

Influence of the content of dispersed fillers of various nature in polyvinylidene fluoride on its structural parameters and thermal conductivity

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Abstract. In this work, a comprehensive study of the effect of graphite and bronze particles on the structure and thermal conductivity of polyvinylidene fluoride (PVDF) was carried out. Based on the experiments carried out, it was found that at the limit of a relatively small concentration of bronze, the melting point of PVDF exceeds, and this was confirmed by an increase in the longitudinal dimensions of the crystallites. With relatively small amounts of fillers contained in the polymer composite materials (PCM, it was written that the change in thermal conductivity occurs mainly due to changes in the polymer structure. It was found out that the change in the structure of the polymer component in the compound and the thermal conductivity largely depends on the nature of the fillers.

1 Introduction

In modern materials science, the need to create new polymer composite materials (PCM) with the desired physical mechanical and thermodynamic properties encourages the science of polymer physics to develop further and find new applications. Polymer binder composites differ from all other traditional materials in their elasticity, lightness, excellent physical and mechanical and anticorrosive properties.

The possibility of scientific and practical ordering of the thermophysical properties of polymer materials (TFP), in particular thermal conductivity (λ), depending on the nature of thermal motion at various levels of structural formation of polymers, accelerates the solution of the problem of obtaining PKM with specified thermophysical properties.

Knowledge of the nature of thermal motion in polymers allows for a deeper and more comprehensive analysis of the heat transfer mechanism in PCM, which is why λ is one of the most important operational properties of polymer materials and compositions based on them.

Thermal conductivity is a thermodynamic characteristic that can also serve to regulate the structure of polymer materials, solving the problems of theoretical modeling of the connections between their physico-mechanical and thermophysical properties [1-4].

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The provision of polymer materials to the increasing needs of various industries is carried out in several directions: new materials are being developed and multi-tonnage polymer materials produced serially by chemical industrial enterprises are being modified.

Modification can be carried out at various stages of obtaining or processing the polymer by chemical and physical methods. The latter are currently used most widely, their general principles are sufficiently fully covered in works [3-7].

One of these polymers, the so-called polyvinylidene fluoride (PVDF), having good mechanical, including antifriction properties, has a fairly low thermal conductivity and a high thermal coefficient of linear expansion (TCLE) $(8-12)10^{-5}K^{-1}$ [7]. This makes it difficult to use it as a structural material for friction units.

It is known that modification of crystalline (CP) polymers based on fillers leads to a change in the polymer structure at different stages of PCM formation. It should be noted that such a ratio of filler to polymer does not always take place, therefore, if a small amount of dispersed filler substance enters the crystallized polymer, its particles mainly act as an artificial nucleating structure (ANS) forming element [8]. Thus, to improve the thermophysical properties of PVDF-based composites, it will be necessary to introduce heat-conducting fillers into them. Graphite and bronze are among such fillers, and their introduction into PVDF leads to an increase in the thermal conductivity of the material.

2 Materials and methods

The degree of crystallinity of the polymer χ and the average size of the crystallites (L) were chosen as structural parameters. The degree of crystallinity of PVDF was determined by radiographic (χ_R) [8], dilatometric (χ_d) and calorimetric (χ_K) [8,10] methods.

An indirect assessment of structural changes in PVDF with a change in the content of fillers was carried out by dynamic scanning calorimetry (DSC) by determining the specific heat capacity of the matrix and its density [6].

Measurements of the thermal conductivity of the PCM in the stationary heat flow mode were carried out at room temperature. The method is based on the registration of the heat flow from a flat source of constant power through the test sample of the PCM to a body with a constant temperature [3].

The density of unfilled and filled PVDF was determined by hydrostatic weighing. Ethyl alcohol was used as an immersion liquid. Quartz optical glass of the KB-I brand was used as a reference for determining the density of the immersion liquid.

3 Results and Discussion

The influence of graphite particles on the structural parameters and thermal conductivity of polyvinylidene fluoride.

The obtained results of the study of the effect of dispersed graphite on the thermal conductivity and structure of PVDF are presented in Figure 1. An indirect assessment of structural changes in PVDF with a change in the content of fillers was carried out by determining the specific heat capacity of the matrix and its density. The melting point T_{pl} of the polymer was determined by the maximum on the curve of dependence $C_p = f(T)$ PCM based on PVDF.

