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The structure, composition and preparation of injection-molded composite materials based on glass-filled polysulfone

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In the course of this study, compositions and designed structures for the polysulfone (PSF) and short glass fibers systems were calculated. Additionally, disperse-filled polymer composite materials (DFPCM) based on PSF-190 were classified in accordance with their respective structures, and the optimal amount of glass fiber (13.5–18.5 vol %) was determined. This article describes the production of DFPCM using PSF and a short glass fiber with a twin-screw extruder (Labtech Engineering Company LTD, model Scientific FIC 20-40). Furthermore, optimal mixing parameters for the creation of composites wherein the glass fiber length exceeds the critical length (l_{cr}) were established. The critical length was calculated, and the curves for fiber size distribution of polysulfone composites were depicted, and a difference in fiber concentration between the dispenser and the extrusion head (up to ~10–15%) was found when the fiber content was at 18–25 vol %. For the first time, optimal parameters (which pertain to medium-filled dispersions) for the structure of DFPCM based on PSF and short glass fiber are able to be demonstrated.

Keywords: *polysulfone, composite materials, critical fiber length, short glass fibers.*

Структура, составы и получение литьевых композиционных материалов на основе стеклонаполненного полисульфона

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Рассчитаны составы и спроектированы структуры для системы полисульфон (ПСФ) + короткие стеклянные волокна. Представлена классификация дисперсно-наполненных полимерных композиционных материалов (ДНПКМ) на основе ПСФ-190 по структурному *принципу, с учетом обобщенных параметров структуры и установлена оптимальная область содержания стеклянного волокна (13.5–18.5% об.). Описана технология получения ДНПКМ на основе ПСФ и короткого стеклянного волокна на двухшнековом экструдере фирмы Labtech Engineering Company LTD марки Scientific FIC 20-40 и определены оптимальные параметры смешения для создания композиций с длиной стекловолокна более $l_{кр}$. Рассчитана критическая длина ($l_{кр}$) и построены кривые распределения волокна по размерам в полимерных композиционных материалах на основе полисульфона. Впервые приведены данные по оптимальным параметрам структуры ДНПКМ на основе ПСФ и коротких стеклянных волокон, которые соответствуют средненаполненным дисперсным системам.*

Ключевые слова: *полисульфон, композиционные материалы, критическая длина волокна, короткие стеклянные волокна, смешение.*

Introduction

In order to improve physicomechanical characteristics, heat-resistant engineering polymers belonging to the polysulfone (PSF) class may be modified by introducing fibrous fillers of different nature, thus making them more diverse and applicable in more situations.

The design of structures and compositions for disperse-filled polymer composite materials (DFPCM) should be performed according to the classification of the system by the structural principle [1].

This work demonstrates data on generation (by extrusion) of a PSF-based composite with varying content of short glass fiber.

The selection of glass fiber content was performed according to the classification of disperse systems by the structural principle: diluted systems (DS), low-filled systems (LFS), medium-filled systems (MFS) and high-filled systems (HFS), taking into account the generalized parameters of the structure for production of injection-molded DFPCM.

The publication [2] showed that, for diluted systems and low-filled systems, insignificant changes in physicomechanical characteristics were observed. The highest values were reached in the production of medium-filled systems below the yield point (MFS-1) and above it (MFS-2).

Materials and Methods

The Russian-made PSF-190 (JSC "G.S. Petrov Institute of Plastics") with the melt flow index (MFI) = 10 g/10 min (340 °C and 2.16 kgf) and the temperature interval of production at 295–305 °C [3], as well as glass roving EC17-1200 made by "Owens Corning", the diameter of its elementary thread is 13 μm and its linear density is 2180 tex [4], were chosen as subjects of research.

[1]Owens Corning catalog, OCV Reinforcements [electronic source]. URL: http://www.ocvreinforcements.com/pdf/products/SingleEndRovings_SE1200_ww_06_2008_Rev0.pdf

Polysulfone PSF-190 was dried at ~145 °C for 4 h in vacuum until the residual humidity was no more than 0.02%.

The mixing of the components and control of fiber content in PSF were performed during extrusion by measuring the PSF feed rate with a gravimetric feeder, at the constant rate of glass roving feed.

The mixing was performed on a twin-screw extruder Labtech Engineering Company LTD (model Scientific FIC 20-40). The scheme of the process, in which glass filled PSF is produced, is shown in Fig. 1.

