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HEAT-RESISTANT GAS-FILLED COMPOSITES BASED ON PHENYLON AND INORGANIC PORE FORMERS

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Abstract

Heat-resistant gas-filled polymer-based composites with inorganic pore formers were developed in the work. Aromatic polyamide phenylon, which is one of the heat-resistant and strongest polymers, was chosen as the polymer base. To reduce the viscosity of its melt during processing, PMS-500 oligosiloxane liquid was introduced into the products. It was established that the optimal content of this modifier is 2 % by mass. At this content of oligosiloxane liquid, the lowest values of polymer composite melt viscosity are observed during processing into products. To create a gas-filled composition, the following pore formers were studied: ammonium chloride (NH_4Cl), magnesium carbonate (MgCO_3), and polyvinyl alcohol (PVA). As a result of their thermogravimetric analysis, it was established that the most suitable pore former for aromatic polyamide is MgCO_3 , the decomposition products of which are able not only to create pores in the polymer, but also to thermostabilize it, which is proven by the increase in the Vicat softening temperature values of the obtained polymer composite materials. A study of the thermophysical characteristics of the developed foams based on phenylon, namely the apparent density, heat capacity, and thermal conductivity. It was established that their values are at the level of the best analogues. Based on the fact that in values of strength (up to 6 MPa) and maximum operating temperature (up to 557 K), the developed foams based on phenylon significantly exceed the best analogues, they can be recommended for use as foams operating at a significant level of loads and temperatures.

Keywords: gas-filled polymers; pore formers; phenylon; foam plastics; thermophysical and physico-mechanical properties.

ТЕРМОСТІЙКІ ГАЗОНАПОНЕНІ ПОЛІМЕРНІ КОМПЗИТИ НА ОСНОВІ ФЕНІЛОНУ ТА НЕОРГАНІЧНИХ ПОРОУТВОРЮВАЧІВ

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Анотація

У роботі розроблені теплостійкі газонаповнені композити на полімерній основі з неорганічними пороутворювачами. В якості полімерної основи було обрано ароматичний поліамід фенілон, який є одним із найбільш теплостійких та міцних полімерів. Для зменшення в'язкості його розтопу при переробці у виробі вводили олігоорганосилоксанову рідину марки ПМС-500. Встановлено, що оптимальним вмістом цього модифікатора є 2 % мас. За цієї концентрації олігоорганосилоксанової рідини спостерігаються найменші значення в'язкості розтопу полімерного композиту при переробці у виробі. Для створення газонаповненої композиції досліджували наступні пороутворювачі: хлористий амоній (NH_4Cl), карбонат магнію (MgCO_3) та полівініловий спирт (ПВС). У результаті проведення їх термогравіметричного аналізу встановлено, що найбільш підходящим пороутворювачем для ароматичного поліаміду є MgCO_3 , продукти розпаду якого здатні не тільки створювати пори у полімері, а і також термостабілізувати його, що доведено збільшенням значень температури розм'якшення за Віка отриманих полімерних композиційних матеріалів. Проведено дослідження теплофізичних характеристик розроблених пінопластів на основі фенілону, а саме удаваної густини, теплоємності та теплопровідності. Встановлено, що їх значення знаходяться на рівні найкращих аналогів. Виходячи з того, що за міцністю (до 6 МПа) та максимальною температурою експлуатації (до 557 К) розроблені пінопласти на основі фенілону значно перевищують кращі аналоги їх можна рекомендувати до використання в якості пінопластів, що працюють при значному рівні навантажень та температур.

Ключові слова: газонаповнені полімери; пороутворювачі; фенілон; пінопласт; теплофізичні та фізико-механічні властивості.

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Introduction

The latest investigations in the field of creating new types of gas-filled polymers are aimed at increasing their heat resistance and mechanical properties in order to be used as highly efficient structural materials [1–5]. To achieve this goal, it is necessary to use high-strength heat-resistant polymers as a polymer base [6–13].

One of the representatives of this class of polymers is the aromatic polyamide phenylon, which exceeds most industrial thermoplastic polymers in terms of mechanical properties and heat resistance [14–18]. However, the high viscosity of the melt poses certain difficulties for the pore formation processes in the polymer. Therefore, it is of great interest to conduct research aimed at finding rational ways to reduce the viscosity of the phenylon melt as well as to identify substances capable of pore formation in the volume of phenylon.

