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Obtaining a Molecular Composite Based on Polytetrafluoroethylene and Silicon Dioxide

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Abstract

A method is proposed for making a composite material based on a molecular mixture of polytetrafluoroethylene and SiO_2 *via* absorbing the on thermal decomposition products of ammonium hexafluorosilicate and polytetrafluoroethylene in ammonia water. Using XRD diffraction analysis, it was evidenced that there is of SiO_2 molecular distribution observed in the composite structure. An influence of the compound introduced upon the yield of fluorosilicon composite output from the gas phase was studied

Key words: polytetrafluoroethylene ammonium hexafluorosilicate, fluorosilicon polymer powder, thermal degradation, kinetics, thermal analysis, structural analysis

INTRODUCTION

Composite materials based on polytetrafluoroethylene (PTFE) and silicon oxide exhibit a number of useful properties, excelling the pure PTFE in the parameters. It should be noted that the introduction of oxygen in the form of oxides in the polymer chain structure causes increasing the heat resistance and several times and improves the compressive strength and the hardness of the material [1]. Several methods were developed for introducing a filling agent in PTFE, but they are all based on the mechanical mixing of the two components and fail in achieving a complete homogenization of the composite [2].

It is obvious, the properties of the composite could completely manifest only in the case of a complete homogenization of its components and developing such a method would provide a breakthrough in the field of the materials science of composite materials. In the case of PTFE the application of a known method of homogenization such as the introduction of one component into the solution of another is impossible owing to the absence of an universal solvent for PTFE and SiO_2.

The analysis of the physicochemical properties of PTFE and silicon compounds demonstrated that only one silicon compound such as ammonium hexafluorosilicate $(NH_4)_2SiF_6$ can be evaporated at the temperature values above 300 °C to be quantitatively condensed under cooling just as PTFE. Consequently, it is possible to obtain a material which is a molecular mixture of condensed PTFE and $(NH_4)_2SiF_6$. An important property of ammonium hexafluorosilicate consists in the possibility of reaction thereof with ammonia water and ammonia according to the following reaction

$$(NH_4)_2SiF_6 + 4NH_4OH = SiO_2 + 6NH_4F + 2H_2O$$

The treatment of the condensed PTFE and $(NH_4)_2SiF_6$ molecular mixture by ammonia water allows one to obtain a molecular mixture of PTFE and SiO_2. In this case ammonium fluoride can be readily removed by means of dissolving [3].

The purpose of this study consisted in developing a technique of quantitative silica penetration into the PTFE polymeric matrix as well as a technology for obtaining a molecular composite consisting of PTFE and SiO_2.

The studies performed earlier demonstrate that the powder-like PTFE and $(NH_4)_2SiF_6$ can be distilled together with the formation of a fluoropolymeric powder, so-called fluorosilicon polymeric powder (FSPP) that contains silicon atoms in the structure.

In order to achieve this goal it is necessary to accomplish a number of tasks. They are: to investigate influencing the amount of $(NH_4)_2SiF_6$ introduced upon the FSPP yield and influencing the $(NH_4)_2SiF_6$ under introduction upon the process of PTFE, thermal decomposition as well as to investigate the properties of the FSPP synthesized by means of thermal analysis and IR spectroscopy methods.

EXPERIMENTAL

Experiments on the recondensation of PTFE and $(NH_4)_2SiF_6$ were carried out in a tube furnace, whereto we placed a nickel retort connected with a sealed tank [4]. In the lower part of the tank there was dissolved ammonia present. Inside the retort we placed the weighed sample portions of PTFE and $(NH_4)_2SiF_6$. The weighed sample portion of PTFE was constant (15 g), whereas the weighed sample portion of $(NH_4)_2SiF_6$ was varied depending on experimental conditions. A vessel was filled with 500 ml distilled water and 100 ml of ammonia solution (25 mass %). The solution was stirred; the vessel was then sealed with a lid. The duration of the experiment was equal to 90 min, the temperature of the distillation process amounted to 575 °C.

