

This paper reports a laboratory study of the physical, mechanical, and thermal properties of designed composite materials based on Phenylone C1 filled with silica gel. Structural plastics, due to their high chemical and wear resistance, sufficient level of physical, mechanical, and thermal properties, can significantly improve the technical characteristics of machines and mechanisms. However, some structural plastics, including Phenylone C1, have a significant drawback – a narrow temperature range of their processing, which leads to a complication of technological equipment and increases the cost of production. It was established that the technical processing of the initial composite material into finished products could be improved by introducing fillers.

The regularities of influence of silica gel content on the level of thermal and physical-mechanical properties of polymer composite materials based on Phenylone C1 have been established. It was found that the introduction of silica gel into Phenylone C1 leads to an increase in stress at the yield strength and modulus of elasticity at compression by 6.3 % and 13.3 %, respectively, compared to the original material. It was established that the heat resistance of the filled composite increases by 11.6 % with a decrease in thermal linear expansion by 10–20 %, depending on the content of the filler.

It was found that with an increase in silica gel concentration in the polymer matrix, the temperature of the onset of active destruction shifts towards higher temperatures. When filled in the amount of 30 % by weight, this temperature reaches 375 °C, which increases the temperature range of processing the designed material by 25 °C.

The study results make it possible to optimize the system of tolerances and landings of parts made of polymer-composite materials, simplify the technology of their manufacture, and, as a result, reduce their cost

Keywords: Phenylone C1, silica gel, heat resistance of composite, processing temperature, physical-mechanical properties, destruction temperature

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DETERMINING THE INFLUENCE OF THE FILLER ON THE PROPERTIES OF STRUCTURAL THERMAL-RESISTANT POLYMERIC MATERIALS BASED ON PHENYLONE C1

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1. Introduction

Modern industry is experiencing an acute shortage of special-purpose structural materials, which are cheaper and have a higher level of properties than existing ones. The introduction of these materials into machine units and mechanisms could increase their reliability and durability, productivity, safety for the environment, etc. In accordance with the principles devised by the European Commission on Key Enabling Technologies (KETs), the creation of such materials is one of the most priority and relevant tasks [1].

When polymeric products are used in the friction nodes, they undergo mechanical stress. High load values make it impossible to apply most polymeric materials in friction nodes due to their low strength and pliability. There are also some restrictions on the use of plastics: the physical-mechanical properties of plastics depend on the physical and phase state during operation. The performance of polymeric materials depends on the nature of the external forces (for example, static or dynamic load). All these factors lead to the fact

that many friction nodes are made of metals and their alloys whose physical-mechanical characteristics outperform those of polymers [2].

Promising structural materials for special purposes are polymers and composites based on them [3–6]. Due to the low level of density, high chemical and wear resistance, sufficient level of physical, mechanical, and thermal properties, parts that are made of them are able to improve the technical characteristics of machines and mechanisms and reduce the cost of production. In addition to advantages, polymer-composite materials (PCMs) have some drawbacks. The main disadvantages include limited (narrow) modes of processing the source material into finished products (parts). This requires the use of high-precision technological equipment, which does not always allow for a low cost of production. That is why designing new or improving existing technologies for producing PCMs at insignificant costs is a relevant task of materials science and mechanical engineering. The basis for reducing the cost of PCM production is the study of the properties of new materials

that could make it possible to optimize the modes of their processing in finished products.

2. Literature review and problem statement

The polymers of structural purpose include polyamides, synthetic materials that contain an amide group (CONH) with which carbon chains of different structures and lengths are connected [7]. According to the structure of the chain of a polymer macromolecule, polyamides are aliphatic and aromatic. They differ from each other both in structure and in the level of properties [7].

Aliphatic polyamides, compared to aromatic ones, have a worse level of physical, mechanical, and thermophysical properties. Therefore, to improve them, fillers of different nature and morphology are used, which are injected into the polymer matrix [8].

