

---

TO THE 100th ANNIVERSARY OF THE KARPOV  
INSTITUTE OF PHYSICAL CHEMISTRY

---

## Composites Based on Polytetrafluoroethylene and Detonation Nanodiamonds: Filler–Matrix Chemical Interaction and Its Effect on a Composite's Properties

A. P. Koshcheev\*, A. A. Perov, P. V. Gorokhov, N. V. Zaripov, A. V. Tereshenkov, and S. A. Khatipov

*Karpov Physicochemical Research Institute, Moscow, 105064 Russia*

*\*e-mail: koscheev@nifhi.ru, apkoscheev@mail.ru*

Received October 17, 2017

**Abstract**—Specific properties of PTFE composites filled with ultradisperse detonation diamonds (UDDs) with different surface chemistries are studied. It is found for the first time that filler in the form of UDDs affects not only the rate of PTFE thermal decomposition in vacuum pyrolysis, but also the chemical composition of the products of degradation. The wear resistance of UDD/PTFE composites is shown to depend strongly on the UDD surface chemistry. The presence of UDDs in a PTFE composite is found to result in perfluorocarbon telomeres, released as a readily condensable fraction upon composite pyrolysis. The chemical interaction between PTFE and UDDs, characterized by an increase in the rate of gas evolution and a change in the desorbed gas's composition, is found to occur at temperature as low as 380°C. It is shown that the intensity of this interaction depends on the concentration of oxygen-containing surface groups, the efficiency of UDDs in terms of the composite's wear resistance being reduced due to the presence of these groups. Based on the experimental data, a conclusion is reached about the chemical interaction between UDDs and a PTFE matrix, its dependence on the nanodiamond surface chemistry, and its effect on a composite's tribology.

**Keywords:** polytetrafluoroethylene, detonation nanodiamond, properties of composites, mass spectrometry

**DOI:** 10.1134/S0036024418060080

### INTRODUCTION

Polytetrafluoroethylene (PTFE) is widely used in technology due to its high thermal stability, chemical inertness, and low friction coefficient. To overcome the main disadvantage of PTFE (its low abrasion resistance), the polymer is usually filled with a variety of dispersed inorganic particles. The properties of PTFE are better improved by introducing nanoparticles, rather than traditional micron-sized fillers. This effect is assumed to be due to more pronounced structurization accompanying PTFE crystallization [1, 2]. The desired improvement of the mechanical properties of a PTFE-based composite can be achieved using much lower concentrations of a nanofiller, compared to those of micron-sized fillers.

The effect a nanofiller's surface chemistry has on the tribomechanical properties of PTFE-based composites has been described in a number of works. For example, the wear resistance of a PTFE composite was found to increase when using a nanofiller pretreated with acids [3] or subjected to thermal treatment in air [4]. The dependence of the tribological characteristics of a PTFE composite reinforced with carbon nanofibers on the surface chemistry of the latter was established in [5]. Introducing fluorosilane

groups into a surface layer of  $\text{Al}_2\text{O}_3$  nanoparticles resulted in pronounced improvement of a composite's properties in [6]. In these works, the tribological characteristics of PTFE composites were assumed to be affected by the surface chemistry of the filler, as a result of the different degrees of nanoparticle distribution in the polymer matrices or the different polymer morphologies. With respect to existing concepts about the structure of PTFE's macromolecular chains and its chemical inertness, no mention of polymer–filler interaction (reaction) or its relationship to the tribological properties of composites can be found for PTFE in the literature.

Ultra-dispersed detonation diamonds (UDDs) synthesized using explosives [7] are a promising nanomaterial that can be used as a filler for polymer composites, due to the inherent properties of diamonds and the presence of reactive groups on a particle's surface. Industrial amounts of UDDs can be produced using current technologies with and without explosives. A great many works have been devoted to studying the properties of polymer composites filled with nanodiamonds (see [8–16]).

For some polymer materials (e.g., PVA, nylon, epoxy resin, and biodegradable polymers), the role

played by UDD surface chemistry in the properties of a polymer composite was shown in [16–22]. The properties of a composite were in these cases governed by the chemical interaction between functional groups on the surfaces of UDDs and the polymer molecules. The effect UDDs have on the tribological characteristics of PTFE has been described in a number of works [23–26]. The main result from these studies was a considerable improvement in the composites' wear resistance even at low filler contents (~1%), with low coefficients of friction being maintained. No data on the role played by UDD surface chemistry in shaping the properties of PTFE composites can be found in the literature.

There have been a great many works on the thermal degradation of bulk PTFE and the chemical composition of the products of degradation under different conditions. The data on the thermal degradation of composites based on PTFE and such traditional industrial fillers as graphite, bronze, and glass fiber indicate the composition of the thermal degradation products is little affected by these fillers [27, 28]. In some works, however, it was found that the filler had a considerable effect on the composition of products of PTFE thermal degradation. This was observed for  $\text{CoF}_3$  [29] and  $\text{NH}_4\text{HF}_2$  [30], where the change in the mechanism of PTFE thermal degradation is due to the evolution of volatile reactive fluorine-containing compounds accompanying the decomposition of the filler. However, there are no data on the effect heat-resistant fillers have on the composition of the gases that evolve upon the degradation of PTFE composites.