Further the mixture of PTFE and $(NH_4)_2SiF_6$ was quantitatively distilled into a vessel with ammonia water. PTFE does not react with water, whereas $(NH_4)_2SiF_6$ is quantitatively converted into SiO_2. The composite obtained consisting of PTFE and SiO_2 was squashed on a filter, dried and investigated by means of thermal analysis, XRD and IR spectroscopy.

The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using a SDT Q 600 combined TGA/DSC/DTA analyzer with TA Instruments Universal V4.2E software for data acquisition; the balance sensitivity was equal to 0.1 μg. The thermal studies of the FSPP were performed in an atmosphere of nitrogen, argon, and air; the heating rate in all cases was equal to 10 °C/min.

The IR spectra were registered with the help of a NICOLET 6700 Fourier spectrometer (Thermo Electron Corporation) in the range of $\nu = 400–4000\ \text{cm}^{-1}$, the allowable error limit of wavenumber scale was equal to $\pm 0.5\ \text{cm}^{-1}$. Samples were prepared by pressing tablets, the ratio between the substance under investigation and KBr amounted to 1 : 300.

The XRD phase analysis was performed using a DRON-3M X-ray diffractometer with a copper anticathode. Registration conditions: I = 25 A, U = 35 kV.

The rate of PTFE thermal decomposition was performed using the method of permanent weighing the mixture of PTFE and $(NH_4)_2SiF_6$ with automatic mass registration. The level of decomposition was determined according to mass caused by forming the gaseous products of $(NH_4)_2SiF_6$ sublimation and of PTFE thermal decomposition. The temperature was maintained to accuracy within ±2 °C.

RESULTS AND DISCUSSION

Determining the optimal amount of $(NH_4)_2SiF_6$ and the influence upon FSPP yield under PTFE and $(NH_4)_2SiF_6$ codistillation

The studies were performed using mixtures consisting of 0, 1, 3, 5, 10, 15, 20, 30 mass % of $(NH_4)_2SiF_6$ and 100, 99, 97, 95, 90, 85, 80, 70 mass % of PTFE, respectively.

It has been determined that the condensation of FSPP (Fig. 1) from the gas mixture resulting from $(NH_4)_2SiF_6$ sublimation and PTFE thermal decomposition products with the further precipitation by ammonia water depends on the initial condition of the mixture loaded into the reactor. The condensation level of PTFE

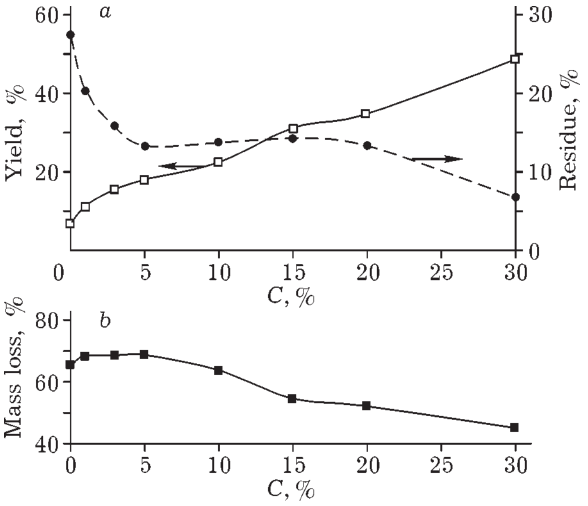

Fig. 1. FSPP yield (*a*) and the mass loss into the gas phase (*b*) depending on the concentration of $(NH_4)_2SiF_6$.

thermal degradation products in the environment of $(NH_4)_2SiF_6$ sublimation with the further treatment by ammonia water exhibits an increase with increasing the concentrations of $(NH_4)_2SiF_6$ in the starting material.

