diffraction reflections of the initial sample points to the presence of only the ( $hk0$ ) reflections ( $l=0$ ) (Fig. 5a), which is accounted for by disordering along the hexagonal axis of the crystalline phase (symmetry group  $p6mm$ ) [7]. The X-ray powder



**Fig. 5.** (a) X-ray powder diffraction pattern of initial UPTFE. (b) X-ray powder diffraction pattern of the UPTFE fraction dissolved at 60 °C and 60 MPa. (c) X-ray powder diffraction pattern of the insoluble UPTFE fraction.

diffraction pattern of the soluble fraction (Fig. 5b) shows, in addition to the major peak at  $d/n = 4.90 \text{ \AA}$  (18.01°) and the amorphous halo at 38.80°, a number of small-angle reflections (at ~2°, 3°, 5°) typical of LMW perfluorinated compounds with a chain length of 15–20 monomer units [13]. It is likely that the small-angle reflections arise from the lowest-molecular-weight component of the LMW fraction, and the peak at  $d/n = 4.90 \text{ \AA}$  (18.01°) is due to the higher-molecular-weight component of the same LMW fraction. The fact that the peaks at ~2°, 3°, and 5° are poorly resolved can be attributed to broad polydispersion. At the same time, peaks at 36°, 49°, and 56° are lacking, which can be explained by disordering of macromolecules along the hexagonal axis of the crystalline phase. This reasoning is in agreement with the results in [9] where

**Table 2**  
X-ray diffraction data.

$a = 5.69 \text{ \AA}$ , $c = 19.42 \text{ \AA}$ , symmetry group $p6mm$			
$2\theta$	$I/I_0$	$d/n$	$hkl$
<b>Initial UPTFE</b>			
17.96	100.0	5.00	100
22.96	1.3	3.92	013
26.94	1.2	3.35	006
29.36	1.2	3.08	015
31.40	5.0	2.88	110
36.44	6.2	2.49	200
46.90	2.4	1.96	117
48.88	2.5	1.89	210
52.88	2.0	1.75	028
56.02	1.8	1.66	300
65.55	1.2	1.44	220
68.64	1.1	1.38	310
<b>Dissolved fraction</b>			
2.78	40.2	32.15474	
3.40	24.4	26.29251	
5.38	8.4	16.61975	
17.90	100.0	5.01374	
31.28	4.9	2.893259	
<b>Insoluble fraction</b>			
18.08	100.0	4.97	100
23.07	1.2	3.90	013
27.04	1.1	3.34	006
29.46	1.1	3.07	015
31.51	3.1	2.87	110
36.58	4.2	2.49	200
49.04	1.7	1.88	210
51.70	1.1	1.79	0011
52.56	1.0	1.76	214
53.04	1.4	1.75	119
55.22	1.0	1.68	0111
56.17	1.2	1.66	300
65.70	0.7	1.44	220
68.90	0.8	1.38	310

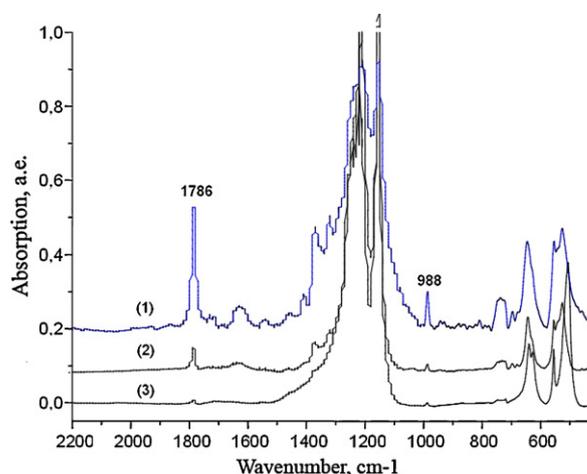
fractions with different molecular weights were removed from UPTFE by sublimation at different temperatures.

Fig. 5c shows the X-ray powder diffraction pattern of the UPTFE fraction insoluble at 60 °C and 60 MPa. As compared with the initial sample, the relative intensity of the peaks at 16°, 23°, 27°, and 29°, which have a nonzero  $l$  index, increases. According to model calculations [7], a higher degree of ordering of helical UPTFE molecules along the hexagonal axis is manifested in the increase in the intensity of these reflections and in the decrease in their width. Thus, efficient removal of the LMW fraction from the matrix formed by UPTFE macromolecules leads to the formation of a more regular crystal structure with symmetry group  $p6mm$ .

The degree of crystallinity of the initial UPTFE and the fractions extracted under different conditions was also studied by X-ray diffraction. It turned out that all samples had a rather high degree of crystallinity (~90%) which did not change upon treatment with  $sc\text{-CO}_2$ . These results are consistent with IR spectroscopy evidence (as shown below).