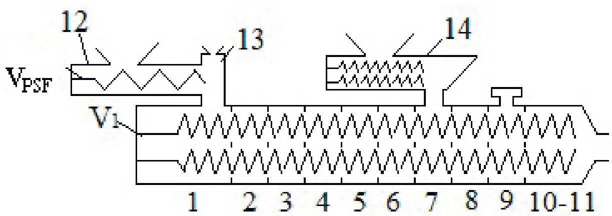

Fig. 1. The scheme of the process in which glass filled PSF is produced (*keys see following in the text*).

The laboratory extruder (Fig. 1), with the screw diameter D_s = 20 mm and L/D_s = 40, has 10 independently heated zones with the following temperatures: zone 1 with 260 °C, zones 2–9 with 310 °C, zones 10–11 with 295 °C. The extruder has a degassing zone (zone 9).

In the process of producing glass filled PSF, the torque was ~35–40 N×m. The rotational speed of the extruder's screws was constant, V_1 = 300 rpm.

The glass roving was introduced into the extruder by two different methods:

Method 1. The glass roving was introduced continuously through a loading spout (position 13) into zone 1 of the twin-screw extruder, at 260 °C, with linear speed of fiber feed V_f = 18 m/min, and the rotational speed of the extruder's screws V_1 = 300 rpm. The glass fiber feed rate was Q_f = 36 g/min.

Polysulfone was introduced by a gravimetric feeder (position 12) into the loading zone of the extruder (zone 1).

The feed speed for PSF (V_{PSF}) was varied between 3 and 10 rpm, and the feed rate Q_{PSF} was changing between 30 and 140 g/min.

Method 2. The glass roving was introduced through a side twin-screw loader (position 14) into the PSF melt, directly into zone 7 of the extrusion cylinder. The linear speed of fiber feed was constant, V_f = 1.3 m/min, and the feed rate was 36 g/min. The rotational speed of the extruder's screws was V_1 = 300 rpm. Polysulfone was introduced in the same way as in Method 1.

Glass fiber concentration in PSF was controlled by measuring the PSF-190 feed rate with a gravimetric feeder (position 12), while changing the rotational speed of the feeder's screw from 3 to 12 rpm, and with the constant glass fiber feed rate Q_f = 36 g/min.

Figure 2 shows the dependency of PSF-190 feed rate on the rotational speed of the feeder's screw (feeder in position 12).

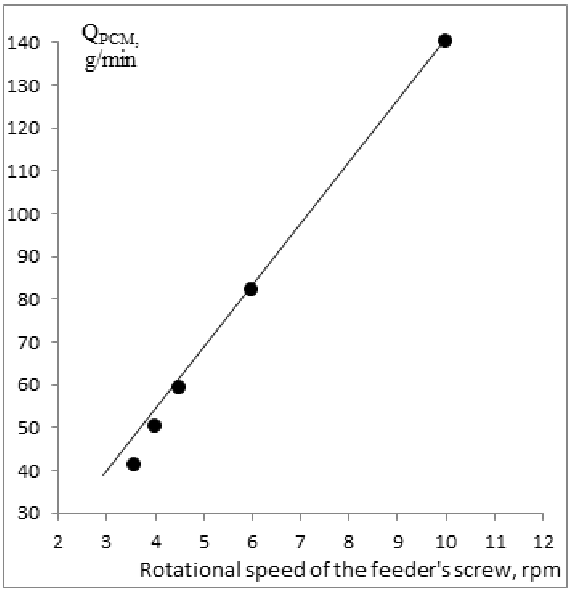

Fig. 2. Dependency of PSF-190 feed rate (Q_{PCM}) on the rotational speed of the feeder's screw (feeder in position 12).

According to Fig. 2, if the rotational speed of the feeder's screw (feeder in position 12) grows from 3 to 10 rpm, then the PSF-190 feed rate increases from 40 to 140 g/min. It may be characterized by a linear function: Q_{PSF} = K(n – 4.2/K) = 14(n – 0.3), for the rotational speed interval between 3 and 10 rpm, n is the rotational speed of the feeder's screw (feeder in position 12), K is a proportionality factor.