With increasing the concentration of $(NH_4)_2SiF_6$ in the mixture up to 30 % the yield of the target product (FSPP) into the solid phase amounts to 50 mass % as compared to the initial weighed sample portion of the mixture (see Fig. 1, *a*), whereas the mass loss amounts to about 45 % (see Fig. 1, *b*). When this residue in the reactor was about 6 mass % (see Fig. 1, *a*).

The mass loss (see Fig. 1, *b*) depending on the amount of $(NH_4)_2SiF_6$ introduced into the mixture (from 1 to 30 %) ranges from 45 to 70 %, respectively. There is also the mass loss at the expense of ammonium fluoride NH4F that is formed from $(NH_4)_2SiF_6$ *via* the reaction of ammonia-driven hydrolysis. Consequently, the greater $(NH_4)_2SiF_6$ content in the initial mixture, the greater is the content of NH_4F in the solution, and the less is the loss in the form of gases.

For example, in the case of the initial mixture composed of 30 mass % of $(NH_4)_2SiF_6$ and 70 mass % of PTFE there theoretically passes into an aqueous solution as much as 19.9 mass % of the additive in the form of NH_4F, whereas 10.1 mass % thereof is formed as SiO_2. Accordingly, when the yield of the FSPP powder into the solid phase amount is to about 50 mass %, the calculated mass fraction of SiO_2 powder in the FSPP powder should be about 20 %, which is confirmed by the derivatographic examination of FSPP samples.

Thus, with increasing the amount of $(NH_4)_2SiF_6$ additive one can observe increasing the yield of the target product (FSPP) and reducing the mass loss caused by passing into the gas phase.

Thermogravimetric analysis and the kinetic parameters of PTFE distillation process with adding 30 % of $(NH_4)_2SiF_6$

The results of thermal studying the mixtures of PTFE and $(NH_4)_2SiF_6$ are presented in Fig. 2. The initial temperature of the mass loss is equal to 200 °C, the final temperature when the mass loss is registered being equal to 585 °C. The region of changing the mass from 100 % (200 °C) up to 84 % (475 °C) is associated with the sublimation of $(NH_4)_2SiF_6$. The samples were prepared as it follows: 10 g of PTFE powder was mixed with 3 g of $(NH_4)_2SiF_6$, from the mixture a weighed sample portion was taken for analysis.

The DTA curve exhibits the absence of PTFE melting maximum [5] because there is $(NH_4)_2SiF_6$ sublimation process occurring. There is only one exothermic peak observed associated with the oxidation process [5] (at a temperature of 565 °C). The data of thermal analysis in the atmosphere of air demonstrate that the thermal degradation of PTFE with the addition of $(NH_4)_2SiF_6$ occurs in a similar manner with respect to the thermal degradation with the use of NH_4HF_2 [6]: first of all there occurs

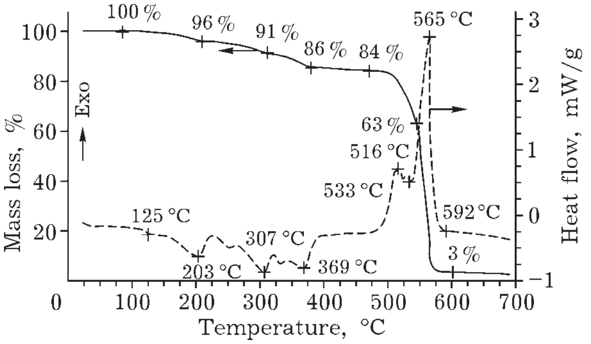

Fig. 2. Derivatographic profile for the mixture of PTFE and $(NH_4)_2SiF_6$ in air. Heating rate being equal to 10 °C/min.