Paper [9] reports the results of comprehensive research into the physical, mechanical, and thermal properties, as well as membranes, of polyamides when introducing various organic and inorganic fillers into their structure. It is indicated that when devising PCM manufacturing technologies, special attention should be paid to interphase interaction and power fields arising in the composite. At the same time, to implement it, special pricey equipment is needed, which increases the cost of PCMs obtained. There are known polymeric composite materials based on aliphatic polyamides, which are filled with organic and inorganic fibers (carbon, basalt, aramid, etc.), dispersed materials (graphite, technical carbon, silicon-containing materials, etc.). Work [10] reports the results of a tribological study into fiberglass-filled polyamide. It has been proven that the designed material is recommended for the manufacture of gears as it has greater durability at friction without oil, compared to metals and alloys. It is indicated that polymeric gear drives have low carrying capacity and limited operating temperatures. The option of overcoming these shortcomings may be the introduction of fillers, nanomaterials, into the structure of aliphatic polyamides. This approach was used in [11] whose authors proposed the introduction of fillers in the form of montmorillonite treated with polyvinylpyrrolidone nanoparticles. The introduction of dispersed fillers makes it possible to receive the desired effect but the cost of such materials usually exceeds the economic effect of their implementation. Along with improving the level of properties of aliphatic polyamides, the cost of making products from them increases in most cases. For example, the price of original polyamide 6 is USD 4–6 per 1 kg while that of a polymer filled with carbon fiber reaches USD 20–25. At the same time, parts made of aliphatic polyamides can work at low temperatures (up to 120–140 °C) and a $p\dot{v}$ factor of up to 5 MPa·m/s, which limits the scope of their application. An option to overcome this disadvantage is to use aromatic polyamides with a high level of operational properties compared to aliphatic. The aromatic polyamide Phenylone C1 is close to metals in terms of its physical-mechanical properties. Thus, its elasticity limit at compression is 240 MPa. However, compared to metals, it has a very significant advantage. Its specific weight is 6–8 times less than that of metallic materials, that is, parts made of Phenylone have a much lower weight than that of metals. However, along with a high level of properties, such materials have a fairly high

cost of up to USD 100 per 1 kg. To reduce the cost of products made of aromatic polyamides, the fillers that are introduced into their composition are cheaper than the original polymer matrix, which can improve the level of the physical, mechanical, and thermal properties of the designed PCMs. One of these fillers is technical carbon; work [12] reports a study into the properties of PCMs based on Phenylone and the specified filler. It has been shown that the introduction of technical carbon into the matrix makes it possible to improve the characteristics of PCMs compared to the base material. However, the cited work reports a study under minor operating modes – pressure up to 1.5 MPa, slip speed up to 1.25 m/s, which limits the scope of such materials. An option to overcome the difficulties may be to use finely dispersed fillers. It is this approach that is applied in [13], which proposed to use low-containing carbon fibers as a filler. It has been shown that metal-containing carbon fibers, which include dispersed metals, are promising fillers for Phenylone C1. At the same time, the use of particles of metals of small size creates additional obstacles regarding the uniformity of their distribution. In addition, the cost of dispersed fillers is quite high, which leads to an increase in the cost of PCM obtained.

It is possible to resolve this issue by using inexpensive fillers with reactive surfaces capable of physical and chemical interaction with polymer molecules. This approach was applied in work [14], which proposed using, as fillers, silicon dioxides, which are widespread (up to 32 % of chemical compounds on Earth are silicon-containing) and cheap. Physical adsorption is possible due to the fact that silicon dioxides have a fairly developed surface (up to 400 m²/g). When processing into products, when high pressures and temperatures apply to the polymer composition, volatile components would be removed from the surface of the filler. At the same time, they form rarefaction in close proximity to the surface of the filler, due to which the molecules of aromatic polyamide are attracted to it partially or completely, thereby filling the irregularities of the surface profile.

Paper [15] reports the results of a quantum-chemical estimation study of PCMs based on the aromatic polyamide Phenylone C1 filled with silica gel. It was established that the chemical interaction of molecules of the source material with the filler is carried out mainly due to the formation of strong hydrogen bonds. These bonds occur between carbonyl oxygen atoms in polymer molecules and active hydroxyl groups on the surface of silica gel particles. Chemical interaction is possible by creating hydrogen bonds between active silanol groups on the surface of silicon dioxide with polyamide molecules.

In [16], it was confirmed that the likely creation of a hydrogen bond between silicon dioxide hydrogen and the oxygen of the amide group of polyamides is due to the fact that such a compound has higher interaction energy due to a lower distance between oxygen and hydrogen atoms. In work [16], the expediency of the introduction of silicon dioxide in Phenylone C1 was substantiated. However, the task of optimizing the content of the filler in the polymer matrix remains unresolved.