Depending on the volume concentration of graphite, λ will have two regions: the values of λ are explained by a small percentage of the filler in the concentration ($\varphi \leq 10\%$); a significant increase in the intensity of heat transfer is explained by an increase in the volume concentration of the filler. Chain structures begin to appear in the volume fractions

of the filler more than 25%, the polymer shunts, which leads to a linear growth of both λ and γ .

A joint examination of these data with the results of determining the degree of crystallinity by X-ray and dilatometric methods makes it possible to assume the presence of the influence of structural changes in PVDF. For a more complete analysis of the polymer-filler interaction process, it is necessary to use DTA and DSC data.

With a volume content of graphite of about 2.5%, the degree of crystallinity determined by dilatometric and X-ray methods has a local maximum, while the crystallite sizes also reach maximum values (Figure 1 a). This assumption is supported by local maxima on the dependences on the φ enthalpy and melting temperature, which according to [6] corresponds to the formation of relatively low-defect crystallites of enlarged sizes. This is also evidenced by the relatively rapid increase in Young's modulus (Figure 1). With a decrease in the distances between the filler particles, the growth of crystallites is hindered due to steric restrictions, so their sizes decrease somewhat and, in the future, stabilize.

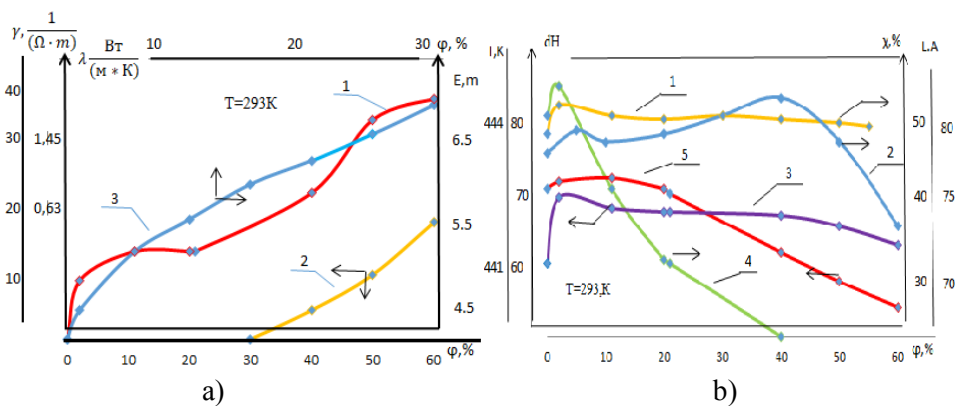


Fig. 1. a)-dependences on the graphite content in PVDF: 1-thermal conductivity λ ; 2-electrical conductivity γ ; 3-Young's modulus E . b)-dependences on the content of Low ash graphite (GLA) in PVDF: degrees of crystallinity 1- χ_r ; 2- χ_d ; 3-enthalpy of melting dH_m ; 4-dimensions of crystallites L ; 5-temper.

When analyzing the effect of GLA on the thermal conductivity of PCM, it is necessary to take into account the additional thermal resistance that occurs at the polymer-filler interface due to the interaction of the polymer not with the entire surface of the filler, but with individual active centers of its surface. This confirms the well-known provisions of the works [6-7]. The decrease in T_{pl} , the discrepancy between χ_d and χ_r , confirms that, despite the significant contribution of the thermal conductivity of the filler to the thermal conductivity of the PCM, the decrease in the growth rate of χ at $\varphi \leq 50\%$, confirms the need to take into account structural changes in the polymer even with significant filler contents (Figure 1).

The properties of the polymer deposited in the boundary layers (BL) [9], due to its relatively small size $\varphi \leq 10\%$, have practically no effect on the interrelation of $C_p^m = f(\varphi)$ thermophysical properties. This can be explained by the increased order of arrangement of the crystalline part in the polymer and the fact that the solid surfaces of the filler particles prevent the movement of molecules [7].

With an increase of φ up to 25%, despite the limitations of the possible sizes of crystallites, the dilatometric degree of crystallinity increases, but the defect of the formed crystallites is so great that X-ray structural data do not record its increase in comparison with the values corresponding to $\varphi = 2.5\%$ (Figure 1 b). As already noted, when the

volume content of the filler exceeds 25%, the structuring of the latter is accompanied by the displacement of the polymer and the contact area of graphite particles.

