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THE STRUCTURE AND PERFOMANCE CHARACTERISTICS OF PSF-NANOCOMPOSITES, MANUFACTURED BY METOD OF SOLID PHASE EXTRUSION

G.S. Baronin[1], P.V. Kombarova[1], D.E. Kobzev[1], A.K. Razinin[1], A.S. Loseva[2]

Departments: «Theory of Machines, Mechanisms and Machine Parts» (1); «CAD Systems» (2), TSTU; kombarova_polina@mail.ru

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Abstract: On the base of studying the structural mechanical relaxational properties and X-ray structural analysis PSF-nanocomposites, manufactured by liquid- and solid-phase technology, the regularities of structure formation and performance characteristics of the nanocomposites, processed by pressure in solid phase were revealed.

Currently one of the fastest growing industries is that of polymers and composites processing. New processing technologies and advanced polymeric materials allow to manufacture the products with an incredibly wide range of performance characteristics. Products made of polymers are widely used in many areas. As a consequence, a set of requirements for the performance characteristics of materials is quite wide and single polymers do not always meet these requirements. One method of modifying the physical properties of polymeric materials is the introduction of additives into a polymeric matrix, including nanocarbon additives. This help to achieve the increase in rigidity, strength, impact resistance, heat resistance, thermal stability of materials, their barrier properties, as well as lowering flammability. Often, in order to satisfy the requirements of new technologies it is enough to modify the widely available polymers by introducing nanocarbon additives or adding other polymers, rather then develop the process of producing new polymers, which significantly reduces the cost of production of composite materials having desired characteristics.

Solid phase technology (**SPE**) is a perspective technological method of processing a wide class of materials, including polymers and composites. All methods of low-temperature deformation of thermoplastics lead to the improvement of mechanical properties of final products comparing to the original material. Products manufactured by solid phase extrusion and die forging possess a significantly higher strength, hardness, high creep resistance under compressive and tensile loads [1].

Polysulfone (**PSF**) is used in production mostly as a heat-resistant thermoplastic with good strength characteristics, and high chemical resistance. These properties of the material, allow to use it for production of specific machine pieces such as enclosures for

rotameters used to measure the flow of various acids and other products for the chemical industry. In medicine, polysulfone is used as dental prostheses, prostheses of the tubular bones, as well as prosthetic artificial heart. Such widespread use of polysulfone in medicine is defined by its bio inertness and nontoxity.

Polysulfone differs from other polymers in improved performance with respect to chemical and biological stability, and in a number of other characteristics it exceeds them many times. Polysulfone has a wide range of applications in the heat technology, since it possesses a valuable combination of heat resistance, high strength and dielectric properties [2–4].

Nanocomposites represent a new direction in the filler systems. These are materials, consisting of two or more phases, in which at least one of the phases has a particle size of at least one dimension less than 100 nm. Good additive dispersion of nanoparticles in a polymer matrix allows to improve the properties of a material using much smaller amount of additive than in the case of traditional additivers (carbon black, aerosil, talc, fiberglass) [5].

Carbon nanomaterials (**CNM**) "Taunit" (nanofibres, multiwall nanotubes) in the form of one-dimensional nanoscale filamentary formations of polycrystalline graphite. Manufacturer of CNM – LLC "NanoTechCenter", Tambov (Table 1).

The technological basis for selection of compositions PSF-composites were considered based on the requirement to achieve the lowest amount of additive (0,5… 1,5 mass fraction) while reaching high levels of performance characteristics of the material. Properties of the modified polymer depend strongly on the technological conditions of its production, including the temperature of the process. Dependence of the necessary pressure for solid molding (R_f) on the temperature and the content of modifying additives for compositions based on the PSF is shown in Fig. 1. It has been shown experimentally that the introduction of small amount of additives (up to 1 mass fraction) reduces the necessary solid extrusion pressure of PSF-composites.

Raising the temperature during processing PSF-nanocomposites reduces the necessary molding pressure due to increased structural mobility of the material.

To assess structural and mechanical properties of polymer nanocomposites based on PSF, manufactured by liquid phase and solid-state technology various methods are used and include the methods of determining the impact strength during abrasion, evaluation of the micro-hardness and strength properties of the material.