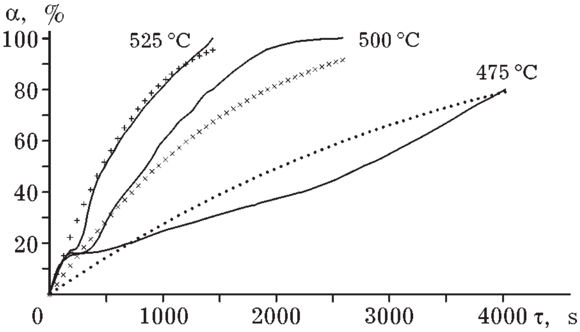

Fig. 3. Level of joint $(NH_4)_2SiF_6$ sublimation and PTFE thermal decomposition (α) depending on time (τ). Solid curves stand for experimental data, points stand for calculated data.

the process of introduced salt decomposition, further there is PTFE thermal degradation observed.

Investigation of the kinetics at the temperature of 575 °C was complicated by a high rate of the process. Experimental studying the effect of temperature on the rate of the mixture thermal degradation and distillation aimed at determining the rate constant and the activation energy values were carried out within the temperature range of 475–525 °C.

Joint thermal PTFE decomposition and $(NH_4)_2SiF_6$ sublimation (Fig. 3) at the temperature of 500 °C and higher is characterized by a uniform decrease in the mass of the sample over time. Increasing the concentration of $(NH_4)_2SiF_6$ exerts almost no effect on the thermal destruction of PTFE. At the temperature of 475 °C there are areas of fast and slow decomposition observed caused by the degradation of the polymer and the sublimation of the additive.

Basing on the data obtained, there have been relationships obtained concerning the level of sample depending on time τ and temperature T within the temperature range of 475–525 °C for PTFE with adding 30 % of ammonium hexafluorosilicate. The process is satisfactorily described by the following equation:

$$\alpha = 1 - \left(2.04 \cdot 10^6 \exp\left[-\frac{147590.2}{RT}\right] \cdot \tau\right)^3$$

The apparent activation energy for the sublimation of 30 % $(NH_4)_2SiF_6$ and the thermal decomposition of 70 % of PTFE is equal to 147 kJ/mol. Consequently, the rate determining stage of the processes is presented by joint degradation and sublimation kinetics; the process could be accelerated by increasing the temperature.

Structural studies of condensed FSPP obtained at different mixture compositions

The molecular structure of the resulting FSPP powders was investigated by means of IR spectroscopy method (Fig. 4). It can be seen