The glass fiber content (φ_f) in polysulfone, at the constant glass roving feed rate Q_f = 36 g/min, was calculated as follows: $\varphi_f = Q_f/(Q_{PSF} + Q_f)$, where Q_{PSF} is PSF-190 feed rate, g/min; Q_f is glass fiber feed rate, g/min; φ_f is glass fiber content in PSF-190, mass fract.

In order to evaluate the influence of the structure on the properties of the glass filled PSF, mass fractions (φ) were re-calculated into volume fractions (φ_{vol}).

Results and Discussion

In order to produce DFPCM based on glass filled PSF with various structures and generalized parameters, compositions for the filler of choice (glass fiber) were calculated. For the short glass fiber, it was experimentally determined that the maximum content of glass fiber φ_{max} = 0.36 vol. fract. This was based on a known approach [4].

The following Table summarizes the compositions, generalized parameters of the structure for the disperse system polymer–glass fiber, and DFPCM classification by the structural principle.

The share of the polymer matrix in the boundary layer and the generalized parameter of the structure M for disperse systems with small specific surface area of the filler were not taken into account in our calculations.

When the DFPCM structure changes from one type to another, the change of the generalized parameter Θ leads to variation in technological characteristics and operational properties.

For example, increase in the coordination number of the lattice Z and packing density kpack; decrease in the amount of polymer interlayer between disperse particles (generalized parameter Θ); and increase in glass fiber content (φ_f) lead to an increase in viscosity; worse reprocessing; and a change in the mechanism of DFPCM fluidity.

During the use of HFS structures with generalized parameter Θ < 0.20 vol. fract. and glass fiber concentration higher than 0.27 vol. fract. in extrusion process, while producing a string, breaks in the latter have been observed, and extrusion became unstable.

To summarize, this granulation method has limitations in the structural parameters of DFPCM. To produce MFS-2 systems with Θ between 0.45 and 0.20 vol. fract., and HFS with Θ < 0.20 vol. fract., it is necessary to use the "granulation on the tip" method.

For further experiments, DFPCM based on glass filled PSF with the following parameters of the structure were produced:

– low-filled systems LFS:

Θ = 0.90 vol. fract. and φ_{vol} = 0.09 vol. fract.;

– medium-filled systems MFS-1:

Θ = 0.73 vol. fract. and φ_{vol} = 0.09 vol. fract.;

Θ = 0.60 vol. fract. and φ_{vol} = 0.135 vol. fract.;

– medium-filled systems MFS-2:

Θ = 0.45 vol. fract. and φ_{vol} = 0.185 vol. fract.;

Θ = 0.40 vol. fract. and φ_{vol} = 0.21 vol. fract.;

Θ = 0.27 vol. fract. and φ_{vol} = 0.25 vol. fract.;

– high-filled systems HFS:

Θ = 0.20 vol. fract. and φ_{vol} = 0.275 vol. fract.

Compositions and generalized parameters of the structure for the glass filled PSF (φ_{max} = 0.36 vol. fract., d =13 μm)

Glass fiber content		Generalized parameters of the structure of DFPCM
φ_{vol}, vol. fract.	φ, mass fract.	Θ, vol. fract.
Low-filled DFPCM with 0.9 > Θ ≥ 0.75 vol. fract.		
0.04	0.09	0.90
Medium-filled DFPCM with 0.75 > Θ > 0.2 vol. fract.		
MFS-1: **0.75** > Θ > 0.45 vol. fract. (DFPCM below the yield point)		
0.085	0.204	**0.75**
0.09	**0.215**	**0.73**
0.11	0.264	0.68
0.135	**0.32**	**0.6**
0.15	0.37	0.56
MFS-2: 0.45 > Θ > 0.2 vol. fract. (DFPCM above the yield point)		
0.183	**0.43**	**0.45**
0.21	**0.50**	**0.40**
0.25	**0.60**	**0.27**
High-filled DFPCM with 0.2 ≥ Θ ≥ 0.0 vol. fract.		
0.275	**0.66**	**0.2**
0.285	0.69	0.016
0.3	0.82	0.01
0.34	0.82	0.01
Ultrahigh-filled DFPCM with Θ < 0 vol. fract.		
0.37	0.864	–0.1

Figure 3 demonstrates the dependency of the short glass fiber concentration in DFPCM (*method 2*) on PSF-190 feed rate, in the feeder in position 12 (2) and in the exit from the extrusion head (1); with the constant fiber feed rate 36 g/min.

