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Binder and polymeric-ceramic material filled with nanosized Al₂O₃

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Abstract. The production of polymer-ceramic materials with high technological and mechanical properties requires the development of effective binders. The article considers the influence of modifiers on the curing process of polymethylsiloxane resin. It is shown that the introduction of modifiers helps to reduce the viscosity of the resin, and in the presence of a hardener, it makes it possible to obtain a binder with a low viscosity and an acceptable gelation time. Polymer-ceramic material based on the developed binder and nanoscale plasma-chemical Al₂O₃ powder has high mechanical properties, reduced shrinkage and porosity.

1. Introduction

The demand in heat-resistant materials for various industries is constantly growing. The use of ceramics is limited by its increased fragility and difficulties in producing of complicated items. That is why it is promising to use polymer-ceramic materials (PCM) based on organosilicon compounds, which are capable to form network structures upon curing. Structural transformations take place when these materials are heated: the detachment of side substituents and the formation of new siloxane bonds occur. After sintering with ceramic powders, such materials demonstrate increased strength, water resistance and the ability to work for a long time at temperatures above 1000 °C [1-5].

To obtain PCM with high mechanical and operational properties, it is necessary to create binders with a regular network structure and advanced technological properties, which are adapted to produce PCM by selected technology.

When creating a binder, an important task is to study the process of its curing. Network structure formation in polymer binder is influenced by its composition, temperature and time of curing, chemical and physicochemical transformations accompanying the process, as well as a number of other factors. Another point is a filler. At the present time, nanosized ceramic powders are widely used in PCM, which make it possible to obtain materials with increased density, strength, and unique electrical, magnetic, and optical properties. The use of nanosized powders, obtained in a high-frequency discharge plasma, is promising, since nanoparticles with an increased specific surface are formed using this method.

The article is devoted to the peculiarities of the curing of polymethylsiloxane resin in the presence of modifiers of various nature and functionality. The properties of PCM, based on developed binder and nanosized Al₂O₃ were examined.

2. Materials and Methods

2.1. Materials

• Polymethylsiloxane resin KM-9K (ZhZKM, Russia) – solid pieces of indeterminate shape from colorless to light yellow color; Ubellode dropping point – no more than 80 °C; mass fraction of non-volatile substances – not less than 95%.

• Octamethylcyclotetrasiloxane (OMCTS) is a colorless liquid; molar mass – 296.6 g/mol; boiling point – 175.8 °C; chemical formula: [(CH₃)₂SiO]₄.

• Vinyl-tris (2-methoxyethoxy)silane (Penta-65) – a transparent colorless liquid; molar mass – 280.4 g/mol.

• Catalyst 230-15 (Cat) – tin diethyldicaprylate – yellow liquid; density – 1165–1176 kg/m³.

• Al₂O₃ with an average particle size of 60 nm; specific surface – 26.5 m^2/g (Baikov Institute of Metallurgy and Materials Science, Russia).

2.2. Methods

2.2.1. Soxhlet extraction. Empty filter paper cartridges were weighed to the nearest 0.0001 g. Powdery specimens in pre-weighed filter paper cartridges were weighed, placed in Soxhlet extractor and subjected to extraction in toluene for 6 h. After that the specimens were dried to the constant weight and weighted again to find weight loss and the degree of curing (β , %):

$$\beta = \frac{[(m_0 + m_1) - (m_2 + m_3)] \cdot 100}{m_{0'}}$$
(1)

where m_0 – weight of a specimen before extraction, g; m_1 – weight of a filter paper cartridge before extraction, g; m_2 – weight of a specimen after extraction, g; m_3 – weight of a filter paper cartridge after extraction, g.

2.2.2. *Rheology*. Rheological studies were carried out on a Brookfield viscometer DV 2T, cone & plate type.

2.2.3. Thermomechanical analysis. The studies were carried out on a TMA Q-400 analyzer (TA Instruments).

2.2.4. Mechanical properties. Flexural strength (σ_{fs}) – ISO 178:2010; compressive strength (σ_{cs}) – ISO 604:2002; volume shrinkage (*Sh*_v) – ISO 3521:1997; apparent porosity (π_a) - ISO 5017:2013.

