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Features of Combined Solid-Phase Extrusion Technology, Structure and Property Formation of Fluoropolymer-Based Nanocomposites

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Abstract

The features of the implementation of the two methods for polymer solid-phase extrusion in a single process cycle as a main instrument for structural modification of polymer systems are considered in this paper. The results of the related research of new methods for obtaining fluoropolymer-based nanocompisites from a gas phase medium are also given as well as the estimation of their performance properties. The work is focused on polytetrafluorethylene-based nanocompisites including metal and ceramic nanoparticles and ultrafine polytetrafluorethylene (**PTFE**), obtained by molecular gas phase mixing. The choice of this polymer is not accidental. Despite its unique physico-chemical properties (its chemical resistance is superior to all other synthetic polymers), the manufacture of PTFE-based products is very hard as the polymer is insoluble and immobile at higher temperatures. So it is actual to develop methods and technologies for its processing. The following methods are used to study performance properties of polymer composites: determination of the specific rate of energy absorption depending on the temperature of samples in the mode of differential scanning calorimetry, measurement of destructive stress value in the cross section of given and modified samples, determination of heat resistance and orientation release stress by charting isometric heat, determination of heat conductivity and thermal diffusivity, estimation of wear resistance under attrition. This research results allowed us to estimate the technological and operational characteristics of the samples used. This led us to the understanding of the nature and impact of the proposed solid-phase method of processing on the structure of PTFE-based polymeric materials and the possibility of regulating their properties. The comparative analysis of the proposed method and traditional methods for processing polymer composites is done. Ways for the practical use of the proposed combined solid-phase instrument and method of the extrusion of multicomponent polymer systems were considered. Further development and adaptation of the proposed method of solid-phase processing of polymeric materials to the modern conditions of domestic and foreign industries are planned.

Keywords

Solid-phase extrusion; polytetrafluoroethylene (PTFE); plastic deformation; strength and thermophysical properties; metal and ceramic nanoparticles.

Introduction

The production of a new type of fluoropolymer-based composites by means of advanced processing technologies providing the manufacture of products with a wide set of performance properties, is an important practical and scientific task of modern material science.

At present the most widely used method for producing materials with a new range of physical and chemical properties is structural modification of polymeric material by special nanosized fillers. The filler concentration in the polymeric matrix can vary greatly depending on the expected results and the processed material features. However, the use of some of them is not always efficient from the economic and practical point of view. Therefore, besides physical and chemical methods of polymer properties modification, the processing methods of structural modification of the material in the solid aggregative state are used.

They provide the creation of the highly-oriented state due to the intensive plastic material deformation development. The processing methods of polymer structure modification include solid-phase ram and hydrostatic extrusion alongside with traditional methods of die forging and sheet forming. Solid-phase extrusion is an advanced processing method of structural modification in the field of plastic mass processing. It results in the sharp productivity increase of the equipment used due to the production run reduction and the improvement of finished product performance properties.

The aim of this work is to intensify processing methods of composite polymeric material structure and property formation as a result of combining two extrusion methods when ram extrusion is implemented gradually together with solid-phase equal-channel angular extrusion. The efficiency of the use of this method for processing polymeric materials is estimated on the basis of the experimental results.

Experimental

Combined solid-phase extrusion process of polymer composites was implemented in a specially made high pressure cell with a transfer chamber which had a diameter of 5 mm and a set of replaceable dies with the different material deformation ratio at a temperature lower than the melting temperature. Fig. 1 illustrates this cell which consists of a force plug – *1*, a matrix – *2*, a polymer tablet – *3*, a die – *4*. It helps estimate the technological parameters of the formation process of the used polymeric systems [3].

The research object was polytetrafluoroethylene (GOST 10007–08) in the form of powder. The following materials were used as modifying extrudants:

– a product obtained by distillation of 97 wt % PTFE charge stock and 3 wt % $(NH_4)_2TiF_6$ at the temperature of 575 °C with the subsequent desublimation by ammonia-water mixture – the PTFE composite with TiO_2 (**TFP**) [1];

– a product obtained by putting nanosized cobalt-containing clusters on fluoropolymer powder microparticles (CoFP) [2].

The main advantage of the obtained PTFE composites is that the used metal and ceramic nanosized clusters attached to the surface of ultrafine PTFE particles cannot agglomerate and at the same time they specifically interact with the external components of the polymer system, maintaining their basic physical properties and forming particular tunable micro-and-macrostructures. The latter are responsible for the change of performance properties in finished products of any practical use (high-frequency insulators, thermal products, anti-friction products, etc.).