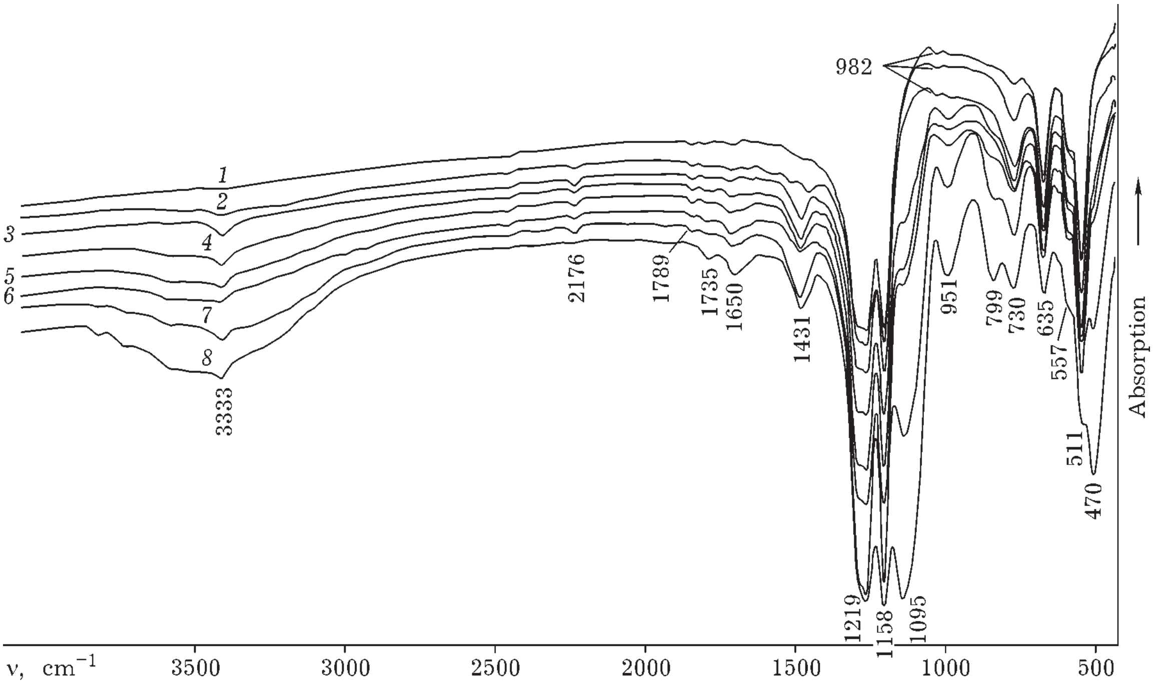

Fig. 4. IR spectra of powders obtained by adding $(NH_4)_2SiF_6$ to the initial mixture (mass %): 0 (*1*), 1 (*2*), 3 (*3*), 5 (*4*), 10 (*5*), 15 (*6*), 20 (*7*), 30 (*8*).

that the IR spectra of FSPP powders have absorption bands similar to IR spectral absorption bands inherent in PTFE [7] (cm^{-1}): 511, 557, 635, 640, 1158, 1219. In the case of mixtures containing 0–3 mass % of $(NH_4)_2SiF_6$ there are bands observed at 982 cm^{-1} those characterize the vibrations of the branched-out CF_3 of CF_2–$CF(CF_3)$–CF_2 type; at a greater amount of adding $(NH_4)_2SiF_6$, up to 30 %, these bands are overlapped by filling agent bands. The bands at 1789 cm^{-1} which characterize the vibrations of the terminal $-CF=CF_2$ group, are observed for all the compounds under investigation. An exception is presented by the mixture consisting of 30 mass % of $(NH_4)_2SiF_6$ and 70 mass % of PTFE: this band is shifted to 1735 cm^{-1}, which is typical for the fluorovinyl group CF=CF within a fluoropolymer chain.

Besides the bands corresponding to the C–F bond, there are bands those characterize the structure of filling agent (SiO_2) of the FSPP composite and the initial compound $(NH_4)_2SiF_6$.

The bands at 3333 and 1431 cm^{-1} indicate N–H bond in the NH^+ ion [8, 9], whereas the bands at 730 cm^{-1} are inherent in Si–F bond within the complex ion SiF_6^{2-} [9–11]. These

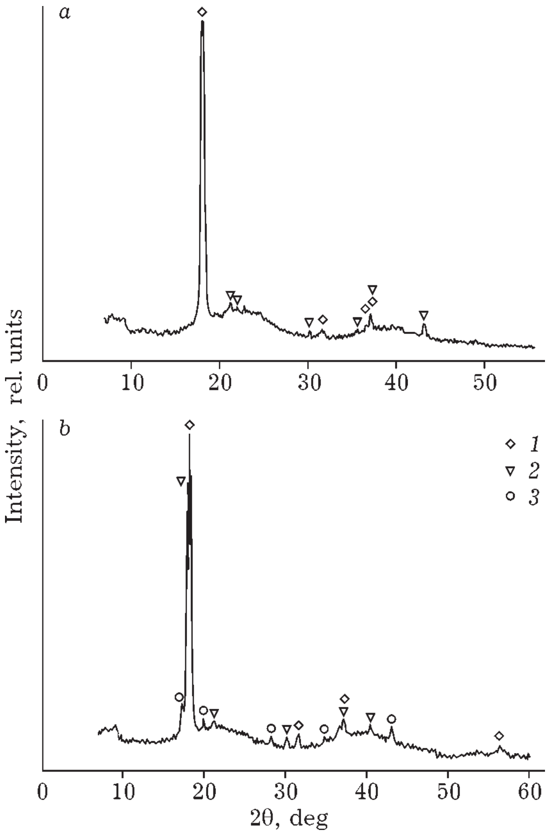

Fig. 5. XRD profiles of FSPP samples obtained by adding 5 (*a*) and 20 % (*b*) of $(NH_4)_2SiF_6$: *1* – $(-CF_2-)_n$, Card 000-47-2217; *2* – $(NH_4)_2SiF_6$, card 000-010269; *3* – $(NH_4)_3AlF_6$, card 000-22-1036.