Table 1

Main characteristics CNM "Taunit"

Description	Value
Outer diameter, nm	8…100
Length, m	10…20
Total impurities including amorphous carbon, %	1.6
Bulk density, g/cm ^{3}	0.4
Effective (pycnometric) density, g/cm ^{3}	1.6
Humidity, %	1.0
Reversible sorption capacity for hydrogen, %	4.8
Specific geometric surface area, m^2/g	90; 130
pH	7
Conductivity, cm/cm	10^0…10^1
Thermal stability, °C	700

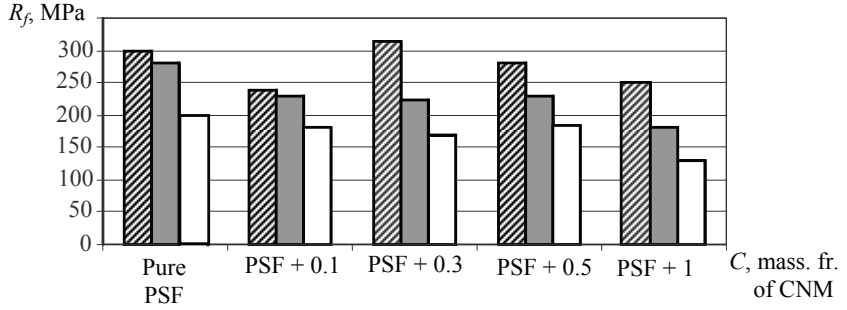


Fig. 1. Diagram of pressure for SPE for PSF-composition λ_{ex} = 1.52:
▨ – T_{extr}= 295 K; ■ – T_{extr} = 338 K; □ – T_{extr} =461 K

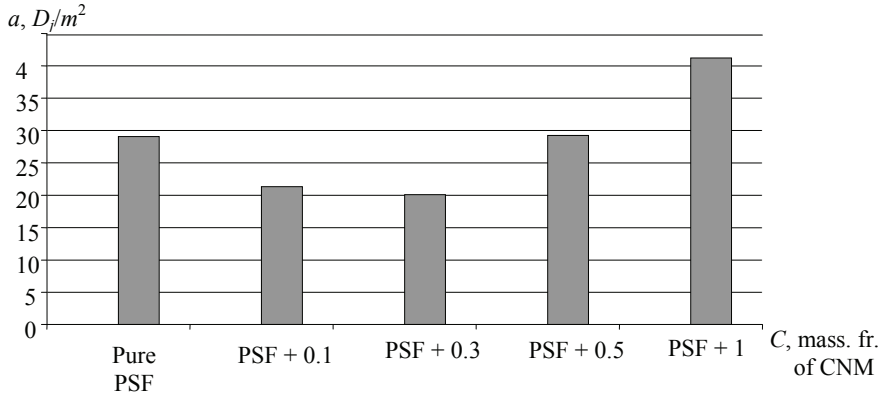


Fig. 2. The profile of the abrasion impact strength of PSF + CNM received via liquid phase extrusion, T_{extr}= 583 K

It is established that the introduction of small additions CNM in the amount of 0.1…0.3 mass fraction into a polymer matrix of PSF reduces the impact strength from 30 to 20 J/m^2. Further increase in the concentration of modifying additive increases the value of impact strength by 40% when the content 1 mass fraction CNM (Fig. 2).

Analyses of structure by X-ray structure analysis is of considerable interest for polymer composites, processed in solid phase using methods of plastic deformation. Methods of low-temperature molding of polymers and composites make it possible to achieve high performance properties of final products as a result of controlled molecular orientation of the structure by forming a desired direction of the directional anisotropy of the material. Results of X-ray structure analysis PSF-composites, depending on the background conditions are presented in Table 2.

It is shown that despite all of X-ray amorphous nature of samples obtained by LPE and SPE, there is some orientation in the material structure of polymer composites. In addition, there is formation of the most common in polymer systems axial texture, that is such a texture where the normal vector to the plane (001) coincides with the direction of liquid-phase or solid-state extrusion. Such structural changes are due to the fact that the macromolecular chains of the initial polymer matrix and carbon nanocrystals acquire a certain orientation along the direction of extrusion.