The solid-phase processing in the mode of combined extrusion of fluoropolymer composites was carried out at the ambient temperature of 22 °C. Solid rods of the cylindrical cross-section with a diameter of 5 mm and a length of 20 mm were used as samples. The composites were produced by the preliminary blending of pulverous PTFE with nanosized fillers TFP and CoFP in the electro-magnetic mixer with the subsequent tabletting and sintering of the products obtained.

The estimation of strength properties in PTFE modified samples, which were processed by combined extrusion under punching stress conditions, was done on a UTC 101-5 machine (GOST 17302–71). The change of strength properties of thermoplasts during the combined solid-phase extrusion process can be explained in terms of plastic deformation mechanism at high pressure values, when the strength of samples is quantified mostly by the existence of different defects especially in the original liquid-phase samples and the decrease in their concentration (microflaws, micropores) in the samples, processed by combined extrusion.

The diagram illustrates the data of critical stress value change in the cross-section of the given and modified polytetrafluoroethylene-based samples (Fig. 2 and 3). The impact ratio of the injected extrudant and the suggested processing on the tablet strength under

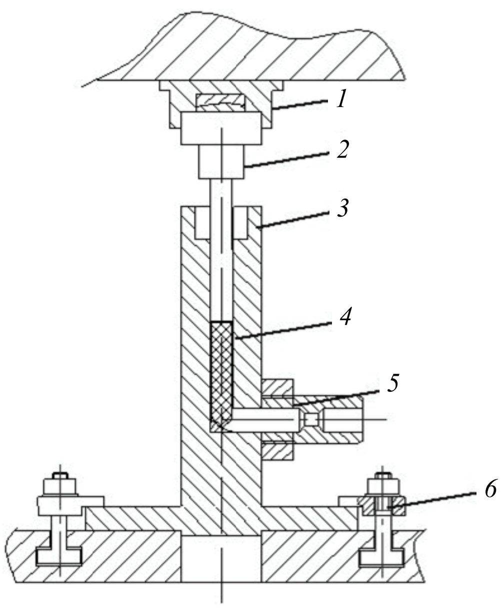

Fig. 1. Experimental cell model for combined extrusion of polymeric materials:
1 – force plug holder; *2* – force plug; *3* – matrix; *4* – polymer tablet; *5* – die; *6* – experimental die holder

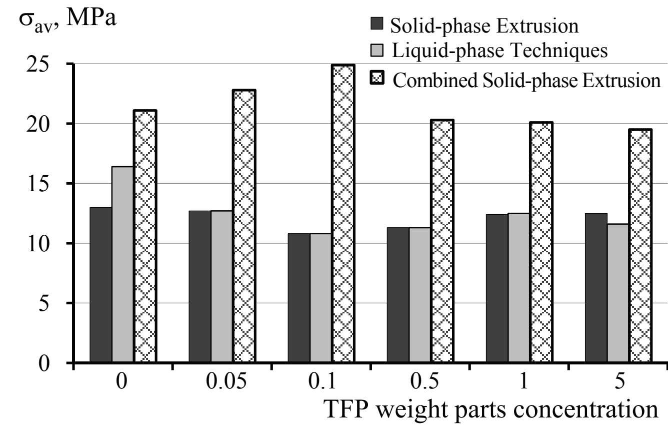

Fig. 2. Diagram of critical stress change in the polymer composite PTFE + TFP section, depending on TFP concentration and processing methods

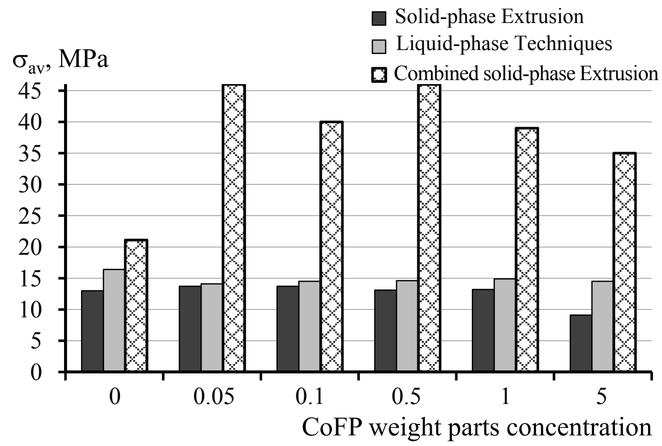

Fig. 3. Diagram of critical stress change in the polymer composite PTFE + CoFP section, depending on CoFP concentration and processing methods

the conditions of critical stress is indicated according to the obtained experimental data. For example, σ_{av} of the composite PTFE + 0.1 wt % TFP is two times greater than properties of the samples, processed by liquid-phase techniques or solid-phase ram extrusion. The same tendency is observed for the composite PTFE + 0.05 wt % CoFP – the similar properties σ_{av} increase three-fold in comparison with the basic substance and samples, produced by ram TFE [6].