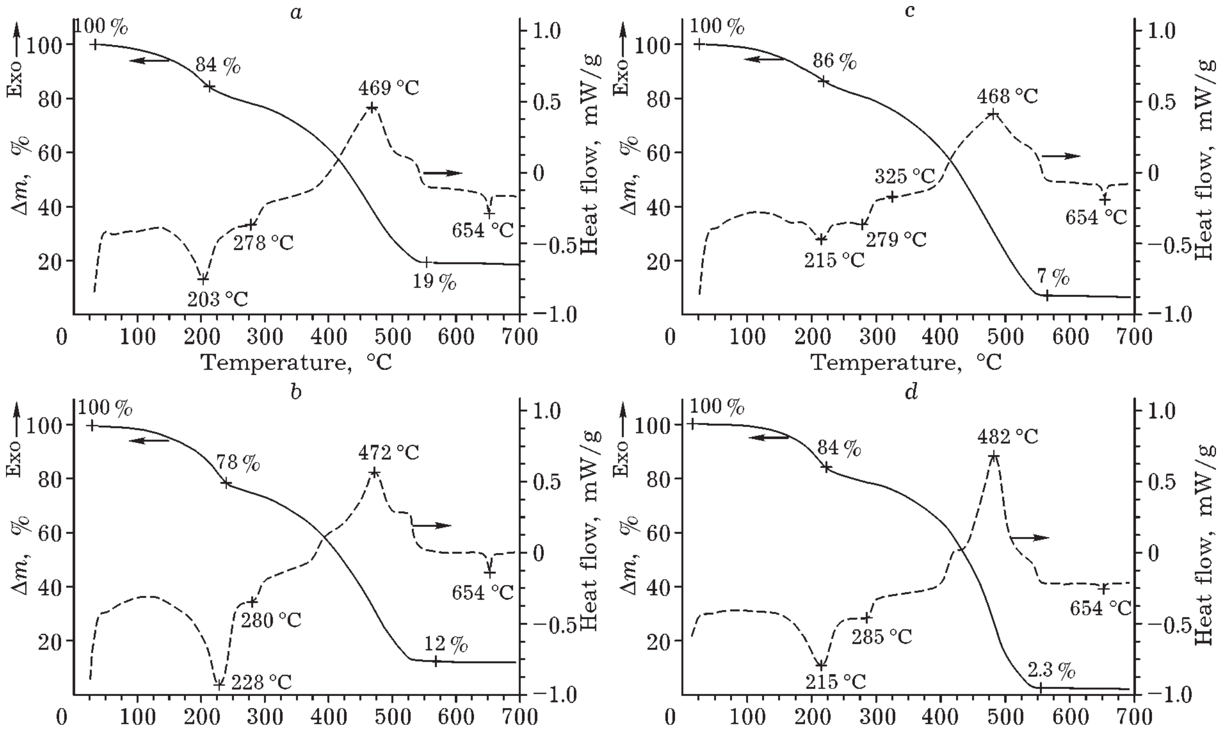

Fig. 6. Derivatographic profiles of synthesized FSPP samples obtained in air from the mixture with the following composition: *a* – PTFE + 30 % of $(NH_4)_2SiF_6$, *b* – PTFE + 20 % of $(NH_4)_2SiF_6$, *c* – PTFE + 15 % of $(NH_4)_2SiF_6$, *d* – PTFE + 10 % of $(NH_4)_2SiF_6$.

bands indicate that the composite structure involves such a compound as $(NH_4)_2SiF_6$.