Structure and properties of modified polymers as a heterogeneous multi-component system in general terms are determined by two factors. The first is founded in the principle of manufacturing the materials by introduction of modifiers into the

Table 2

Results of the PC-analysis of PSF-nanocomposites

Composite, production technology	The degree of deformation, λ_{extr}	Temperature of SPE, T_{extr}, °C	Crystal-identity	The degree of orientation, according to [5]
PSF reference LPE	–	–	X-ray amorphous	0.14
PSF reference SPE	1.52	25		0.22
PSF reference SPE		130		0.12
PSF +1 mass fraction CNM, SPE		190		0.21
PSF +1 mass fraction CNM, LPE	–	–		0.18
PSF +1 mass fraction CNM, SPE	1.52	25		0.20

polymeric matrix, which have different physical and chemical structure, particle size and shape and their amount in the system. The second factor is the result of the changes of physical properties and structure of the polymeric matrix which are caused by the interactions at the interface line of the polymer – is solid. The total change in the properties of the modified system in comparison with the initial polymer is a result of the simultaneous action of both factors. However, in all cases, the most important condition of the reinforcing action of modifiers in such systems - the adhesion of polymers to the surface of the modifier and, hence, the nature of relationships at the interface line of the polymer – is the modifier. Physical interaction of the polymer with the modifier's particle surface determines the deformability of the polymer, the nature of the stress concentration on the modifier's particle surface and conditions of fracture of the polymer composites [6].

Considerable interest in studying the properties of polymer composites is the method of evaluation of micro hardness, which has been developed in the metallographic studies. Application of this method is associated with the determination of depth and size of micro marks (indentations) of the diamond- pyramid shaped indenter. The results of such test are primarily dependent on the shape of the indenter and the amount of the applied load [7]. In addition, measurement of micro-hardness is made with application of very small loads, which makes this method convenient for testing of polymers and composites based on them. Micro-hardness expands the study of properties of polymer nanocomposites in relation to their physical and structural heterogeneity.

In analyzing the concentration dependence of micro hardness on the content of nano additives CNM it is found that with small amount of modifying additive 0.1…1 mass fraction per 100 mass fraction of the polymer a significant increase in micro-hardness is observed. It has been experimentally determined that the characteristics of the composite material depend on the direction of the indentation of the sample during the experiment in relation to the orientation of the extrudate as a result of solid-state ram extrusion (Fig. 3, 4).

While evaluating the physical and mechanical parameters in a shear strength of polymer composites which have undergone SPE process compared with LPE-polymer, substantial increase should be noted in the strength characteristics of the material in a direction perpendicular to the orientation of the polymer structure (Fig. 5).

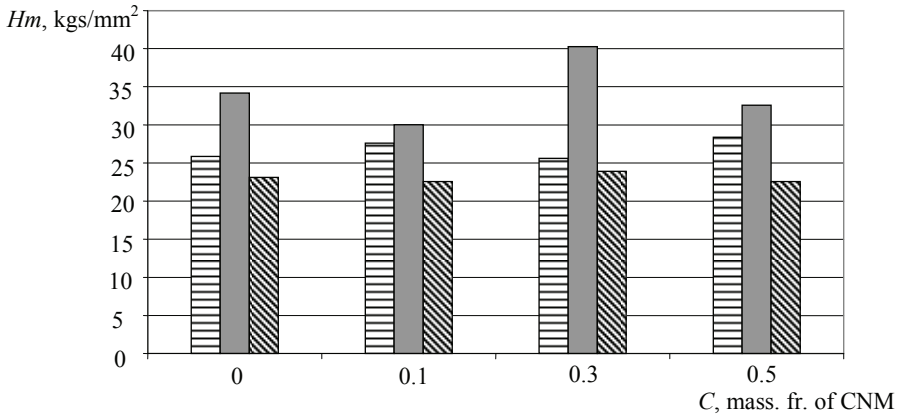


Fig. 3. Concentration dependence on the micro hardness of PSF-nanocomposite:
– liquid phase sample, the direction of indentation parallel ( )
and perpendicular ( ) direction of orientation of the sample in ram
extrusion mode SPE, the degree of deformation $\lambda_{extr} = 2.07$
and $T_{extr} = 461$ K (30 gm test load, hold time 10 sec)