It was established experimentally that the polymeric material processed by combined extrusion, has the bigger Shore hardness (GOST 24621–91) (Fig. 4).

Results and Discussion

For the practical analysis of the material behaviour in the combined extrusion process, the impact estimation of boundary layers "polymer-filler" and the sufficiently reasonable conclusion about the deformation process intensification and the physical mechanism determination, the research of thermal and physical properties of polymer systems was done by the method of diffrential calorimetry. Thermal and physical research by differential scanning calorimeter proved the dependence of the maximum speed of energy absorption by samples of the polymer system in PTFE melting area on the concentration of nanosized composites TFP, CoFP (Fig. 5, 6).

It should be noted that the largest effect in all the research methods used is observed when small amounts of modifiers are added, exactly 0.05 and 0.1 wt % for 100 wt % of PTFE. Besides this combined extrusion allows to improve the surface quality of obtained extrudates due to the material heating (plasticity increase) at the first stage of solid-phase processing during the intensive plastic deformation course.

Heat resistance and the level of orientation release stress refer to some of the most important performance properties which determine the perspective and the scope

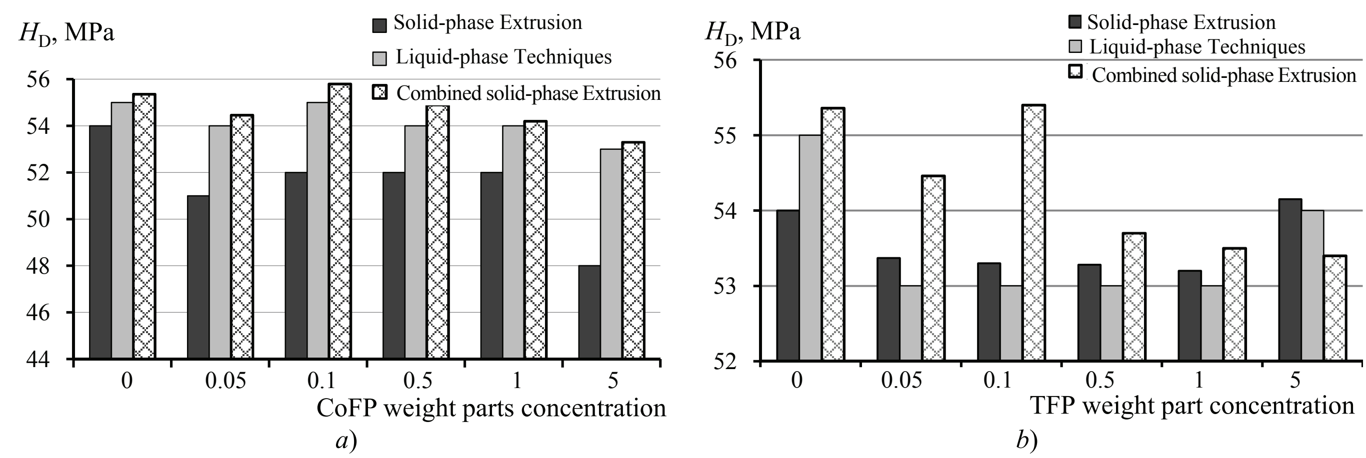

Fig. 4. Diagram of the change in hardness value of PTFE + CoFP polymer composite (*a*), PTFE + TFP (*b*)

