PRODUCTION OF MOLECULAR COMPOSITES BASED ON POLYTETRAFLUOROETHYLENE AND TITANIUM DIOXIDE

A.L. Lashtur

Scientific Supervisor: Asst. A.S. Kantaev

Linguistic Advisor: Senior teacher, N.V. Daneykina

Tomsk Polytechnic University, Russia, Tomsk, Lenin str., 30, 634050

E-mail: all1@tpul.ru

Abstract

The method of creation of composition material on the basis of molecular mixture of polytetrafluorethylene and TiO2, by absorption of the products of thermal decomposition of polytetrafluoroethylene and ammonium hexaflorotitanate on ammonium water is offered. Molecular distribution of TiO2 in the structure of composite is well-proven by the X-ray diffraction analysis. Influence of the entered connection on the yield of titanium-fluorpolymeric composite from a gas phase is researched.

Key words: polytetrafluorethylene, ammonium hexaflorotitanate , titanium-fluorpolymeric powder, thermal destruction, process kinetics, thermal analysis, structural analysis.

Introduction

Composition materials on the basis of polytetrafluorethylene (PTFE) and titanium oxide possess a number of useful properties excelling clean PTFE by their characteristic features. It is necessary to notice that introduction of oxygen in the form of oxides into the structure of polymeric chain promotes heat-resistance, increases durability at compression and hardness of material by several times [1]. A few methods of filler introduction into PTFE have been worked out, but all of them are based on mechanical mixing of two components and do not allow obtaining complete homogenization of composite [2].

Obviously, the properties of a composite can develop to a full degree only during complete homogenization of its components, and finding such a method will allow making breakthrough in area of materials science of composition materials. In case of PTFE well-known methods of homogenization, such as the method of introduction of one component into the solution of the other is impossible because of absence of universal solvent for PTFE and TiO_2.

The analysis of physical and chemical properties of PTFE and compounds of titanium showed that ammonium hexaftorotitanata $(NH_4)_2TiF_6$, as well as PTFE, evaporates at a temperature higher than 300°C and condenses quantitatively at cooling.

Thus, it is possible to get material consisting of a condensate with molecular mixing of PTFE and $(NH_4)_2TiF_6$. Important property of ammonium hexaftorotitanata is that it can react with ammonia and ammoniun water on the reaction given below (1).

$$(NH_4)_2TiF_6 + 4NH_4OH = TiO_2 + 6NH_4F + 2H_2O \quad (1)$$

Processing of molecular mixture of condensed PTFE and $(NH_4)_2TiF_6$ with ammoniun water will allow getting molecular mixture of PTFE and TiO_2. Ammonium fluoride is easily removed by dissolution [3].

The aim of research was the development of a method of quantitative introduction of titanium dioxide into a polymeric matrix from PTFE and technology of receiving molecular composite of PTFE and TiO_2. Preliminary research shows that mixture of powdery PTFE and $(NH_4)_2TiF_6$ are sublimated with formation of fluorpolymeric powder, which has an atom of titanium of the given titanium-fluorpolymeric powder (of TFPP) in its composition.

For the achievement of the set aim it is necessary to solve the following tasks:

1) Research the influence of amount of introduced $(NH_4)_2TiF_6$ on the output of TFPP;
2) Research the influence of introduced $(NH_4)_2TiF_6$ on the process of thermal decompositesition of PTFE;
3) Study properties of synthesized TFPP by means of methods of thermal analysis.

Development and results

Research was conducted for mixtures containing 1, 5, 10, 15, 20 and 30% by mass of $(NH_4)_2TiF_6$ and 99, 95, 90, 85, 80 and 70% by mass of PTFE accordingly.

Condensation of TFPP from gas mixture of $(NH_4)_2TiF_6$ and PTFE sublimation with the subsequent precipitation by ammonium water depends on proportion of a mixture loaded in a reactor. The degree of condensation of thermal destruction products increases with the increase of concentration of $(NH_4)_2TiF_6$ in a mixture.