Based on our review, there is reason to believe that it is a relevant task to study the design of PCMs based on aromatic polyamide, which has a high level of physical, mechanical, and thermal properties with a low cost of finished products.

3. The aim and objectives of the study

The purpose of this study is to determine the effect of the filler on the characteristics and properties of polymeric-composite materials obtained using a simple technology of their processing. This will make it possible to substantiate the feasibility of using parts made from the designed PCMs in mechanisms and machines under different operating conditions.

To accomplish the aim, the following tasks have been set:

- to investigate the physical, mechanical, and thermo-physical properties of experimental samples made from the designed PCMs, based on the aromatic polyamide Phenylone C1 and silica gel;
- to analyze the effect of silica on the resistance of Phenylone C1 and PCMs based on it to the action of temperature.

4. The study materials and methods

The aromatic polyamide of the brand Phenylone C1 was chosen as a polymeric base. This polymer is obtained during the reaction of polycondensation at the interaction of diamines (75 % μ -phenylenediamine and 25 % n -phenylenediamine) from dechlorane hydride miso phthalic acid [17]. The general structural formula of the polymer is shown in Fig. 1.

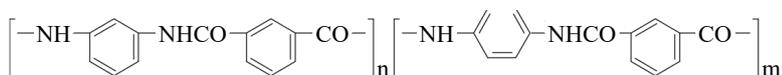


Fig. 1. The structural formula of the aromatic polyamide Phenylone C1

Phenylone C1 in its original form is a pink-white press material with a bulk density of 0.2–0.4 g/cm³, the main particle size is 20–40 μm , which meets the requirements set by TU 6-05-221-101-71.

The level of the physical, mechanical, and thermal properties of articles made from Phenylone C1 is given in Table 1.

Table 1

Properties of the aromatic polyamide Phenylone C1 [18]

| Property indicator | Value |
|---|-------|
| Density ρ , kg/m ³ | 1,330 |
| Strength, MPa: | |
| – at stretching, % | 110 |
| – at bending | 150 |
| Stress at yield strength under compression σ_y , MPa | 240 |
| Impact viscosity a_n , kJ/m ² | 40 |
| Hardness HB, MPa | 280 |
| Vick softening point T_{VC} , °C | 275 |
| The temperature of onset of active destruction T_D , °C | 350 |

Amorphous silicon dioxide, silica gel grade, with a high degree of chemical purity, obtained in the laboratory of polymeric materials and nanocomposites at the Department of Innovative Engineering of the State University “Ukrainian State Chemical Technology University”, was chosen as a filler. The structural formula of silica gel is shown in Fig. 2.



Fig. 2. The structural formula of silica gel

We have chosen the products and modes of silica gel synthesis based on earlier study [17] in order to obtain a filler with the most developed specific surface (Fig. 3).

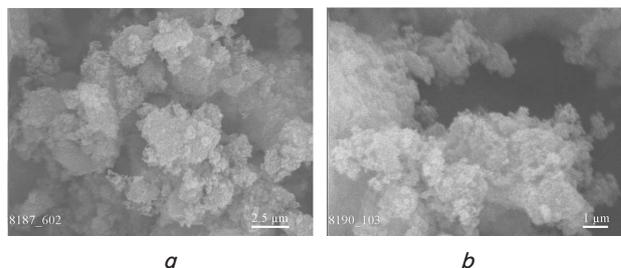


Fig. 3. Micrometric images of silica gel filler particles, magnification: a – $\times 320$; b – $\times 550$

The micrometric images of filler particles were acquired using an electron microscope (Superprobe-733 (Jeol)).

The density of the polymers and PCMs on their basis was determined in line with ISO 1183, using a hydrostatic weighing method, at the analytical scales VLR-200, with a module for hydrostatic weighing.

The stresses at yield strength (σ_y) and elasticity module (E) when compressing the initial polymers and PCMs on their basis were determined in line with ISO 604 and GOST 9550-81 at the universal breaking machine 2167 R-50 according to ISO 604.

The Vick softening point T_{VC} was determined at the device FWV-633/10 in accordance with ISO 1183-1.

We measured the linear thermal expansion of materials α in accordance with GOST 15173-70 at the device DKV-4.

The resistance to the effect of the temperature by the study objects was measured using a thermogravimetric analysis method, according to ISO-11358, by the methods of scanning by temperature and time at the TGA Q50 derivatograph.