Objects of research. The aromatic polyamide phenylon C1 (poly meta-, paraphenylene isophthalamide) was chosen as the polymer matrix. Press material phenylon C1 is a fine pink powder with a bulk density of 200–300 kg/m³.

In order to improve the rheological properties of the phenylon the oligodimethylsiloxane brand PMS-500 was added, which is a colorless liquid resistant to high and low temperatures.

To implement the processes of pore formation in the volume of the polymer substances were used that decompose when heated in the temperature range of 610–630 K with the release of gaseous products. It is at these temperatures that phenylon turns into a viscous state, and gaseous products decompose to form pores in the volume of the polymer.

Ammonium chloride (NH₄Cl), magnesium carbonate (MgCO₃) and polyvinylalcohol (PVA), which are fine powders with a basic particle size of 20–40 mkm, were used as pore formers.

The production of samples for research was carried out as follows:

1. Drying the material at a temperature of 453 K for 40 minutes in order to release moisture, this is an agent of the destruction of phenylon.

2. Forming products by hot pressing at a temperature of 603 K and a specific pressure of 40 MPa followed by cooling under pressure.

3. Foaming of samples at a temperature of 613 K for 15÷20 minutes.

Research methods

The dynamic melt viscosity of the original and modified phenylon was determined by viscosimetric method according to ISO 6721-10:2015. Temperature resistance of the study objects was measured by thermogravimetric analysis in accordance with ISO-11358 on a Q-1500D derivatograph of the F. Paulik system; J. Paulik, L. Erdey. The softening temperature by Vicat was determined according to ISO 1183-1 on FWV-633/10. The density of the materials was determined by hydrostatic weighing according to ISO 1183-1. Stress at the yield strength in compression (σ_y) of materials was determined on a universal bursting machine 2167 P-50 in accordance with ISO 604. The heat capacity of samples of foamed phenylon C1 was determined in accordance with GOST 23630.1-79 on the device IT-C-400. The thermal conductivity of the samples of foamed phenylon C1 was determined in accordance with GOST 23630.2-79 on the device IT- λ -400.

Investigations of the surface morphology of samples from the original and foamed phenylon C1 were performed by optical microscopy on an “MBP-1” device equipped with a 5 MP SIGETA digital camera.

Research results

Aromatic polyamide phenylon has a high melt viscosity, which creates a significant barrier to pore formation in the mass of the polymer.

Oligodimethylsiloxane-based modifiers are used to improve the viscosity characteristics of the polymer. Their introduction into the composition of phenylon contributes to a significant reduction in the viscosity of the polymer melt. At a temperature of 613 K and a shear stress of 2.0 MPa, the melt viscosity decreases by an order of magnitude [19–21].

The results of studies of dynamic melt viscosity of the obtained polymer composite materials (PCs) as a function of temperature (T) and the concentration of the modifier (C) in the polymer are shown in Fig. 1.

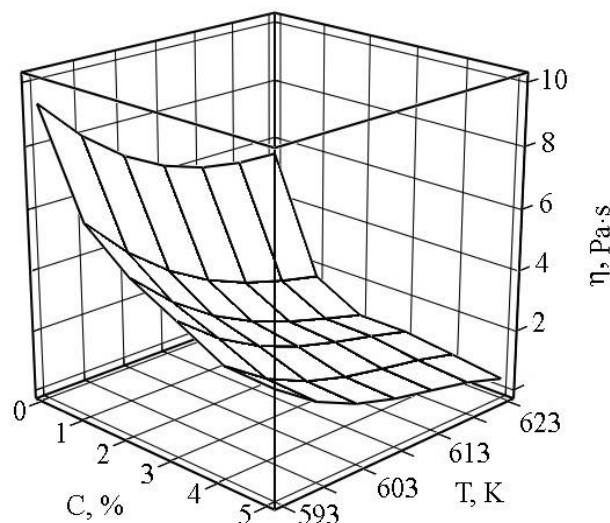


Fig. 1. Dependences of the dynamic melt viscosity (η) of a PCs based on phenylon and PMS-500 on the temperature (T) and concentration (C) of the modifier in the composition of phenylon

According to the obtained results the introduction of PMS-500 in phenylon C1 allows to reduce the dynamic viscosity of the PC melt based on it. In this case an intense decrease in dynamic viscosity is observed in composites with a PMS content of up to 2 %. A further increase in the concentration of the modifier does not significantly affect the decrease in viscosity and at certain values the incompatibility of the components and visible phase separation, which leads to a decrease in mechanical properties. At the same time, the temperature has a significant effect on the dynamic viscosity of the PC melt. The presence of a modifying agent that acts as an interstructural plasticizer increases the mobility of structural elements, which intensity increases with increasing temperature. This reduces the melt viscosity of the polymer to the point of its thermal degradation.