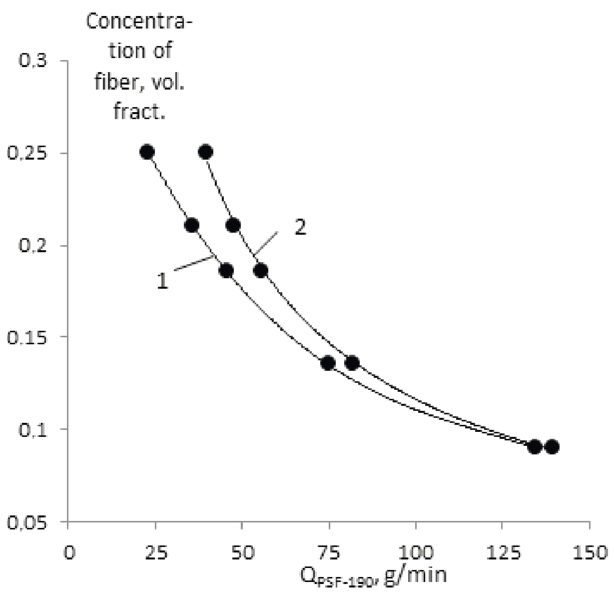

Fig. 3. Dependency of glass fiber concentration in DFPCM on PSF-190 feed rate, in the feeder 12 (2) and in the exit from the extrusion head (1).

Figure 3 shows that the feed rate data for the extrusion head and the gravimetric feeder are the same in the 75–150 g/min area; further decrease in the feed rate to 25 g/min leads to a difference of ~15%.

In the process of the introduction of continuous glass fiber and production of PSF-based DFPCM, grinding and shortening of the fiber occur in the extruder, which undoubtedly influences the physicomechanical characteristics of the glass-filled material.

The publication [4] shows that production of highly durable glass filled composites with short fibers, based on polymer matrices, requires that the following condition is satisfied: fiber length (l_f) should exceed the critical fiber length (l_{cr}).

The critical length (l_{cr}) for "Owens Corning" EC17-1200 glass fiber in PSF was calculated using the following formula:

$$l_{cr} = \frac{\sigma_f}{2\tau} \cdot d$$

If we assume that $\tau \approx \frac{\sigma_{flow}}{\sqrt{3}}$, then

$$l_{cr} \approx 0.866 \cdot \frac{\sigma_f}{\sigma_{flow}} \cdot d$$

where σ_f – tensile strength of glass fiber (2700 MPa); d – fiber diameter (13 μm); σ_{flow} – flow stress of PSF-190 (76 MPa); τ – shear stress on the fiber–polymer matrix boundary, MPa.

The calculated critical length for "Owens Corning" EC17-1200 glass fiber in PSF is ~220 μm.

To investigate the distribution of glass fiber in PSF by size, we used the Mikrofot type 5PO-1 device, made by "Moskinap", Russia. The samples of glass fiber for this experiment were obtained by two-step annealing of DFPCM in a muffle furnace, in accordance with GOST-15973-82.

Figure 4 shows distribution by length for glass fiber in PSF-based DFPCM, depending on the method of introduction (*method 1* – curve 5 and *method 2* – curves 1–4), with different fiber content.

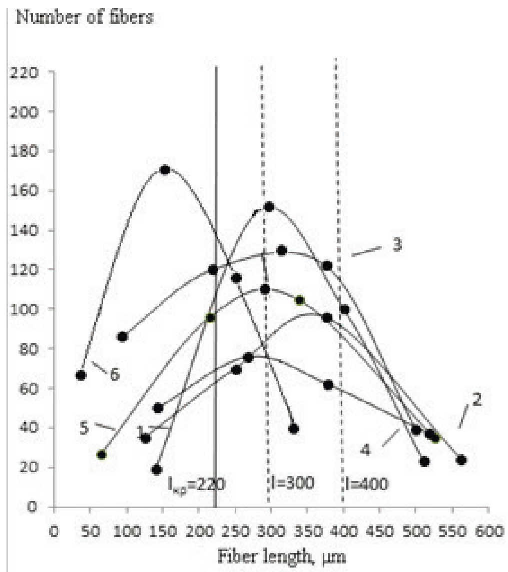

Fig. 4. Distribution of glass fiber by length in PSF-190. Introduction by *method 1* (curve 5) and *method 2* (curves 1–4). Fiber content: 13.5 vol % (1, 5), 18.5 vol % (2), 21 vol % (3), and 25 vol % (4).