5. Results of studying the properties of polymeric-composite materials

5.1. Results of studying the physical, mechanical, and thermal properties of the designed composite materials

In order to establish the optimal formulation of the composition, the concentration dependences of the elasticity limit at compression (σ_y) and module (E) of elasticity (Fig. 4) were studied.

Based on the obtained results, it was established that the introduction of silica gel into Phenylone C1 leads to an improvement in the level of physical-mechanical properties in the region of filler concentrations from 0 to 30 % by weight. With a further increase in the concentration of filler from 30 to 40 % by weight, there is a slight decrease in the PCM characteristics. When the filler content exceeds 40 % by weight, it leads to a sharp deterioration in the physical-mechanical properties of PCMs.

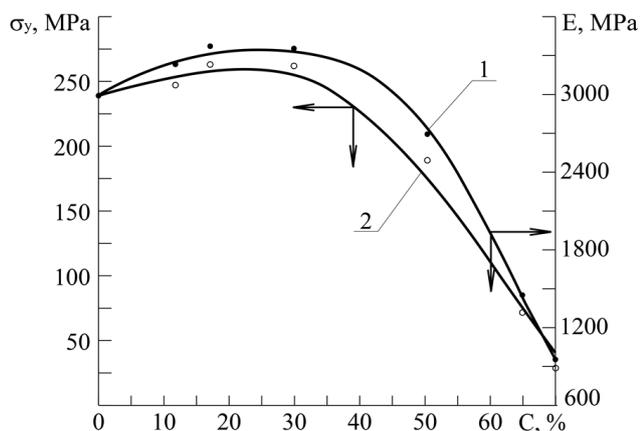


Fig. 4. Dependence of the physical-mechanical properties of the polymer-composite material based on Phenylone C1 on the content of silica gel, wt %: 1 – stress at the yield strength; 2 – elasticity module at compression

According to the results from our thermal physical study (Fig. 5), it was established that the introduction of silica gel into Phenylone C1 leads to an improvement in the level of thermal properties in the region of the examined filler concentrations.

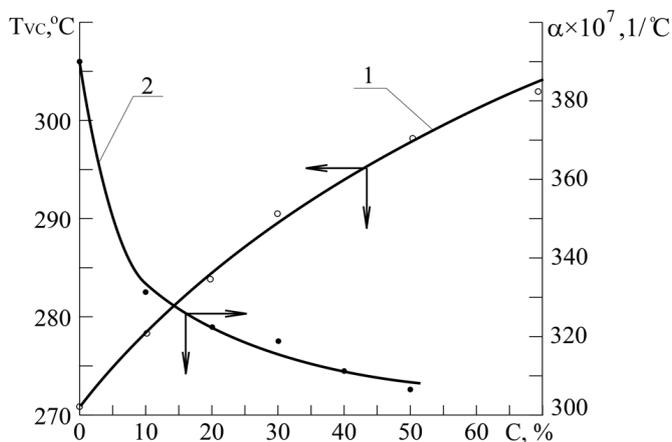


Fig. 5. Dependence of the thermal properties of the polymer-composite material based on Phenylone C1 on the content of silica gel, wt %: 1 – Vic softening point; 2 – coefficient of thermal linear expansion

The heat resistance values of the designed PCMs reach 307 °C, at 70 wt % of filler content in the polymer matrix. This makes it possible to expand the operating temperature range of parts made from the designed PCMs by 10–12 %, towards higher values.

The thermal expansion of the designed PCMs is reduced by 10–20 % depending on the content of the filler with an increase in the content of filler in the polymer matrix. This makes it possible to use parts made from the designed PCMs in moving joints in pairs with metal at the minimal probability of their jamming.

We fit the curves (Fig. 4, 5) acquired from the Mathcad software (USA) using the *regress* function. The error of experiments did not exceed 7 %. The value of the approximation accuracy for stresses at the yield strength, the module of elasticity at compression, the Vick softening point, and the

coefficient of thermal linear expansion is, respectively, 0.970; 0.979; 0.981; 0.971.

5. 2. Results of studying the influence of silica on the resistance of Phenylone C1 and the composite based on it to the effect of temperature

To increase the level of technological properties, we studied the influence of silica on the resistance of Phenylone C1 and the PCM based on it to the action of temperature in accordance with the results of the thermogravimetric study (Table 2).