At the same time, the total surface area of the filler interacting with the polymer decreases, which leads to a decrease in its effect on structure formation in the polymer matrix. If the PCM can be represented as a matrix heterogeneous system before the start of filler structuring [3-4], then after the occurrence of direct filler-filler contacts, a model with mutually penetrating components is more suitable.

Limiting the number of possible conformations of macromolecules near solid surfaces leads, with a further increase in the relative volume of the boundary layer, to loosening of the packaging of the latter, which is accompanied not only by amorphization of the binder, but also by a further increase in the defect of the crystallites.

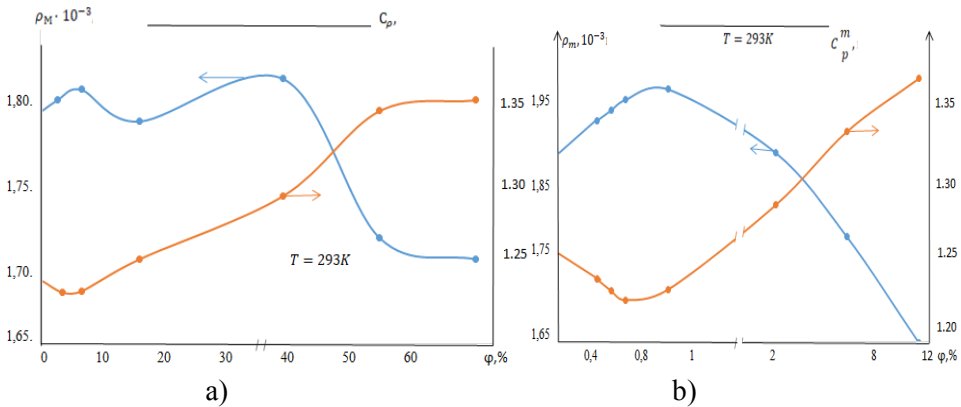


Fig. 2. a)-influence of graphite content in PVDF on its density and specific heat capacity b)-dependence of the specific heat capacity and density of the polymer component in the PCM of the PVDF+Br composition. from the content of fillers.

Influence of the concentration of bronze particles in polyvinylidene fluoride on its structural parameters and thermal conductivity.

Based on the obtained experimental values of C_p and p of the compositions, based on the additivity of the heat capacity, mass and volume of the components, we calculated the heat capacity (C_p^M) and the density of the polymer matrix ρ_m (Figure 2.b).

Thermodynamic factors have a significant impact on the size of the crystallites in the low concentration of fillers. One of the thermodynamic parameters that quantify the state of the crystalline structure of a polymer is its melting point T_{pl} , according to which some conclusions can be drawn about the change in the longitudinal dimensions of the crystallites [4-5, 10-11].

The same was found in the course of the conducted studies that the introduction of bronze particles into PVDF in small concentrations ($\phi \leq 2.1\%$) leads to an increase in the T_{pl} of the polymer. This is due to an increase in the longitudinal dimensions of the crystallites in accordance with the work [78].

The growth of T_{pl} may be due to the fact that crystallization begins at high temperatures under the influence of solid surfaces of bronze particles. Therefore, at the same melt cooling rate, the time of non-isothermal crystallization in the filled PVDF is longer than the unfilled one, and the crystallites have time to grow to large sizes accordingly. As the filler content increases, the influence of the kinetic factor increases, which is the reason for the decrease in the temperature of T_{pl} in the studied PCM with a high filler content.

The introduction of a small amount of bronze particles $\varphi = 2.1\%$ into PVDF leads to a decrease in the density of the polymer binder (Figure 2 b). A further increase in the filler concentration leads to a significant decrease in the ρ_m of the polymer matrix. Observed changes in the specific heat capacity of the polymer matrix correlate with changes in its density. The process of polymer crystallization in a wide range of changes in the concentration of fillers is influenced by two main factors: interaction with the filler and the presence of the filler in the polymer, which leads to a change in its viscosity [4].

The influence of these factors depends both on the nature of the filler surface and on its content in the polymer. With an increase in the filler content, the influence of the increased viscosity of the polymer prevails, which prevents the development of the crystallization process. Therefore, ρ_m in highly filled PVDF samples decreases to values characteristic of the amorphous state. Along with this, the reason for the decrease in the ρ_m of highly filled PVDF is the increased macrodeficiency of samples, these reasons determine the type of concentration dependencies $C_p^M = f(\varphi)$ and $\rho_m = f(\varphi)$. Since the dispersion of bronze differs slightly from the dispersion of graphite, but these fillers have a different nature, it is appropriate to compare the nature of the change in ρ_m and C_p^M , as well as other TFS for PCM with one and another fillers.