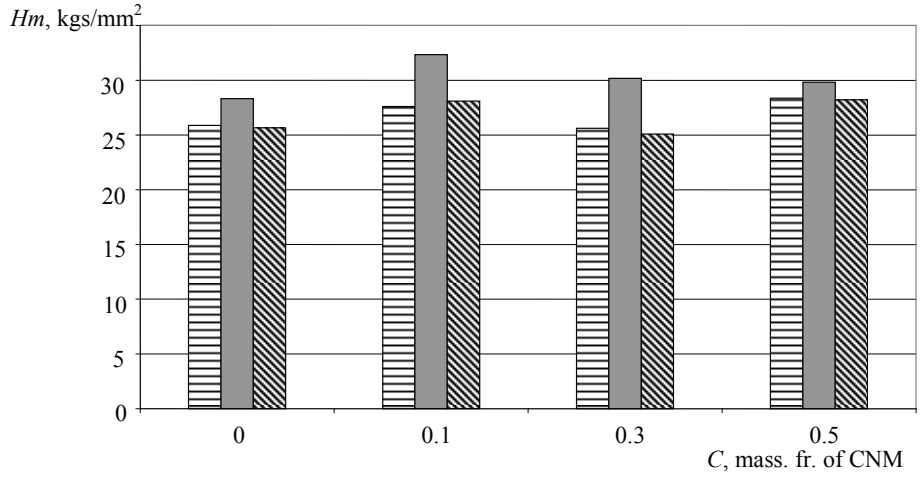


Fig. 4. Concentration dependence on the micro hardness PSF-nanocomposite:
– liquid phase sample, the direction of indentation parallel ( )
and perpendicular ( ) direction of orientation of the sample in ram
extrusion mode SPE, the degree of deformation $\lambda_{extr} = 1.52$
and $T_{extr} = 461$ K (30 gm test load, hold time 10 sec)

The greatest increase in shear strength is observed after treatment of composite PSF + 1 mass fraction CNM at a temperature of SPE in the vicinity of T_c (461 K), compared with the material processed under liquid-phase extrusion.

The full impact of nano-sized additive on the structure and properties of polymer composite can be studied by studying the shrinkage processes under conditions of isometric heating to determine the quantitative and qualitative performance indicators of materials show heat resistance temperature and the magnitude of its residual stresses (Fig. 6). The temperature of heat resistance is one of the important criteria for determining the performance of polymer products produced by the methods of plastic deformation. From a practical point of view, the relatively low level of residual stress and high temperature heat resistance, ie maximum temperature at which the material retains its performance properties, demonstrates the admissibility of the test material.

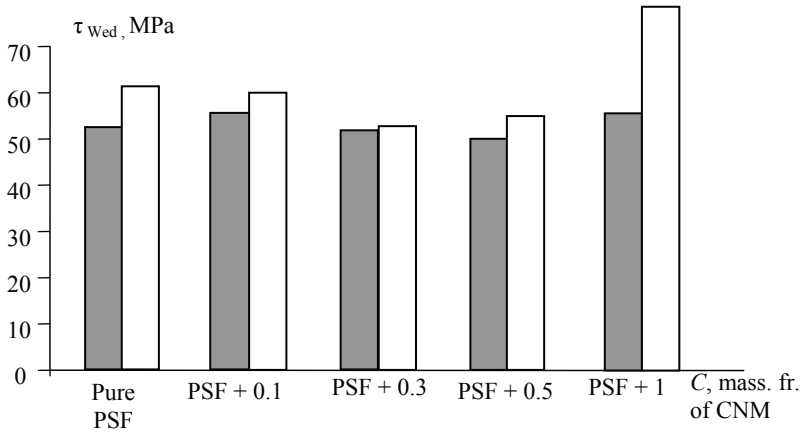
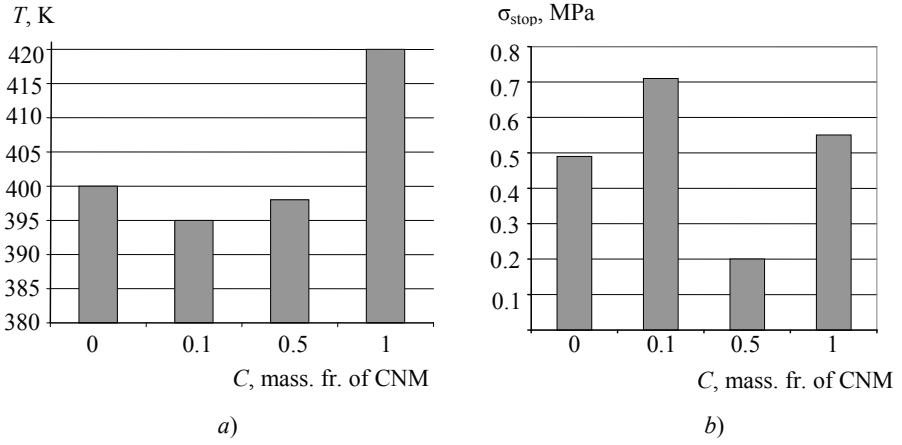