As a result of the research, PCs based on phenylone were obtained, the dynamic viscosity of the melt of which was significantly lower than that of the original phenylone, which contributed to better pore formation when creating foams based on phenylone. Therefore, as a basis for the production of foam selected PC based on phenylon which included 2 wt.% of polydimethylsiloxane (PMS-500).

To obtain a phenylon-based foam the substances were used that form pores in the polymer. One of the methods to achieve this effect is the introduction into its composition of a pore-forming agent, which when heated decomposes with the release of gaseous products that form

pores in the polymer during its transition to a viscous-fluid state.

For this purpose, a thermogravimetric analysis of compounds that decompose with the release of gaseous products during the transition of phenylon to a viscous-fluid state was performed. Compounds with a high level of thermal stability, which is close to the processing temperature of phenylon, are selected as gas creators. Fig. 2 shows the thermogravimetric curves of the substances selected as pore formers.

The thermogravimetric analysis of the above compounds indicates that PVA decomposes and loses mass when heated in the range of the investigated temperatures to 648 K. Compounds NH_4Cl and MgCO_3 begin to decompose intensively at temperatures from 498 to 648 K. PVA decomposes into acetaldehyde and carbon dioxide - magnesium on carbon dioxide and magnesium oxide, and ammonium chloride - on ammonia and hydrogen chloride.

Decomposition of PVA is carried out in a sufficiently wide range of temperatures, which will not allow obtaining the desired effect when foaming phenylon. The decomposition temperature of ammonium chloride is slightly lower than the transition of phenylon to a viscous-fluid state. In the process of decomposition, harmful substances are released into the environment. The decomposition of MgCO_3 occurs at temperatures that are almost identical to the transition temperature of phenylon to a viscous-fluid state, which allows the use of this material as an effective pore-forming agent in the formation of phenylon-based foam.

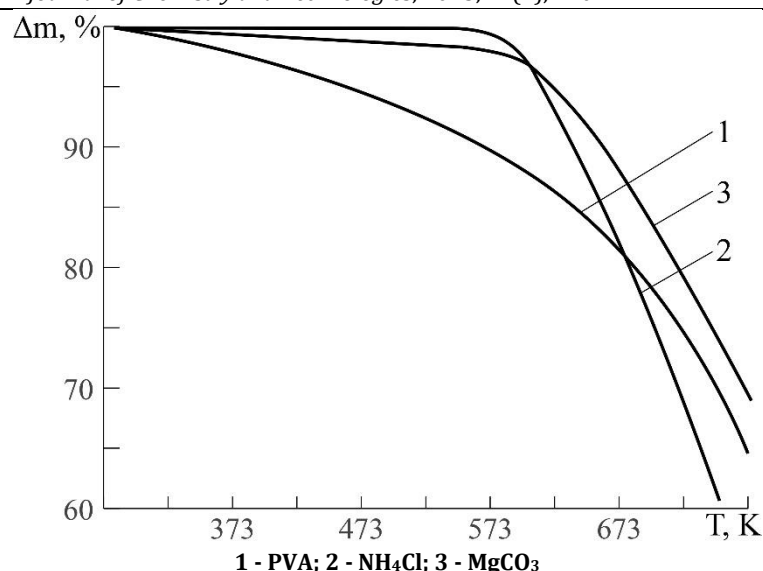


Fig. 2. Thermogravimetric curves of compounds

Therefore, for further research magnesium carbonate (MgCO₃) was chosen as the pore former.

To determine the time of complete decomposition of MgCO₃, at which the maximum release of gaseous components that foam phenylon occurs, we studied the kinetics of decomposition of MgCO₃ at a temperature of 593K, which corresponds to the initial temperature of processing phenylon [22]. Fig. 3 shows the results of these investigations.

According to them, it was obtained that the most intense mass loss of MgCO₃ occurs in the initial period of time up to 400 seconds. With a further increase in exposure at temperature, the intensity of mass loss slows down and its values stabilize from 900 sec., that indicates almost complete decomposition of MgCO₃. Thus the optimal holding time of the polymer composition based on phenylon and MgCO₃ for the formation of high-quality gas-filled material should be in the range from 900 to 1000 seconds.