Table 2

Resistance of Phenylone C1 and the PCM based on it to the action of temperature

| Material | Resistance of Phenylone C1 and the PCM based on it to the action of temperature, determined by the loss of their weight (%) when heated (°C) | | | | |
|---|--|-----|------|------|------|
| | 0 % | 5 % | 10 % | 20 % | 30 % |
| 100 % Phenylone C1 | to 350 | 410 | 420 | 429 | 436 |
| 90 % Phenylone C1+10 % SiO ₂ | to 362 | 415 | 425 | 434 | 442 |
| 80 % Phenylone C1+20 % SiO ₂ | to 370 | 421 | 445 | 463 | 475 |
| 70 % Phenylone C1+30 % SiO ₂ | to 375 | 425 | 450 | 467 | 479 |

According to our research, it was established that with an increase in the concentration of silica gel in the polymer matrix, the temperature of the onset of active destruction shifts towards higher temperatures, and, at 30 % filling, this temperature reaches 375 °C. That leads to an expansion of the processing temperature interval of the designed PCMs by 25 °C compared to those non-filled with Phenylone C1. Increasing the temperature interval of processing PCM greatly simplifies the technology of manufacturing parts from materials based on Phenylone C1 and leads to a decrease in their cost.

6. Discussion of results of studying the properties of polymeric-composite materials

A slight decrease in the characteristics of PCMs (Fig. 4) at the concentration of filler from 30 to 40 % by weight is associated with the beginning of the formation of local clusters of the filler. Further deterioration of the studied characteristics with the content of silica gel from 40 to 70 % by weight is due to the complexity of its uniform distribution in the polymer matrix. It should be noted that the dependences of stresses at the yield strength and the module of elasticity when compressed on the content of silica gel in Phenylone C1 (Fig. 4) are extreme. In this case, the maximum level of properties is achieved at 20–30 % by weight of silica gel in the designed PCMs. Increasing the concentration of filler above 30 % by weight leads to a deterioration in its distribution in the matrix, and, as a result, to a decrease in the specified indicators.

The aromatic polyamide Phenylone C1 refers to polymers that can work at high temperatures (up to 300 °C) and, at the same time, articles made from it, compared to other polymers, do not have a large temperature expansion. The limiting operating temperatures of the aromatic

polyamide Phenylone are determined by its heat resistance, due to the fact that Phenylone does not decompose to the softening temperature (up to 290 °C) [19]. The expansion of the processing temperature interval of the designed PCM (Fig. 5, Table 2) by 11.6 % is a consequence of the interaction of the filler with the polymer. This interaction leads to a restriction of temperature movement of the Phenylone C1 macromolecules when it interacts with the silica gel surface. As a result of this restriction of movement of macromolecules, there is also a decrease in the temperature linear expansion, depending on the content of the filler, by 10–12 %.

The limiting factor of the proposed method for obtaining PCM based on Phenylone C1 and silica gel is the impossibility of receiving a monolithic structure of the PCM, due to the uneven distribution at the concentration of filler exceeding 40 % by weight. The caveat of this study is the lack of intermediate values of the silica gel content (the step is 10 % by weight). In the future, it is necessary to carry out research on changes in the properties of PCMs based on Phenylone C1 and silica gel in a smaller step (3...5 % by weight) in the concentration range of the latter to 30–35 % by weight.

Thus, it is possible to recommend the PCM, based on Phenylone C1 with a filler concentration, silica gel, of up to 30 % by weight, for mobile joints of machines and mechanisms operating at temperatures up to 300 °C. Future stud-

ies in this area should address the impact of the duration and techniques of mixing the PCM components on the quality of their distribution.

7. Conclusions

1. It was established that the introduction of silica gel in the amount of 30 % by weight into Phenylone C1 leads to an increase in stress at the yield strength and elasticity module at compression by 6.3 % and 13.3 %, respectively. A further increase in the concentration of the filler leads to a deterioration of the specified parameters, which is explained by its local clusters in the matrix. The increase in heat resistance to 307 °C, as well as the decrease in thermal linear expansion by 10–20 %, depending on the content of the filler, are due to the physical and chemical interaction of Phenylone C1 molecules with the active surface of silica gel.

2. It was found that the introduction of silica into Phenylone C1 helps improve the stability of the resulting PCM. Thus, the temperature of the onset of active destruction at 30 % filling of the original matrix reaches 375 °C, which is 25 °C higher than the indicators of the corresponding material. Expanding the temperature interval of processing the designed PCM simplifies the technology of manufacturing parts and, as a result, their cost.

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