Fig. 5. Diagram of changes in the strength in shear τ_{Wed} PSF-composites obtained by extrusion at λ_{extr} = 2.07, T_{extr} = 461 K:
■ – liquid phase; □ – solid phase



a) *b*)

Fig. 6. The dependence of the deformation heat resistance of the T_m (*a*) and the level of residual stresses σ_{stop} (*b*) of samples composed from the PSF + CNM in relation to CNM content in the polymer matrix, obtained by SPE at a degree of deformation λ_{extr} = 2.07 and T_{extr} = 461 K

Conclusions

From the presented experimental data the influence of modifying nano additives on the formation properties of composites is clearly shown. Analysis of the experimental results reveals that the best performance characteristics belong to the composite containing 1 mass fraction CNM, as it demonstrates the maximal temperature of heat resistance, the highest strength indices and the value of impact toughness of the material. The experimental results allow us to state that the methods of physical modification of the structure and properties of polysulfone with small additions of nano-sized carbon material and methods of solid-state technologies can achieve high performance characteristics of final products and samples by forming a desired direction of the anisotropy of the material as a result of a controlled molecular orientation structure.

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Структура и эксплуатационные свойства ПСФ-нанокомпозитов, прошедших обработку давлением в твердой фазе

Г.С. Баронин[1], П.В. Комбарова[1], Д.Е. Кобзев[1], А.К. Разинин[1], А.С. Лосева[2]

Кафедры: «Теория машин, механизмов и детали машин» (1); «Системы автоматизированного проектирования» (2), TSTU; kombarova_polina@mail.ru

Ключевые слова и фразы: диффузионные свойства; микротвердость; нанокомпозит; пластическое деформирование; полисульфон; релаксационные свойства; рентгеноструктурные исследования; твердая фаза; твердофазная экструзия.

Аннотация: На основе изучения структурно-механических, релаксационных свойств и рентгеноструктурного анализа ПСФ-нанокомпозитов, полученных жидкофазной и твердофазной технологией, выявлены закономерности формирования структуры и эксплуатационных свойств нанокомпозитов, прошедших обработку давлением в твердой фазе.

Struktur und Anwendungseigenschaften von den die Bearbeitung durch den Druck in harten Phase durchgegangenen PSF-Nanokompositen

Zusammenfassung: Auf Grund der Erlernung der strukturmechanischen, relaxationischen Eigenschaften und der röntgenstrukturellen Analyse der PSF-Nanokompositen, die durch Flüssigphasen- und Hartphasentechnologien erhalten wurden, sind die Gesetzmäsigkeiten der Formierung der Struktur und der Anwendungseigenscheften der die Bearbeitung durch den Druck in harten Phase durchgegangenen Nanokompositen gezeigt.

Structure et propriétés d'exploitation des nanocomposites PSF soumis au traitement sous la pression dans une phase solide

Résumé: A la base de l'étude des propriétés structurelles, mécaniques et de relaxation ainsi que de l'analyse aux rayons X des nanocomposites PSF obtenus par la technologie de phase liquide et solide, sont relevées les régularités de la formation de la structure et des propriétés d'exploitation des nanocomposites PSF soumis au traitement sous la pression dans une phase solide.

Авторы: ***Баронин Геннадий Сергеевич*** – доктор технических наук, профессор, директор научно-образовательного центра (НОЦ) ТамбГТУ – ИСМАН «Твердофазные технологии»; ***Комбарова Полина Владимировна –*** аспирант кафедры «Теория машин, механизмов и детали машин»; ***Кобзев Дмитрий Евгеньеви –*** аспирант кафедры «Теория машин, механизмов и детали машин»; ***Разинин Алексей Константинович*** – аспирант кафедры «Теория машин, механизмов и детали машин»; ***Лосева Алёна Сергеевна*** – студентка кафедры «Системы автоматизированного проектирования», ГОУ ВПО «ТГТУ».

Рецензент: ***Лазарев Сергей Иванович*** – доктор технических наук, профессор, заведующий кафедрой «Прикладная геометрия и компьютерная графика», ГОУ ВПО «ТГТУ».