In this work, the chemical interaction of a nanoscale filler with an inert polymer matrix was studied experimentally. The role played by the filler's surface chemistry in this interaction, and the effect it has on the properties of UDD/PTFE composites, were established.

## EXPERIMENTAL

PTFE powders of grades PN90 and F-4 were used to manufacture the polymer composites. The two types of UDDs studied in [31], SN7 (VNIITF, Snezhinsk) and K2 (KSU, Krasnoyarsk), were used as fillers. Modified SN7 UDDs, heated in air at 420°C (sample SN7-oxy), were also used. UDD/PTFE composites were manufactured by processing polymer–filler mixtures with different UDD contents in a knife mill, followed by compacting of the blend and sintering in air at 380°C.

The surface chemistry of the UDD samples was determined via thermal desorption mass spectrometry (TDMS) [31, 32]. For analysis, each UDD sample was heated to 1100°C at a rate of 15 K/min in vacuum, with the evolved gases being directed from the sample heating chamber to the mass spectrometer MX-7304.

The thermal degradation of PTFE composites filled with UDDs (0.03–10 wt %) at temperatures of up to 700°C and a heating rate of 5 K/min in vacuum was monitored using an MX7304 mass spectrometer (mass range  $m/z$ , up to 250 Da), and the gas products of each sample's thermal degradation were analyzed.

The measuring procedure was described in detail in [33]. A Varian MAT731 magnetic mass spectrometer ( $m/z$  range, up to 1400) was used to widen the range of mass numbers, improve the sensitivity of analysis, and register not only gaseous but also low-volatile (condensing) products of the polymer samples' thermal decomposition. In this device, each sample is introduced directly into the region of ionization, the maximum sample temperature being around 450°C.

Commercially available F4K20, F4S15, F4KS2, and F4UV20 PTFE composites filled with coke, cobalt blue, and glass and carbon fibers were also studied by means of mass spectrometry. FEP Teflon copolymer (DuPont) with highly branched chains and radiation-modified (20 Mrad, ~330°C) cross-linked unsaturated F-4 [33] were used as model fluoropolymers with chemically modified chain structures.

The tribological characteristics of the polymer composites (wear, coefficient of friction) were determined using an UMT tribometer according to the finger-disk scheme (dry friction on metal) at a sample load of 5 MPa and a sliding speed of 1 m/s.

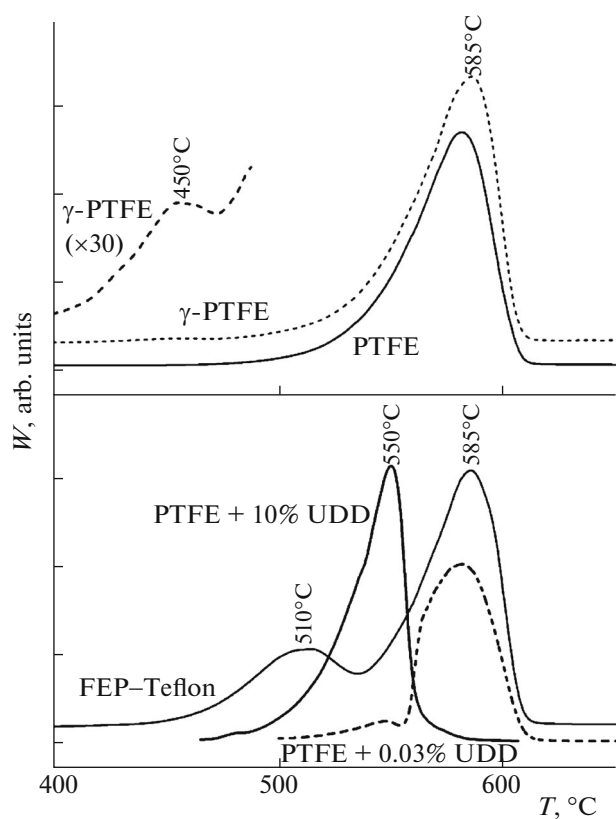
## RESULTS AND DISCUSSION

### *Thermal Degradation of UDD/PTFE Composites*

The vacuum pyrolysis of the samples was studied according to the mass spectrometry technique described in [33]. Composite samples based on PTFE (grade F-4) with different contents of K2-type UDD were used. The initial PTFE (without filler) was characterized by a one-peak temperature profile of gas evolution with a maximum at around 580°C (Fig. 1). According to the mass spectrometry data (Fig. 2), monomer  $\text{C}_2\text{F}_4$  ( $m/z = 31, 50, 81, 100$ ) with around 3%  $\text{C}_3\text{F}_6$  ( $m/z = 69, 131, 150$ ) was in this case the main volatile product, which agreed with the data in [34].