### 3.1. IR spectroscopy study of UPTFE fractions

Figs. 6 and 7 show the IR spectra of the initial UPTFE, the fraction obtained at 50 °C and 17 MPa, and the insoluble fraction. All spectra show the bands characteristic of PTFE [8]. The strongest absorption bands at 1211 and 1154  $\text{cm}^{-1}$  are due to C–F stretching vibrations in  $\text{CF}_2$  groups. The  $\nu(\text{C}=\text{C})$  vibration is observed as an inflection at ~1233  $\text{cm}^{-1}$ . In a low-frequency region, wagging vibrations  $\gamma_{\omega}(\text{CF}_2)$  are observed at 639  $\text{cm}^{-1}$ . The bands at 555 and 516  $\text{cm}^{-1}$  arise from bending and rocking vibrations of  $\text{CF}_2$  groups, respectively. For the samples under consideration, the intensity ratio of these bands remains the same. As is known, the PTFE

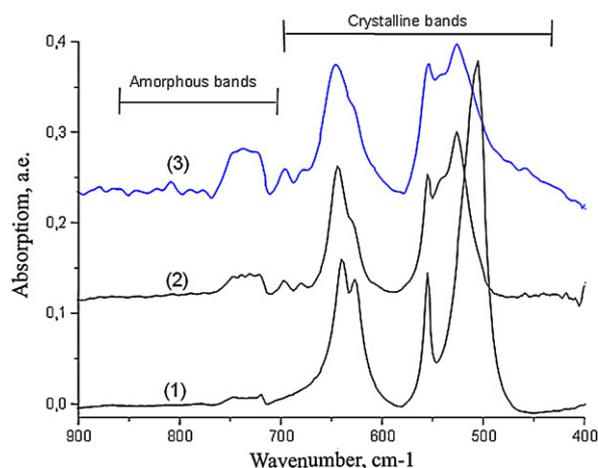


**Fig. 6.** IR spectra of (curve-1) the fraction dissolved at 50° and 15 MPa, (curve-2) initial FORUM UPTFE and the insoluble fraction (curve-3).

molecules have a helical conformation characterized by a doublet at 640 and 625  $\text{cm}^{-1}$ . The band at 625  $\text{cm}^{-1}$  is believed to reflect the change in the sense of the helix from left- to right-handed, and the band at 640  $\text{cm}^{-1}$  reflects the existence of a regular helix in the PTFE structure [15].

As follows from Fig. 7 (curves 1–3), all fractions have different the  $I_{640}/I_{625}$  ratios. The ratio is largest for the LMW fraction (curve-3) and lowest for the HMW fraction (curve-1). Such a behavior is due to the fact that the number of transitions from left-handed to right-handed helices increases with an increase in the macromolecule length.

At the same time, all spectra (Fig. 6, curves 1–3) show the bands at 1786 and 988  $\text{cm}^{-1}$ , which, according to quantum-chemical calculations [16], are responsible for vibrations of terminal  $-\text{CF}=\text{CF}_2$  and  $-\text{CF}_3$  groups, respectively. The stronger these bands, the higher the content of the LMW fraction in a sample. Fig. 6 demonstrates that the intensities of these bands in the spectrum of the extracted fraction (Fig. 6, curve-1)  $I_{1786}/I_{1154} \cong 0.5$ ,  $I_{988}/I_{1154} \cong 0.17$  are considerably higher than for the initial UPTFE ( $I_{1786}/I_{1154} \cong 0.04$ ,  $I_{988}/I_{1154} \cong 0.03$ ) and the insoluble fraction (Fig. 6, curve-2)  $I_{1786}/I_{1154} \cong 0.02$ ,  $I_{988}/I_{1154} \cong 0.01$ . This is evidence that the extracted fraction contains considerably larger amounts of  $-\text{CF}=\text{CF}_2$  groups and pendant  $-\text{CF}_3$  groups. It can be assumed that the macromolecules of this fraction have small molecular weights, so that the terminal groups account for higher percentages



**Fig. 7.** IR spectra (400–900  $\text{cm}^{-1}$ ) of (curve-1) the insoluble fraction, (curve-2) the initial sample and (curve-3) the fraction dissolved at 50° and 15 MPa.

of the MW. At the same time, the removal of the LMW fraction from the initial sample leads to a decrease in the content of terminal  $-\text{CF}=\text{CF}_2$  groups. It is worth noting that the intensity ratio and shape of the amorphous and crystalline bands (778 and 503–512  $\text{cm}^{-1}$ , respectively) remain almost unaltered (Fig. 7, curves 1–3), which is evidence of the same amorphous disordering in all samples.

#### 4. Conclusions

Upon treatment with  $\text{sc-CO}_2$ , the LMW UPTFE fractions are dissolved to form an extra free volume in the initial matrix, which leads to an increase in the specific surface area of the insoluble fraction. After removal of the LMW fraction from UPTFE, the macromolecules of the HMW fraction insoluble in  $\text{sc-CO}_2$  form a crystal structure of symmetry group  $p6mm$  more regular with respect to the hexagonal axis. The LMW fraction contains phases with different molecular weights and packing. The shortest molecules form planar layers and longer oligomers have symmetry group  $p6mm$ . IR spectroscopy and X-ray diffraction have demonstrated that all samples have a high degree of crystallinity and identical amorphous disordering. TGA and IR spectroscopy have shown that dissolution of the LMW fraction begins with the lowest-molecular-weight component and, as the pressure and temperature in the autoclave increase, components with increasing molecular weight are dissolved and removed from the initial sample in the course of fractionation.

Thus, varying the experimental conditions, i.e., pressure and temperature in the autoclave, makes it possible to isolate PTFE fractions of different molecular weights.

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