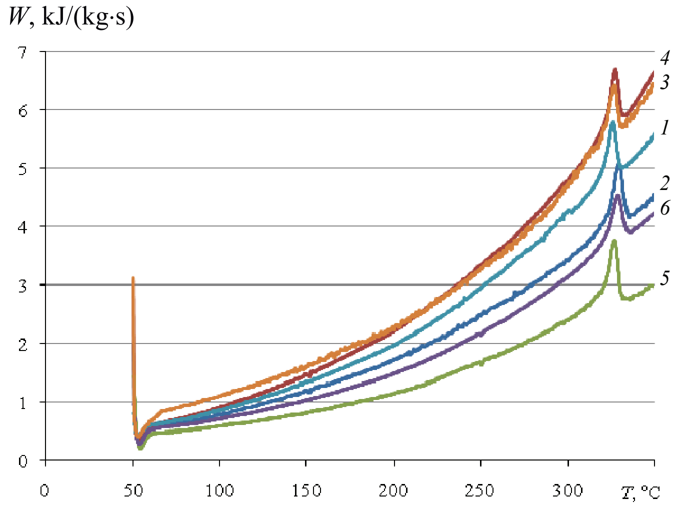

Fig. 5. Diagram of the dependence of the specific rate of energy absorption *W* by the polymer composite PTFE+TFP samples on temperature:
1 – PTFE primary; *2* – PTFE + 0.05 TFP; *3* – PTFE + 0.1 TFP; *4* – PTFE + 0.5 TFP; *5* – PTFE + 1 TFP; *6* – PTFE + 5 TFP

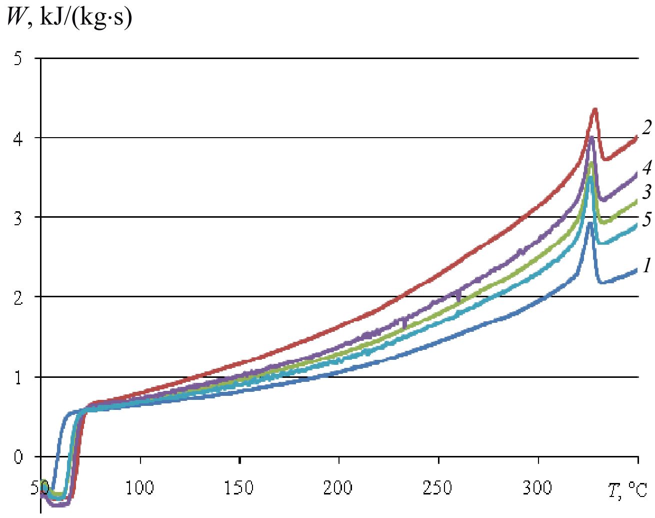

Fig. 6. Diagram of the dependence of the specific rate of energy absorption *W* by the polymer composite PTFE+CoFP samples on temperature:
1 – PTFE primary; *2* – PTFE + 0.05 CoFP; *3* – PTFE + 0.1 CoFP; *4* – PTFE + 0.5 CoFP; *5* – PTFE + 1 CoFP; *6* – PTFE + 5 CoFP

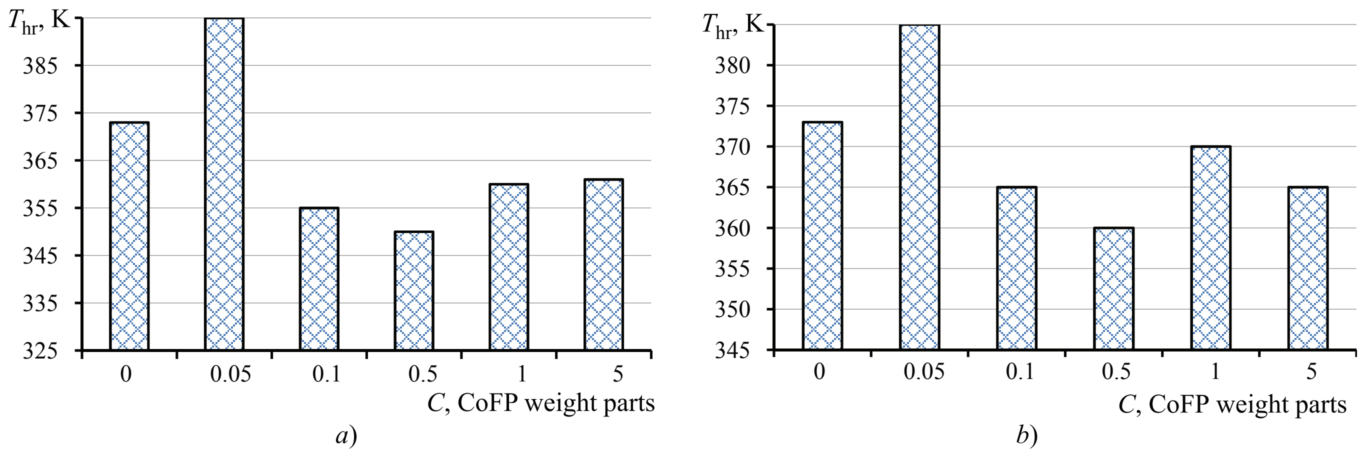

Fig. 7. Diagram of the dependence of heat-distortion temperature T_{hr} in the polymer composite PTFE+CoFP samples (*a*), PTFE+TFP (*b*) on CoFP concentration

of practical application of the products obtained (Fig. 7, 8). The research was done on the pilot setup using a specially developed program for data collection and charting isometric heat [4, 5].