Additional gas release was observed for the UDD/PTFE composite at around 550°C. This peak predominated at high UDD concentrations (Fig. 1). Numerical processing of the temperature profiles of gas evolution presented in Fig. 1 revealed the temperature of degradation corresponding to a half-weight loss to be reduced from the 570°C registered for PTFE to 540°C for the polymer matrix with 10% UDD.

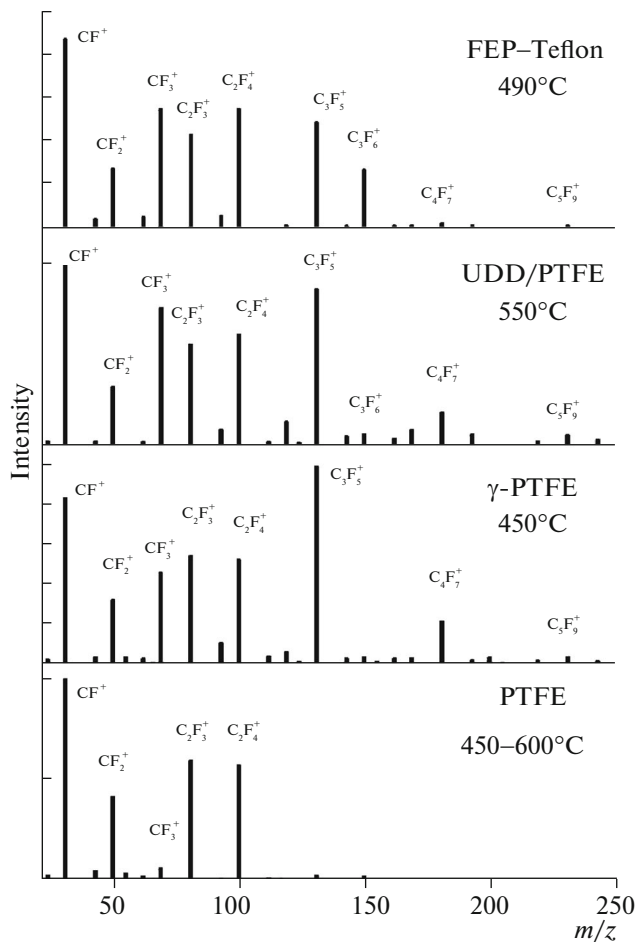
In contrast to the initial PTFE, the mass spectra of the volatile products released from the UDD/PTFE composite during pyrolysis were characterized by increased intensity of the  $\text{CF}_3^+$  and  $\text{C}_3\text{F}_5^+$  fragments and the emergence of such heavier fragments as  $\text{C}_4\text{F}_7^+$



**Fig. 1.** Temperature profiles of total gas release (total ion current in a mass spectrometer) for different PTFE samples heated at a rate of 5 K/min in vacuum.  $W$  is the rate of gas evolution.

and  $C_3F_9^+$  (Fig. 2). According to the NIST mass spectra library,  $C_6F_{12}$ ,  $C_7F_{14}$ , and  $C_8F_{16}$  molecules can be present in products of the thermal degradation of UDD/PTFE composite.

Additional low-temperature gas release was also observed for the FEP copolymer and  $\gamma$ -modified PTFE at around 450 and 500°C, respectively (Fig. 1). As with the UDD/PTFE composite, the mass spectrometry data in these cases showed that fluorocarbon



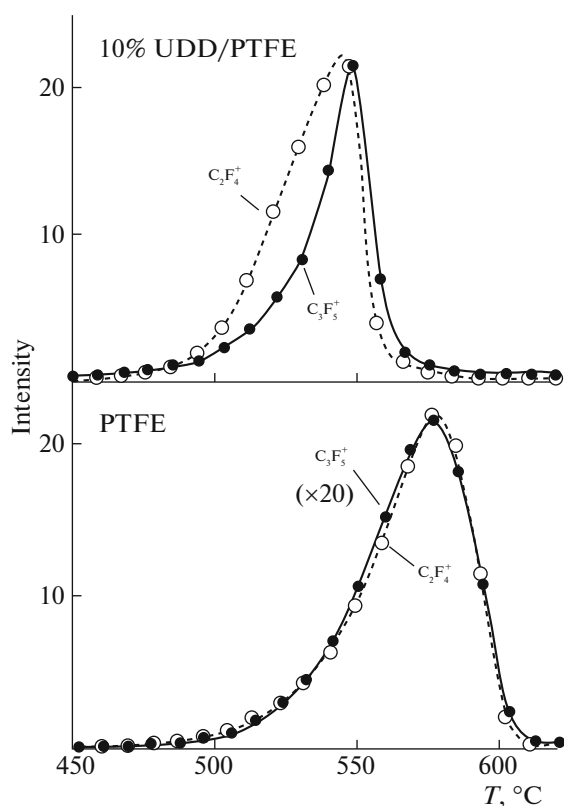
**Fig. 2.** Mass spectra of the volatile products released upon the pyrolysis of different PTFEs.

molecules different from the  $C_2F_4$  monomer, the main product of the thermal degradation of PTFE, were released (Fig. 2, Table 1).