Bronze and graphite differ from each other in nature, degree of dispersion and thermodynamic activity - therefore, variations of ρ_m and C_p^M in crystalline polymers, in particular PVDF, vary depending on the thermodynamic activity of fillers. Also, the different effects of graphite and bronze on the PVDF structure are the cause of the changes observed in the thermal conductivity of the filled PVDF.

The thermal conductivity of bronze is significantly greater than PVDF, however, despite the contribution of the filler, the growth λ of the filled PVDF in the region of low bronze contents is very weakly expressed, which is due to the influence of the decrease in ρ_m . The introduction of small amounts of graphite into PVDF leads to a more significant increase in the thermal conductivity of PCM. It should also be noted that despite the higher thermal conductivity of bronze, the concentration dependence $\lambda=f(\varphi)$ of the composition of PVDF+ Br. in the entire studied area, the content is lower than in the case of graphite filling. The reason for this conclusion is the different effect of these fillers on the density of the polymer binder.

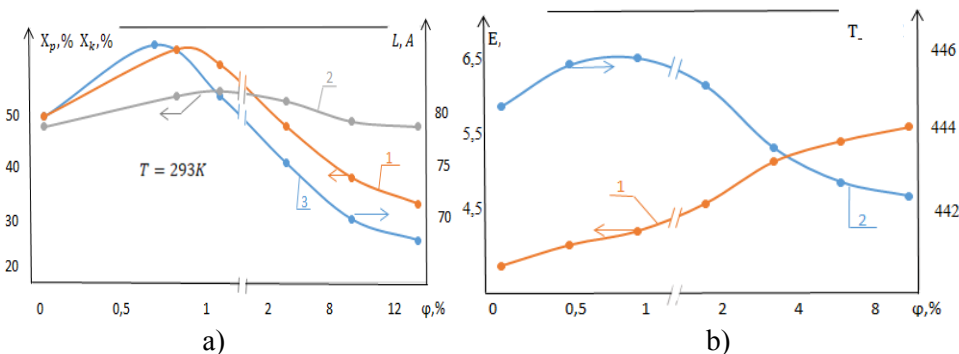


Fig. 3. a)-influence of the bronze por ash content in PVDF on: degrees of crystallinity (1- $\gamma_r\%$, 2- $\gamma_k\%$); longitudinal size of crystallites (3-L). b)-dependence on the content of bronze powder in PVDF: 1- modulus of elasticity of PCM; 2-melting temperature of PVDF.

The macro-defect of the polymer matrix structure in the case of graphite injection is significantly less than when PVDF is filled with bronze, which reduces the scattering of

phonons on defects in the polymer structure and contributes to an increase in the thermal conductivity of compositions based on PVDF and graphite.

Thus, the change in the thermal conductivity of PCM in the region of relatively low filler content is mainly due to changes in the polymer structure. The quantitative characteristic of such structural transformations is the change in the degree of crystallinity and the average size of PVDF crystallites in the compositions of both compositions, as well as the Young's modulus and melting temperature (Figure 3 b). The increase in highly charged compositions with the further increase in the content of fillers, despite the decrease in ρ_m lymer, is due to the dominant influence of the own contribution of fillers. The latter statement is also confirmed by the results of the study of the specific volumetric electrical conductivity of the filled PVDF. For high-filled PVDF (Figure 3.) with the same volume content of fillers, a higher value of the specific volumetric electrical conductivity γ is characteristic of PVDF filled with bronze, compared with compositions containing graphite.

With an increase in the filler content, the influence of the increased viscosity of the polymer prevails, which prevents the development of the crystallization process. Therefore, ρ_m in highly filled PVDF samples decreases to values characteristic of the amorphous state. Along with this, the reason for the decrease in the ρ_m of the highly filled PVDF is the increased macro defect of the samples (Figure 4.). As the content of electrically conductive fillers increases in the process of heat transfer in compositions, the role of the electronic component of thermal conductivity increases, although the participation of free electrons is possible even with small thicknesses of the polymer located between two filler particles. That is, in this case, filler-polymer type contact is carried out between the filler particles. A qualitative confirmation of this is an increase in the specific electrical conductivity γ already in the region of comparatively small filler contents, as evidenced by the type of dependence $\gamma = f(\varphi)$.