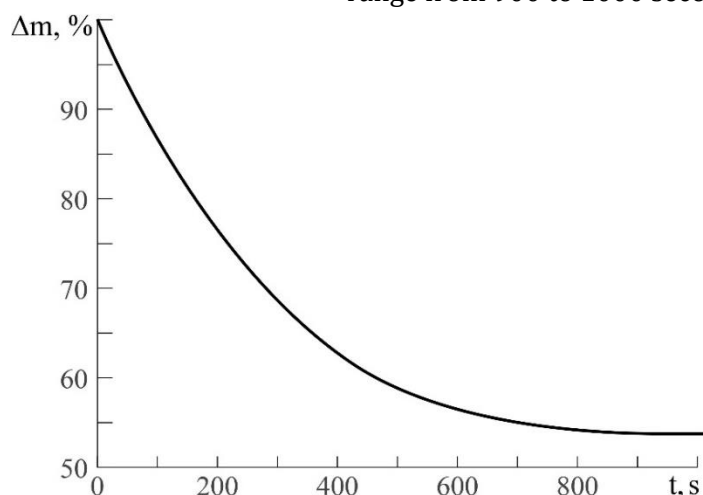


Fig. 3. Dependence of mass change (Δm) MgCO₃ on exposure time (t) at a temperature of 593 K

It should also be noted that the decomposition of MgCO₃ releases carbon dioxide and magnesium oxide, which, like most oxides, can have a heat-stabilizing effect on phenylon, which further increases its heat resistance and increases the operating temperature range of products from it. To support this assumption investigations have been performed to determine the effect of magnesium oxide on the softening temperature by

Vicat of phenylon-based PCs. Table 1 shows the results of the investigations.

It has been established that as the concentration of magnesium oxide in phenylon increases to 20 % softening temperature by Vicat increases from 546 to 600 K. This indicates the thermostabilizing effect of magnesium oxide on phenylon, which in turn expands the range of operating temperatures of its products.

Softening temperature by Vicat values for phenylon and based on it PCMs		
Nº	Materials	Softening temperature by Vicat T _{Vc} , K
1	100 % phenylon	546
2	95 % phenylon + 5% MgO	552
3	90 % phenylon + 10% MgO	557
4	85 % phenylon + 15% MgO	559
5	80% phenylon + 20% MgO	560

Based on the conducted studies it can be concluded that the most effective is the use of MgCO₃ as a foaming agent. Its use as a pore former allows not only to obtain phenylon-based foam due to the release of CO₂ during its decomposition, but also to improve its heat resistance due to the heat-stabilizing action of magnesium oxide, which is a by-product of thermal decomposition of MgCO₃.

Of particular interest there are investigations of the thermophysical characteristics of the developed foams based on phenylon, namely the apparent density, heat capacity, and thermal conductivity. These characteristics are especially relevant for foamed materials due to the fact that they are often used as thermal insulation materials.

Fig. 4 shows the concentration dependence of the apparent density of the developed phenylon-based foams.

According to presented investigations, as the concentration of magnesium carbonate in phenylon increases, there is a significant decrease in the apparent density, which is due to an increase in the amount of carbon dioxide, which is a pore former in the volume of the polymer. At the same time, exceeding the concentration of the pore-forming impurity above 15 % is not expedient, as there is a stabilization of the values of the apparent density, as well as some decrease in the mechanical characteristics of the obtained foam.

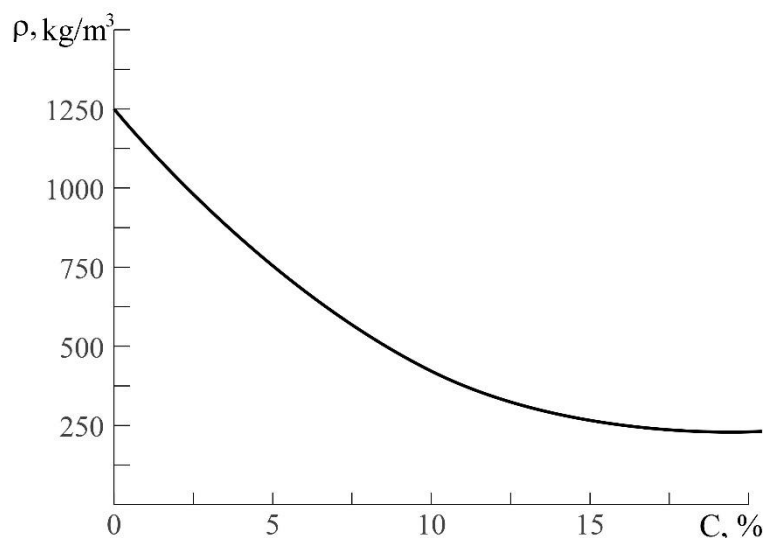


Fig. 4. Concentration dependence of the apparent density (ρ) of the developed foams based on phenylon filled with MgCO₃