The temperature profiles shown in Fig. 3 for the ion fragments in the mass spectra of the evolved gases are identical for all fragments of the mass spectrum of the initial PTFE, so the thermal degradation of PTFE

**Table 1.** Characteristic mass spectra intensities of molecular fragments (arb. units) in gas mixtures evolved from different types of PTFE in the temperature range of 200–700°C

Fragment	F-4	0.03% UDD/F-4	10% UDD/F-4	FEP Teflon	$\gamma$ -F-4
$CF_2$	1	1	1	1	1
$C_2F_3$	1.66	1.70	1.70	1.66	1.68
$C_2F_4$	1.44	1.60	1.69	1.59	1.54
$CF_3$	0.22	0.32	1.36	0.60	0.44
$C_3F_3$	0.010	0.026	0.176	0.056	0.048
$C_2F_5$	0.001	0.006	0.21	0.015	0.024
$C_3F_5$	0.095	0.21	1.33	0.47	0.36
$C_3F_6$	0.046	0.098	0.17	0.23	0.096



**Fig. 3.** Temperature profiles of the mass spectra peaks of degradation products  $C_2F_4^+$  ( $m/z = 100$ ) and  $C_3F_5^+$  ( $m/z = 131$ ) for PTFE and UDD/PTFE composite.

can be considered to proceed via a single-stage mechanism. The desorption profiles of the mass spectrum components differ considerably for the UDD/PTFE composite (Fig. 3). This proves that the thermal degradation of the composites proceeds via several possible mechanisms, since a temperature dependence is observed for the composition of the products of thermal degradation. This dependence was also observed for the FEP Teflon copolymer and the  $\gamma$ -modified PTFE. There was no difference between the parameters of thermal degradation (the composition of the products and the temperature desorption profiles) of PTFE composites with conventional fillers (coke, cobalt blue, and carbon and glass fibers) and the PTFE matrix.

It should be noted that the above results were obtained using a procedure in which the volatile products of polymer degradation that evolved in the sample heating chamber were introduced into the mass spectrometer, so a highly volatile (gas) fraction was mainly considered. At the same time, no information could be obtained on the low-volatile fraction that condensed on the walls of the vacuum chamber. To overcome this methodological shortcoming, each sample was introduced directly into the mass spectrometer's region of

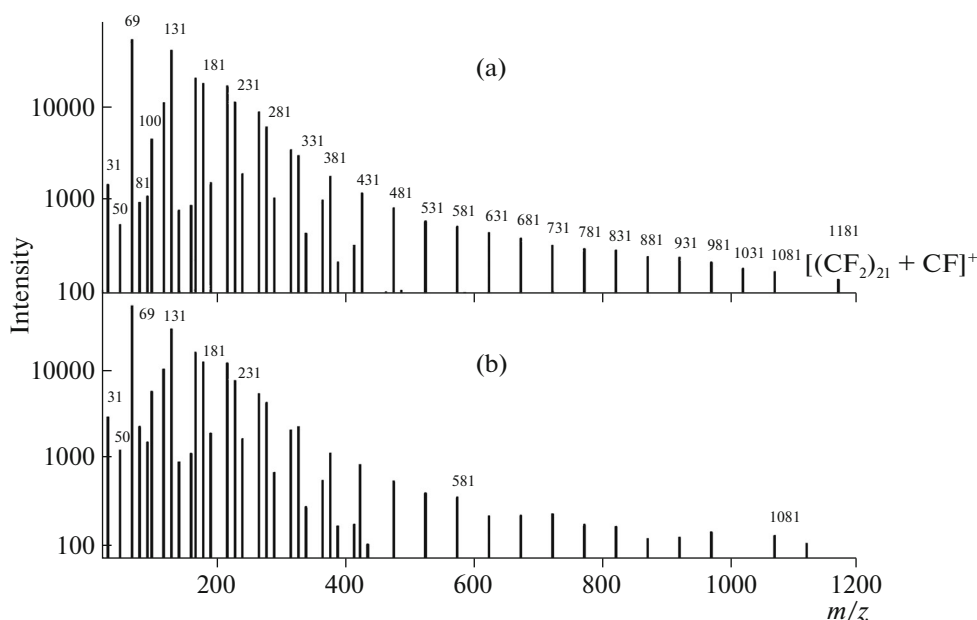
ionization. Although this technique limited the range of sample heating ( $\sim 400^\circ\text{C}$ ), that of the mass spectrum's mass was broadened considerably, and the sensitivity of analysis was increased. The condensing volatile products of polymer thermal degradation were registered in this case as well.