Information-measuring system of nondestructive testing helped determine heat conductivity and thermal diffusivity of the sampling material by a probe method. The experimental research done allowed us to determine all thermal and physical properties in one nondestructive test (Fig. 9, 10). Changes in energy conditions of the modified nanocomposite, concerning a small amount of extrudants in comparison with the given polytetrafluorethylene, stipulate the increase in all properties of the system.

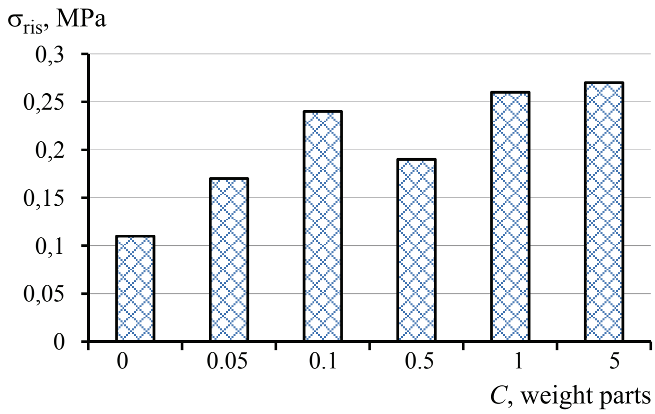

Fig. 8. Diagram of the dependence of the orientation release stress σ_{ris} in the polymer composite PTFE+CoFP samples on CoFP concentration

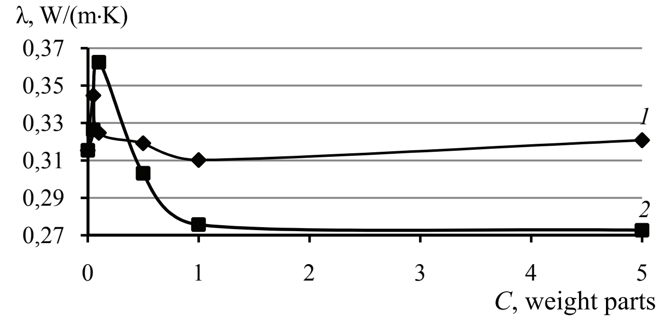

Fig. 9. Diagram of the dependence of heat conductivity in PTFE polymer composite samples on TFP concentration (*1*), CoFP (*2*)

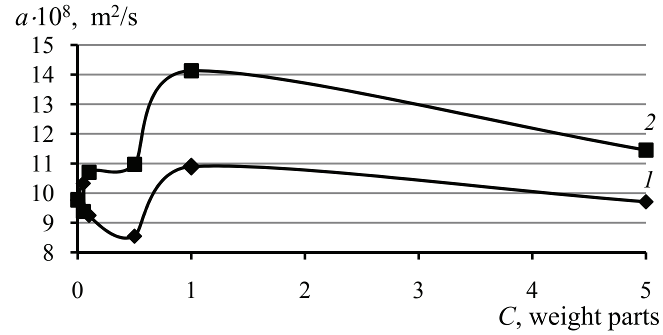

Fig. 10. Diagram of the dependence of thermal diffusivity in PTFE polymer composite samples on TFP concentration (*1*), CoFP (*2*)

It is planned to develop a set of formulas for composite materials based on thermoplasts as a result of the practical application of the suggested technique. These composites will have properties meeting the requirements for the use of products according to their specific area. The presence of the moulding die in the solid-phase processing flow chart allows to produce not only strengthened tablets of different shapes and parameters but also finished profiled products with a specified set of parameters. The research results prove that the use of this device is perspective for the establishing and successful activity of new enteprises, and for increasing competitiveness of the existing polymer processing plants, due to the introduction of energy-efficient solid-phase technologies [6].

Conclusion

As a result of the theoretical and practical analysis of the behaviour of PTFE-based composites in the combined extrusion process, quite reasonable conclusion about the deformation process intensification as material structural modification by the gradual intensive plastic flow process taking place at different structural levels (nano-, micro- and macro-) can be made. The scope of the levels depends on the sample geometry and parameters of structural defects (nonuniformity), and the observed changes in properties and the type of defect structure depend on specific conditions and type of loads [7].

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