Fig. 4 indicates that, when glass fiber is introduced into the loading zone of the extruder (*method 1*, curve 5), intensive grinding of glass fiber occurs, as a result of dry friction with granulated PSF, screws and the extrusion cylinder in the loading zone. In these conditions, fiber length in the composite material is less than l_{cr}, and the average length $l_{average}$ ≈ 150 μm.

The introduction of glass fiber directly into the PSF melt in zone 7 of the extrusion cylinder (curves 1–5) also results in fiber grinding (*method 2*). However, in this case, fiber length for the 13.5 vol % and 18.5 vol % situations is $l_{average}$ ≈ 400 μm, which is almost double of the critical length of fiber in PSF (l_{cr} ≈ 220 μm). For composites with 25 vol % fiber content, the average length is ca. 300 μm, which is approximately 1.5 times higher than l_{cr}.

The tensile strength of the DFPCM based on PSF and glass fiber, with $l_{average}$ ≈ 400 μm and fiber content 13.5–18.5 vol %, reaches the maximal value of 120 MPa. This is 1.7 times higher than for the polymer matrix, and it is no worse than for foreign-made analogs.

When glass fiber is introduced by *method 1*, fiber length in the composite material is less than l_{cr} ($l_{average}$ ≈ 150 μm), and the tensile strength of the DFPCM does not exceed 75 MPa, which is almost the same as for PSF. In this case, glass fiber does not work as a reinforcing filler.

Conclusions

PSF formulations containing short glass fibers were designed based on the theory of lattices and packing. They were classified by the structural principle, and the optimal glass fiber content was determined to be 13.5–18.5 vol %.

The production technology of DFPCM based on PSF and short glass fiber (*method 2*) was described, and the optimal mixing parameters to create composites where glass fiber length exceeds l_{cr} were determined.

For the very first time, data on the optimal parameters of the structure for DFPCM based on PSF and short glass fiber was presented, which conform to the parameters of medium-filled disperse systems.

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The authors declare no conflicts of interest.

References:

1. Simonov-Emel'yanov I.D. Building structures in dispersion-filled polymers and properties of composite materials. *Plasticheskie massy* = Polymer Science and Technology. 2015;9(10):29-36 (in Russ.).

2. Mikhaylin Yu.A. Heat resistant polymers and polymeric materials. Saint Petersburg: Professiya Publ., 2006; 261-298 (in Russ.).

Список литературы:

1. Симонов-Емельянов И.Д. Построение структур в дисперсно-наполненных полимерах и свойства композиционных материалов // Пластические массы. 2015. № 9-10. С. 29–36.

2. Михайлин Ю.А. Термоустойчивые полимеры и полимерные материалы. СПб.: Профессия, 2006. 259 с.

3. Baranov A.B., Peksimov O.E., Prudskova T.N., Andreeva T.I., Simonov-Emel'yanov I.D., Shembel N.L. Study on technology characteristics materials based on polysulfone. *Tonkie khimicheskie tekhnologii = Fine Chemical Technologies*. 2016;11(5):87-90 (in Russ.). https://doi.org/10.32362/2410-6593-2016-11-5-87-90

4. Simonov-Emel'yanov I.D., Spembel' N.L., Prokopov N.I., Ushakova O.B., Surikov P.V., Markov A.V. Methods for determination of technological properties of fillers and polymer materials. Moscow: Publishing and Printing Center of MITHT, 2014;63-74 (in Russ.).

3. Баранов А.Б., Пексимов О.Е., Прудскова Т.Н., Андреева Т.И., Симонов-Емельянов И.Д., Шембель Н.Л. Исследование технологических характеристик материалов на основе полисульфона // Тонкие химические технологии. 2016. Т. 11. № 5. С. 87–90. https://doi.org/10.32362/2410-6593-2016-11-5-87-90

4. Симонов-Емельянов И.Д., Шембель Н.Л., Прокопов Н.И., Ушакова О.Б., Суриков П.В. Методы определения технологических свойств наполнителей и полимерных материалов. М.: ИПЦ МИТХТ, 2014. С. 63–74.

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