The composition of the products of the FEP Teflon copolymer's thermal degradation was determined using this approach. No heavy  $C_xF_y$  fragments with  $m/z > 300$  were registered in the mass spectra, the main products being  $C_2F_4$  and  $C_3F_6$ . The mass spectra of the products released from the UDD/PTFE composite and radiation-modified PTFE are shown in Fig. 4. There is a striking similarity between the mass spectra of these PTFE-based materials. The presence of  $C_nF_{2n+1}$  homologs in the mass range of up to 1200 Da is typical of both cases, the data being limited by the mass spectrometer's operational mass range. According to the obtained data, the mechanisms of the thermal degradation of the radiation-modified PTFE and UDD/PTFE composites share some common features. The changes in the macromolecular structure that occur due to the UDDs in the polymer matrix are therefore assumed to be similar to the ones that take place in the irradiated polymer.

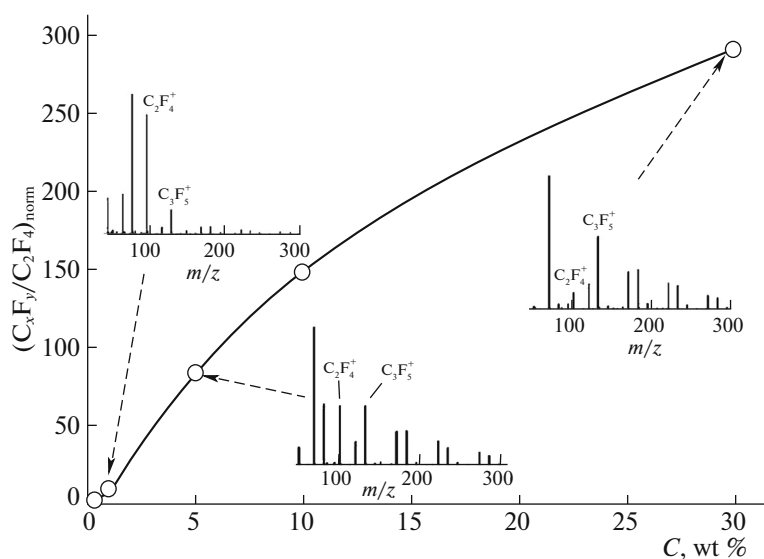
No mass spectra coinciding with the ones shown in Fig. 4 were found in the available mass spectra databases. The mass spectra of the Forum ultrafine organofluorine material manufactured from PTFE by gas-dynamic means [35] are similar to the ones in Fig. 4. We may therefore assume the thermal degradation of UDD/PTFE composites is accompanied by the formation and separation of perfluorocarbon compounds (telomers) containing more than 20  $-\text{CF}_2-$  units.

To quantify the thermal degradation of the composite, the amounts of  $C_2F_4$  monomer and the heavy  $C_xF_y$  fraction released upon heating the composite samples to  $420^\circ\text{C}$ , were determined from the total intensity of the mass spectrum peaks with  $m/z = 31, 50, 81, 100$  and  $m/z = 69, 131, 169, 181$ , respectively. Figure 5 shows the  $C_xF_y/C_2F_4$  ratio grew monotonously along with the concentration of the UDD filler. At a UDD content of 30 wt %, this ratio was around 300 times higher than that of the initial PTFE.

It should be noted that according to weight loss measurements, nearly half the polymer matrix degraded after being heated for 60 min at  $450^\circ\text{C}$  and high concentrations of UDD. Under the same conditions, only several percent of the initial PTFE degraded. The presence of the UDD particles under certain conditions is thus assumed to accelerate the thermal degradation of PTFE and shift the path of PTFE thermal degradation, so heavy fluorocarbon compounds form instead of  $C_2F_4$  monomer.



**Fig. 4.** Mass spectra of thermal degradation products: (a) radiation-modified PTFE (F4 irradiated); (b) UDD/PTFE composite (F4 + 10% UDD), measured with high sensitivity in a wide range of mass numbers at temperatures of around 410°C. A homologous series of  $[(CF_2)_n + CF]^+$  ionic fragments was registered in both cases.



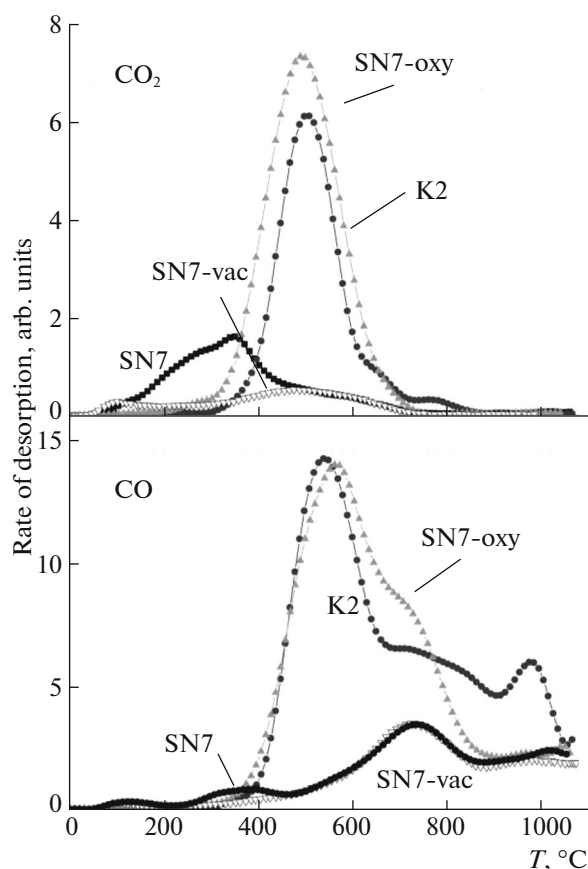
**Fig. 5.** Normalized ratio of the amount of the heavy  $C_xF_y$  fraction (the sum of mass spectra peaks with  $m/z = 69, 131, 169$ , and  $181$ ) and  $C_2F_4$  monomer (the sum of mass spectra peaks with  $m/z = 31, 50, 81$ , and  $100$ ), evolved from UDD- K2/PTFE composites after programmed heating to 420°C in vacuum, as a function of UDD concentration ( $c$ ). The value of  $(C_xF_y/C_2F_4)_{\text{norm}}$  is assumed to be 1.0 for the initial PTFE. The mass spectra of the products of thermal degradation at different UDD concentrations are shown in the inserts.