There are a number of bands observed which are inherent in such a compound as $SiO_2 \cdot nH_2O$ (cm^{-1}): 470, 799, 951, 1095, 1650. The absorption bands at 470 and 1095 cm^{-1} correspond to asymmetric and symmetric vibrations of Si–O–Si fragment, respectively; the bands at 799 and 951 cm^{-1} is characterize silicate ion SiO_3^{2-} [12], whereas the band at 1650 cm^{-1} corresponds to the crystallization water H–O–H [8]. In the IR spectra of the samples synthesized from the mixtures with the mass fraction of $NH_4)_2SiF_6$ ranging within 1–20 %, there is a weak absorption band observed at 2176 cm^{-1} that can be attributed to C=N bond [12]. However, in order to confirm this assumption, additional structural studies are required.

With increasing the content of $(NH_4)_2SiF_6$ in the mixture, an increase in the intensity of the bands corresponding to $SiO_2 \cdot nH_2O$ group is observed.

From the data presented in Fig. 5 one can see that the FSPP sample consists of PTFE and an insignificant impurity of $(NH_4)_2SiF_6$. Figure 5, *b* also exhibits a small admixture of $(NH_4)_3AlF_6$, formed as a result of corrosion of aluminum structures of the laboratory setup.

The thermal decomposition FSPP powders (Fig. 6) occurs in another manner than the thermal decomposition of PTFE and FORUM®, the PTFE thermal destruction product [5]. The temperature of beginning the mass loss is just the same for all the samples being equal to 125 °C, whereas the temperature of finishing the mass change for all the samples is equal to 550 °C. All the samples of FSPP are characterized by a stepwise mass change with increasing the temperature, and in all cases one can observe two fractions having different thermal stability. It is known [5] that the thermal stability of polymers depends directly on the molecular mass. The fraction of low molecular phase in the samples of FSPP under study is equal to 15–20 % with respect to the initial weighed sample portion. The DSC curve for all the samples of FSPP demonstrate an exothermic peak within the temperature range of 469–482 °C, which appears to be associated with oxidation processes [5] in the polymer component of the FSPP. As compared to the initial PTFE, the FSPP samples exhibit the 469–482 °C peak to be 80 °C shifted to a low temperature region, which, to all appearance, could be caused by the presence of a low molecular polymer component (15–20 %) in the FSPP.

As a result of the thermal and structural investigation of the composite FSPP materials obtained it has been found that the polymeric component exhibits a structure similar to a FORUM(®) material [5], but at the same time it has individual features such as the presence of the amino group in the structure and a filling agent such as SiO_2. These properties are directly dependent on the method of obtaining the FSPP product. The technique proposed is remarkable by the simplicity of equipment required for the process.

CONCLUSION

1. We have proposed a method that allows developing a technology for synthesizing molecular composites based on PTFE and SiO_2.

2. In order to introduce SiO_2 into PTFE it is optimal to use $(NH_4)_2SiF_6$.

3. The optimal mass ratio between the components is 70 % of PTFE + 30 % of $(NH_4)_2SiF_6$.

4. The yield of the product into the solid phase is equal to at least 50 mass %.

5. As the source of PTFE one could use wastes, chippings and spent PTFE products.

6. The level of PTFE decomposition (thermal degradation) with 30 mass % of $(NH_4)_2SiF_6$ added as a function of temperature and time can be described by the following equation

$$\alpha = 1 - \left(2.04 \cdot 10^6 \exp\left[-\frac{147590.2}{RT}\right] \cdot \tau\right)^3$$

7. Using IR spectroscopy, it has been proved that all the FSPP samples synthesized contain O–Si–O bonds in the structure and exhibit all the characteristic bands inherent in PTFE.

8. The XRD phase analysis does not reveal SiO2 crystals in the structure of FSPP, which indicates the fact that SiO_2 is involved in the molecular structure of the polymer.

9. The method proposed is simple in equipment design; it does not require for expensive reagents and could be implemented in the industry.

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