The results of studies of the heat capacity of the developed phenylon-based foams (Fig. 5) showed that as the temperature increased, its values increased and reached a maximum within the glass transition temperature of phenylon. The change in heat capacity with increasing concentration of magnesium carbonate is a consequence of the fact that when the polymer is foamed, the absorbency of the material increases.

Of particular interest is the study of thermal conductivity of gas-filled compositions based on phenylon as the developed PCs can be

recommended for implementation as thermal insulation materials (Fig. 6).

The change in thermal conductivity of gas-filled phenylon with increasing concentration of porophore and increasing temperature is a consequence of the fact that in the volume of the polymer there is a two-phase system "gas-polymer". As the concentration of porophore increases, the amount of gas component increases, its thermal conductivity is much lower than in the polymer matrix. This contributes to the total reduction of this figure in the gas-filled polymer.

Some increase in thermal conductivity with increasing temperature is a consequence of increasing the thermal motion of the structural elements of the gaseous and solid components of phenylon-based foams, which contributes to the intensity of heat transfer processes.

As a result of investigations of heat capacity and thermal conductivity developed by PCs based on phenylon, it was found that the values of the obtained foams are at the level of the best foreign analogues and exceed them [23–25].

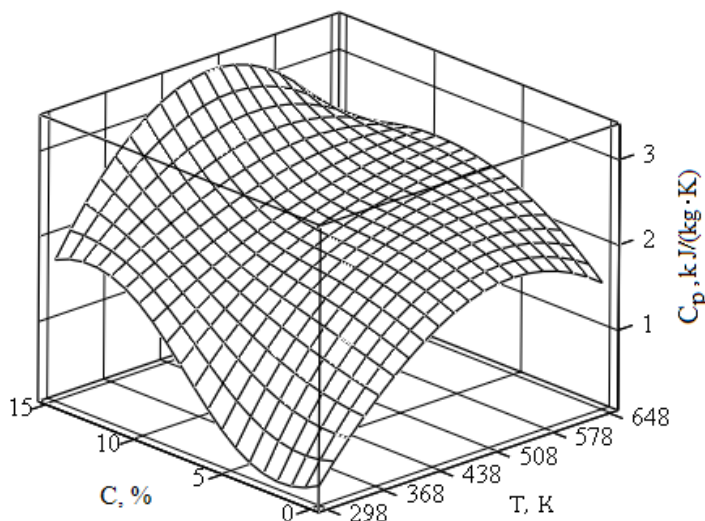


Fig. 5. Dependence of the change in heat capacity coefficient (C_p) of the PCs on the temperature (T) and concentration (C) of the foaming agent $MgCO_3$ in the composition of phenylon

The particular interest is the study of the morphology of the surface of composite materials based on phenylon.

Following the technique of foaming phenylon-based compositions, and obtaining foamed

samples, an optical examination of their surface was performed, which indicated the presence of fine-grained polymer in the volume. The pore size is about 50–150 micrometers (Fig. 7).