#### *Effect of UDD Surface Chemistry on the Properties of UDD/PTFE Composites*

UDD powders K2, SN7, and SN7-oxy (subjected to thermal oxidation in air) were used to clarify the effect UDD surface chemistry has on the thermal degradation of PTFE and the tribological properties of

the polymer composite. The composition and structure of UDD surfaces were studied via thermal desorption mass spectrometry (TDMS).

The total concentration of surface groups, determined from the number of desorbed species at temperatures of up to 1100°C in vacuum, can be as high as



**Fig. 6.** Temperature profiles of CO and CO<sub>2</sub> desorption for UDDs of various types when heated in vacuum at a rate of 15 K/min.

20 wt %, with CO and CO<sub>2</sub> being the main components. Figure 6 gives the temperature dependence of the rate of CO and CO<sub>2</sub> desorption for different UDD samples. According to these data, the main difference between SN7- and K2-type UDDs is the concentration and composition of the surface functional groups. The decomposition of these groups is accompanied by the evolution of CO and CO<sub>2</sub>. The content of oxygen-containing groups in K2-type UDDs is much higher than in those of the SN7 type.

**Table 2.** Properties of PTFE composites with 2.5% UDD

Parameter	Polymer matrix	K2	SN7 (I)	SN7(II)	SN7-oxy
<i>c</i> , arb. units	—	5.3	1.0	?	4.9
<i>K</i>	0.23	0.17	0.18	0.17	0.18
<i>W</i> , arb. units	100	24	5.7	29	21

*c* is the total amount of evolved CO and CO<sub>2</sub>, calculated from the area of the thermal desorption profiles and normalized to 1.0 for SN7; *K* is the coefficient of friction; *W* is the rate of stationary wear, normalized to 100.0 for the initial polymer; I is the composite bulk; II is the near-surface region of the composite.

Carboxyl (range of CO<sub>2</sub> desorption, 200–400°C) and carbonyl groups (CO desorption at around 800°C) on the SN7-type UDD surface were detected by means of TDMS, the spectra being processed according to the procedure described in [36]. There were mainly anhydride groups on the K2-type UDD surface (range of CO and CO<sub>2</sub> desorption, 500–700°C). The thermal oxidation of SN7 in air removes carboxyl groups with formation of anhydrides. The concentration and structure of oxygen-containing surface groups in the case of the SN7-oxy sample are similar to those of the K2 sample.

Introducing UDDs into PTFE greatly increased the wear resistance of the composite, with the coefficient of friction remaining about the same, as was observed in other studies. The wear resistance depended nonmonotonically on the UDD content, reaching a maximum near ~3–5%. However, the data in Table 2 show that at the same filler concentration, the wear of the composite depended largely on the type of UDDs. This effect was most pronounced when using the SN7-type UDDs with the lowest content of oxygen-containing groups on their surfaces. The wear rate of the PTFE composite when using the K2 and SN7-oxy UDDs was 4 times higher than for the SN7 UDDs. This rather unexpected result was the first evidence of the effect UDD surface chemistry has on the tribology of PTFE composites. From a practical point of view, the UDDs with the lowest concentration of oxygen-containing groups on their surfaces should be used in manufacturing UDD/PTFE composites.

The sintering at ~380°C is the necessary stage to attain the required properties of PTFE-based materials. The UDD surface chemistry affects even the appearance of the composites after sintering. The bulks of the SN7-containing composites were more darkly colored than their ~0.5-cm-thick surface layers or the composites filled with K2 and SN7-oxy UDDs, which are characterized by high concentrations of oxygen-containing groups. Upon sintering in vacuum, no light-colored surface layers were observed for the CH7/PTFE composite. Our study of the tribological properties of the bulk and near-surface region of the sintered SN7/PTFE composite showed the wear rate of the near-surface region to be much lower than that of the bulk, the first being close to the values obtained for the composites filled with highly oxidized UDDs (K2 and SN7-oxy) (Table 2). According to the mass spectrometry data, the patterns of the thermal destruction of the near-surface layers of SN7/PTFE composite were also similar to those for the composite with an oxidized UDD surface.