The formation of a quasi-metallic composite polymer system is due to the appearance of directly contacting or separated by a thin dielectric layer of particles. If the filler particles are in contact with each other, then along with the activated conductivity, quasi-metallic conductivity is carried out through "bridges" between the particles [3, 7]. With an increase in the filler content, the thickness of the dielectric layers between the particles decreases, which leads to a significant increase in the conductivity of the system, due to the contribution of the electronic component [6]. With significant electrical conductivity of the filler, the thermal conductivity of the PCM can be further increased due to the formation of a filler-filler type contact between the filler particles.

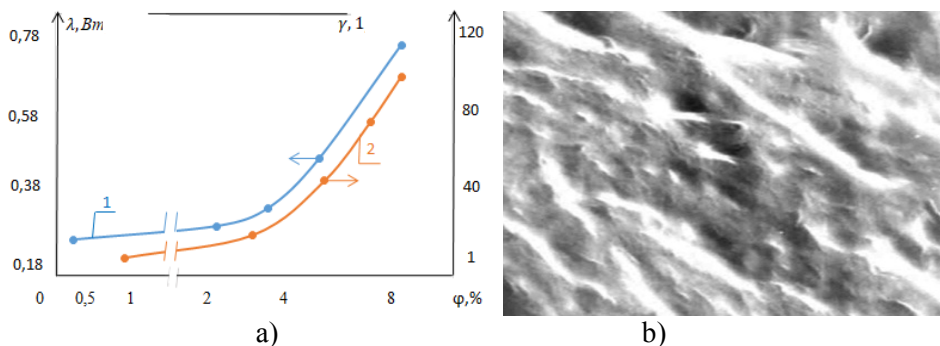


Fig. 4. a)-dependence on the content of bronze powder in PVDF: 1-thermal conductivity of PCM; 2- electrical conductivity of PCM. b)- supramolecular structure of PVDF containing 3% bronze.

Thus, a joint analysis of the impact of fillers of different nature (graphite, bronze), which differ in the degree of dispersion, shows that these fillers are one of the factors that can change the structure and mechanism of heat transfer of PVDF-based PCM.

4 Conclusion

Based on the electronic mechanism of thermal conductivity and electrical conductivity, it can be concluded that the characteristics of graphite are in the same order as those of a number of metals. It should be noted that graphite is characterized by anisotropy of a number of properties (thermal, electrical conductivity, thermal expansion, etc.). For example, the anisotropy of thermal conductivity can vary widely [3]. An exceptionally valuable feature of technical graphite is its ability to be structured into chain complexes, providing compositions with good electrical properties. An exceptionally valuable feature of technical graphite is its ability to be structured into chain complexes, providing compositions with good electrical properties. The study of heat transfer processes in PCM showed that despite the contribution of more heat-conducting bronze compositions are less than in the case of filling them with graphite. The reason for such a discrepancy between the thermal and electrically conductive properties of the filled PVDF is the different ratio between the thermal and electrical conductivity of bronze and graphite.

The study of heat transfer processes in PCM showed that despite the contribution of more heat-conducting bronze compositions are less than in the case of filling them with graphite. The reason for such a discrepancy between the thermal and electrically conductive properties of the filled PVDF is the different ratio between the thermal and electrical conductivity of bronze and graphite.

The thermal conductivity of bronze is several times greater than that of graphite, and the electrical conductivity is several orders of magnitude greater. Therefore, bronze's own contribution to the electrically conductive properties of compositions is manifested to a much greater extent than its contribution to heat transfer processes [7].

A qualitative confirmation of this is an increase in the specific electrical conductivity (γ) already in the region of relatively small filler contents, as evidenced by the type of dependence $\gamma = f(\varphi)$.

With significant electrical conductivity of the filler, the thermal conductivity of the PCM can be further increased due to the formation of a filler-filler type contact between the filler particles.

A joint analysis of the impact of fillers of different nature (graphite, bronze), which differ in the degree of dispersion, shows that these fillers are one of the factors that can change the structure and mechanism of heat transfer of PVDF-based PCM.

The increase in highly filled compositions as the content of fillers increases further, despite the decrease in the density of the polymer matrix, is due to the dominant influence of the own contribution of fillers.

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