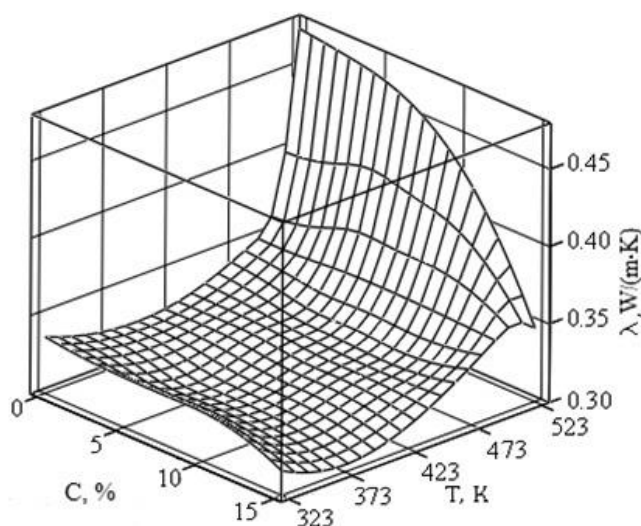
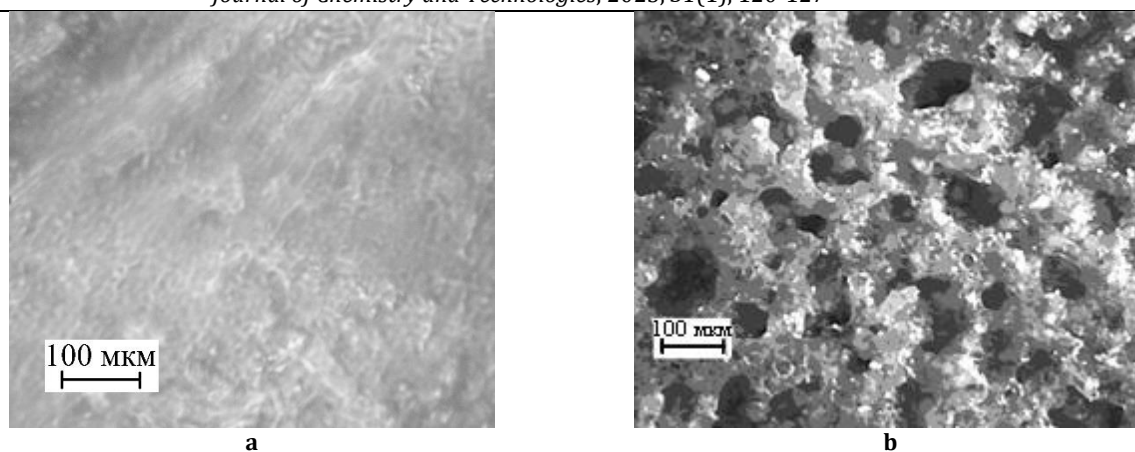


Fig. 6. Dependences of thermal conductivity (λ) of the PCs on the temperature (T) and concentration (C) of the foaming agent $MgCO_3$ in the composition of phenylon

At the same time, according to a visual assessment, it can be said that the quality of their distribution in the volume of the polymer matrix is quite high. It is of interest to compare the properties of the obtained gas-filled material based on phenylon with known industrial

analogues. Their comparative analysis is shown in Table 2.

Based on a comparative analysis it can be argued that in most respects foamed phenylon exceeds the most common in the industry foams based on polymers currently in use.



a – before foaming; b – after foaming

Fig. 7. Morphology of the surface composition of the composition phenylon C2 + 2 % PMS + 10 % MgCO₃

The maximum allowable operating temperature in most known polymers is about 373 K, while the foamed phenylon reaches a temperature of 557 K. The minimum allowable

operating temperature of the known foamed polymers is about 213 K, and the foamed phenylon – 193 K.

Table 2

Comparative analysis of the properties of the developed foams based on phenylon with similar materials used in industry

№	Indicator of properties	Values of property indicators				
		phenylon-based foam	expanded polystyrene	polyethylene foam	PVC foam	polyurethane foam
1	Density, kg/m ³	230	40–600	20–70	90–120	60–220
2	Stress at the yield strength in compression, MPa	6.0	0.8–4.0	-	0.4–0.7	2.0–10.0
3	Maximum operating temperature, K	557	373	358	343	440
4	Minimum operating temperature, K	193	-	-	-	-
5	Thermal conductivity, W/(m·K)	0.3–0.4	0.2	0.3–0.4	-	0.4–0.6

An excellent indicator is also the stress at the yield strength under compression, which in the developed PCs reaches the mark of 6.0 MPa, in contrast to other foam polymers, which have values in the range of 3–5 MPa.

Conclusion

1. Studies have been carried out aimed at reducing the viscosity of the phenylone melt. As a result of modification of phenylon with organosilicon liquid PMS-500 its viscosity is reduced by 7–10 times that considerably simplified process of pore formation and promoted improvement of quality of the received material.

2. The influence of magnesium carbonate on the processes of pore formation in phenylon and its thermophysical characteristics has been established. The optimal concentrations of the pore former in the polymer composition were determined.

3. A comparative analysis was obtained of the properties of the developed foams based on phenylon with similar materials used in industry. It is established that the developed materials significantly exceed the known analogues in terms of physical-mechanical and thermophysical properties.

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