This behavior can be explained by the diffusion of oxygen into a composite sample upon sintering, and the subsequent oxidation of the UDD surfaces, which alters the character of the interaction between the UDDs and the PTFE matrix. In addition, this allows us to exclude one more concept explaining the



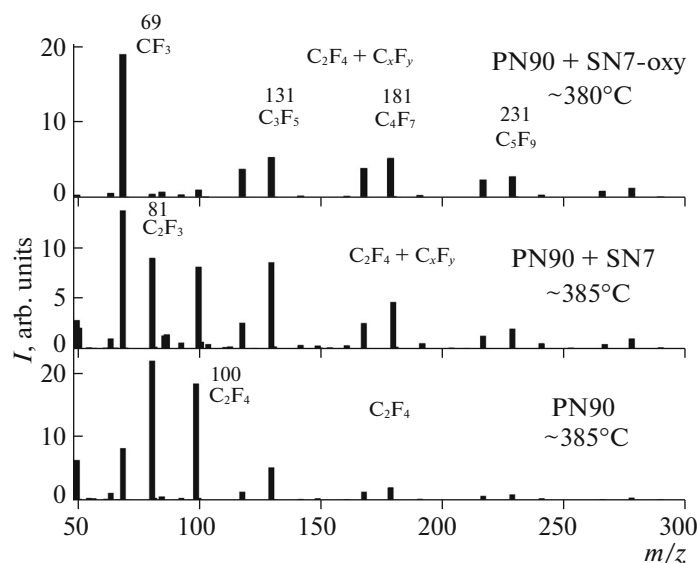


Fig. 7. Mass spectra of the volatile products that evolve upon the sintering of grade PN90 PTFE and PTFE composites containing different UDDs in vacuum.

observed dependence of the composites' wear resistance on the properties of UDDs: the hypothesis that the UDD surface chemistry affects the degree of nanoparticle dispersion in the polymer matrix when manufacturing the composite. The spatial distribution of the filler depends only on the modes of dispersion of the blends containing UDD and PTFE powders. This parameter is thus the same for two regions (the near-surface layer and the bulk) of the SN7/PTFE composite that are characterized by different properties.

The obtained data on the substantial effect the nanodiamond surface chemistry has on the tribological properties of PTFE composites must be considered in technological practice when preparing composites with improved properties. To achieve the maximum reproducible effect of the filler, the UDDs must be preliminarily modified and the composites must be sintered under the conditions described in [37].

The presence of UDDs resulted in increased weight loss of the composite upon sintering, the magnitude of which depended on the type of UDDs. The weight loss was likely due to the effect the UDDs had on the polymer's thermal degradation at relatively low temperatures (380°C). To verify this assumption, the composition of gaseous products released from the composites under sintering in vacuum was studied via mass spectrometry. The parameters of composite sintering reproduced in the experiment were sample size, rate and duration of heating. According to the data shown in Fig. 7, the main product identified upon the sintering of the initial PTFE was  $C_2F_4$  monomer. For the SN7/PTFE composite, the product of degradation also contained heavier  $C_xF_y$  compounds. These compounds were the dominant products for the

SN7-oxy filler. These results led to the conclusion that chemical interaction occurs between PTFE and UDDs upon sintering. As a result of this interaction, the supramolecular structure of the polymer can be transformed upon crystallization. The nature of this interaction depends on the UDD surface chemistry.

The homogenization of PTFE powder–filler blend using high power mechanical dispersers (mills) is one of the steps in the preparation of PTFE composites. Chemical processes can in this case be intensified due to the mechanical activation of the powder particles' surfaces. Two composite samples were prepared to clarify the role played in UDD–PTFE interaction by the mechanochemical processes that accompany the mechanical dispersion stage of composite manufacturing. The first sample was homogenized conventionally using a mill; the second one, via thorough manual mixing until a homogeneous composition was formed. No appreciable differences in the products of the thermal degradation at 420°C were revealed for these composites by mass spectrometry. Evolution of the heavy  $C_xF_y$  products was observed in both cases, with the mass spectra being identical. This data showed the chemical reactivity of the UDD with respect to PTFE was due to the specific properties of the UDD surfaces, rather than to mechanochemical activation.

## REFERENCES

1. A. A. Okhlopkova, S. N. Popov, S. A. Sleptsova, et al., *Zh. Strukt. Khim.* **45**, 172 (2004).
2. V. N. Aderikha, V. A. Shapovalov, and Yu. M. Ple-skachevskii, *J. Frict. Wear* **29**, 120 (2008).