The degree of condensation of thermal destruction products of PTFE in gaseous medium of $(NH_4)_2TiF_6$ increases with the increase of concentration $(NH_4)_2TtiF_6$ in an initial load. From experimental data it is evident, that the highest yield YFP is observed at introduction of 30% $(NH_4)_2TiF_6$into PTFE.

When the concentration of $(NH_4)_2TiF_6$ increases to 30% the yield of the final product (YFP) of about 40% by mass from the initial sample weight of mixture in a hard phase is provided, and percentage of gas losses is slightly more than 20% , but residue in a reactor makes about 40% by mass.

When the concentration of $(NH_4)_2TiF_6$ decreases to 20% by mass, losses in the form of gases increase to 30% and the yield of the final product also decreases by 10%. The percentage of residue changes proportionally to the losses in a reactor.

Thus, it is obvious that the optimal amount of addition of $(NH_4)_2TiF_6$ makes 30% by mass, which provides the maximum yield of the final product (YFP).

Joint thermal decomposition of PTFE and sublimation of $(NH_4)_2TiF_6$ at a temperature of 500^0C and higher possesses high speed of process, while the sublimation of addition $(NH_4)_2TiF_6$ accelerates the process of decomposition, which can be noted on the lines at 500^0C and below and is expressed by a smooth concavity on the area from 30% to 60%.

The presence of the second component $(NH_4)_2TiF_6$ practically does not affect the speed of process. Time of complete decomposition and sublimation is practically the same as for other fluorides examined within the framework of this work.

On the basis of the resultin data dependences (2) of the degrees of joint sublimation of addition $(NH_4)_2TiF_6$ and thermal decomposition of PTFE (α) on the time (τ) and temperature (T) within the interval of temperatures 475…525ºC. Process is well described by equalization of contracting sphere.

$$\alpha = 1 - \left(1 - 1{,}32 \cdot 10^{8} \cdot \exp\left[-\frac{174453}{R \cdot T}\right] \cdot \tau\right)^{3} \quad (2)$$

Apparent energy of sublimation process activation of 30% (NH4) 2TiF6 and thermal decomposition of 70% PTFE makes the 174kJ/mol. As a result the limiting step of this process kinetics of chemical reaction. A method of process acceleration is temperature increase.

Thermal decomposition of TFPP powders differs from PTFE and FORUM ® the product of thermal degradation of PTFE [7]. The temperature of weight loss start is the same for all the samples and is 160 ° C and the final temperature of the end of mass change of the samples is 550 ° C.

Step weight change is characteristic for all samples of TFPP and two fractions with different thermal stability are clearly seen. Low-molecular phase comprises 15-20 % of the original sample. Endothermic peak, located in the region of 380 - 390 °C on DSC (differential scanning calorimetry) curve, is observed for all samples. This is due to removal of crystal water from the inorganic component of fluorpolymeric composite, [8] , wherein a peak is characteristic only for concentrations of mixture of above 10 %.

As a result of structural and thermal studies of resultin composite materials of TFPP it has been found out that the polymeric component has a similar structure to the material FORUM ® [7], but also has individual characteristics: the presence of an amine group in the structure, the presence in the form of TiO_2.

Conclusion

1. A method which allows working out the technology of synthesis of molecular composite on the basis of PTFE and TiO_2 is offered.
2. It is most optimal to use $(NH_4)_2TiF_6$ for introduction of TiO_2 in PTFE.
3. Optimal correlation of PTFE + 30 % by mass $(NH_4)_2TiF_6$.
4. The yield of the final product in a hard phase makes no less than 40 % by mass.
5. As a source of PTFE it is possible to use wastes, shaving and wastes from PTFE.
6. Degrees of decomposition (of thermal degradation) of PTFE with addition of 30 % by mass $(NH_4)_2TiF_6$ on temperature and time is described by equalization

$$\alpha = 1 - \left(1 - 1{,}32 \cdot 10^{8} \cdot \exp\left[-\frac{174453}{R \cdot T}\right] \cdot \tau\right)^{3}$$

7. The proposed method is characterized by simple hardware design, lack of expensive reagents and can be implemented in industry.

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