3. S. Lai, T. Li, X. Liu, et al., *Macromol. Mater. Eng.* **289**, 916 (2004).
4. S. Lai, T. Li, X. Liu, et al., *Tribol. Int.* **39**, 541 (2006).
5. Y. Shi, X. Feng, H. Wang, and X. Lu, *Wear* **264**, 934 (2008).
6. D. L. Burris, S. Zhao, R. Duncan, et al., *Wear* **267**, 653 (2009).
7. V. Yu. Dolmatov, *Ultradisperse Diamond of Detonation Synthesis* (SPb. Gos. Politekh. Univ., St. Petersburg, 2003) [in Russian].
8. V. N. Mochalin and Yu. Gogotsi, *Diam. Relat. Mater.* **58**, 161 (2015).
9. A. Kausar, *Polym. Plast. Technol. Eng.* **53**, 550 (2014).
10. V. A. Gerasin, E. M. Antipov, V. V. Karbushev, V. G. Kulichikhin, G. P. Karpacheva, R. V. Talroze, and Y. V. Kudryavtsev, *Russ. Chem. Rev.* **82**, 303 (2013).
11. V. Yu. Dolmatov, *Ross. Nanotekhnol.* **2**, 19 (2007).
12. A. Kausar, *Am. J. Polym. Sci. Eng.* **3**, 149 (2015).
13. B. Bai, P. Wang, L. Yang, and Y. He, *Adv. Mater. Res.* **79–82**, 1839 (2009).
14. T. S. Kurkin, A. N. Ozerin, A. S. Kechev'yan, L. A. Ozerina, E. S. Obolonkova, M. A. Beshenko, and V. Yu. Dolmatov, *Polymer Sci., Ser. A* **50**, 43 (2008).
15. N. F. Attia, J. P. Rao, and K. E. Geckeler, *J. Nanopart. Res.* **16**, 2361 (2014).
16. A. Stravato, R. Knight, V. Mochalin, and S. C. Picardi, *J. Therm. Spray Technol.* **17**, 812 (2008).
17. T. S. Kurkin, E. P. Tikunova, M. Yu. Yablokova, A. S. Kechev'yan, M. A. Beshenko, V. Yu. Dolmatov, and A. N. Ozerin, *Dokl. Chem.* **59**, 53 (2014).
18. U. Maitra, K. E. Prasad, U. Ramamurty, and C. N. R. Rao, *Solid State Commun.* **149**, 1693 (2009).
19. V. N. Mochalin, I. Neitzel, B. J. M. Etzold, et al., *ACS Nano* **5**, 7494 (2011).
20. S. Morimune, M. Kotera, T. Nishino, et al., *Macromolecules* **44**, 4415 (2011).
21. M. Comet, V. Pichot, B. Siegert, et al., *J. Nanosci. Nanotechnol.* **10**, 4286 (2010).
22. D. Miliaieva, S. Stehlik, P. Stenclova, and B. Rezek, *Phys. Status Solidi A* **213**, 2687 (2016).
23. V. Yu. Dolmatov, *Ross. Nanotekhnol.* **2**, 19 (2007).
24. S.-Q. Lai, L. Yue, T.-S. Li, and Z.-M. Hu, *Wear* **260**, 462 (2006).
25. D. P. Lee, J. Y. Lim, D. S. Lim, et al., *J. Nanosci. Nanotechnol.* **9**, 4197 (2009).
26. J.-Y. Lee and D.-S. Lim, *Surf. Coat. Technol.* **188–189**, 534 (2004).
27. L. Odochian, C. Moldoveanu, A. M. Mocanu, and G. Carja, *Thermochim. Acta* **526**, 205 (2011).
28. C. M. Simon and W. Kaminsky, *Polym. Degrad. Stab.* **62**, 1 (1998).
29. V. Yu. Filatov, A. V. Murin, S. A. Kaznenkov, S. V. Khitrin, and S. L. Fuks, *Russ. J. Appl. Chem.* **84**, 147 (2011).
30. V. M. Buznik, Yu. E. Vopilov, A. N. D'yachenko, et al., *Materialovedenie*, No. **5**, 16 (2012).
31. A. P. Koshcheev, *Ros. Khim. Zh. (ZhRKhO Im. D.I. Mendeleeva)* **52** (3), 88 (2008).
32. A. P. Koshcheev, P. V. Gorokhov, M. D. Gromov, A. A. Perov, and U. Ott, *Russ. J. Phys. Chem. A* **82**, 1708 (2008).
33. A. P. Koshcheev, P. V. Gorokhov, A. A. Perov, N. Yu. Petrenko, and S. A. Khatipov, *Russ. J. Phys. Chem. A* **82**, 1715 (2008).
34. J. C. Siegle, L. T. Muus, T. P. Lin, and H. A. Larsen, *J. Polym. Sci. A* **2**, 391 (1964).
35. V. M. Buznik, et al., *Khim. Interesah Ustoich. Razvit.* **5**, 605 (2004).
36. O. Shenderova, A. Koscheev, N. Zaripov, et al., *J. Phys. Chem. C* **115**, 9827 (2011).
37. A. P. Koshcheev, A. V. Tereshenkov, N. V. Zaripov, et al., RF Patent No. 2495886, *Byull. Izobret.* No. 29 (2013).

*Translated by D. Yakusheva*