3. Results and discussion

Silicon compounds have increased thermal stability due to the high strength of the Si-O bond (the energy of Si-O bond is 369 kJ/mol). Among the other silicon compounds, silicone resins, in particular polymethylsiloxane resins, are used as polymer precursors for PCM for their ability to form network structures with high density at elevated temperatures [6]. The curing of silicon resins is accompanied by different structural transformations that help to increase the ceramic yield.

Polymethylsiloxane resin KM-9K was chosen as the main object of the present study for its ability to cure at elevated temperatures. The curing of KM-9K was investigated by the methods of Soxhlet extraction and rotational viscometry. The density of the network structure was calculated, resulting on thermomechanical analysis (TMA).

By Soxhlet extraction it was found that the degree of curing of KM-9K, after curing at different temperatures, is insufficient (Figure 1).

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Figure 1. Degree of curing via time for KM-9K at temperatures: 1 – 110 °C; 2 – 130 °C; 3 – 150 °C

It is seen from figure 1 that the curing of KM-9K proceeds slowly, the maximum degree of curing does not exceed 70 % and is achieved only after 160-180 min. This is due to the low content of reactive hydroxyl groups in KM-9K. To obtain PCM with high mechanical properties, a higher degree of curing is required.

KM-9K is a solid substance at room temperature. To use this resin as a binder and to obtain highly filled PCM, it has to be heated to a liquid state. The change in the viscosity of KM-9K upon heating is shown in Figure 2.



Figure 2. Change in the viscosity of KM-9K during heating

It was found that softening of KM-9K is observed at 60-70 °C, and at 80 °C a transition to a liquid state occurs. The intense increase in the viscosity of KM-9K at temperatures above 120 °C is explained by the formation of a network structure during curing.

Regulation of viscosity and the curing process of KM-9K was carried out by mixing it with lowmolecular-weight silicones: octamethylcyclotetrasiloxane (OMCTS) and vinyl-tris (2-methoxyethoxy) silane (Penta-65). OMCTS is an active diluent for KM-9K. It is a low-viscosity liquid (dynamic viscosity is 2.45 mPa·s at 20 °C), which could form joint network structures with KM-9K during heating due to the opening of its ring at the presence of catalyst. Penta-65 was used to improve the interaction of the binder with the filler. The content of finishing agent in a binder, as a rule, does not exceed a few percent.

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We added from 1 to 5 pbw of Penta-65. The effect of the amount of the modifiers on the viscosity of KM-9K was investigated (Figure 3).



Figure 3. Dependence of the initial viscosity of KM-9K on the content of modifiers at 100 °C: 1 – Penta-65; 2 – OMCTS

Both modifiers significantly reduce the initial viscosity of KM-9K: stabilization of viscosity values is achieved with the introduction of 10 pbw OMCTS and 3 pbw Penta-65. At the same time, these modifiers have no significant effect on the rate of curing of KM-9K. That is why catalyst (Cat) – tin diethyldicaprylate – was used to speed up the curing process. Further studies were carried out using the following binder:

100 pbw KM-9K + 10 pbw OMCTS + 3 pbw Penta-65 + 1.0 pbw Cat (Binder)

The degree of curing the cured Binder, established by Soxhlet extraction, was more than 90 %.

The effect of the temperature regime of curing on the change in the viscosity of KM-9K and the Binder was studied (Figure 4).



Figure 4. Viscosity via time for KM-9K (1, 2, 3) and the Binder (4, 5, 6) at temperatures: 1 - 100 °C (1, 4); 2 - 110 °C (2, 5); 3 - 120 °C (3, 6)

The obtained dependences were used to determine the gelation times (tg) of KM-9K and the Binder by plotting the dependence $1/\eta = f(t)$ and extrapolating the straight section of the viscometric curves (at $\eta \rightarrow \infty$) to the abscissa axis [7]. The results are shown in Table 1.

	Curing temperature, °C	<i>t_g</i> , мин
KM-9K	100	180
KM-9K	110	118
KM-9K	120	57
Binder	100	151
Binder	110	76
Binder	120	5

Table 1. Gelation times of the investigated compositions.

It was established that the dependences of the viscosity (η) of all compositions on the curing time (t) at the selected temperatures are described by the equation

$$ln\eta = ln\eta_0 + k_n \cdot t, \tag{2}$$

where $\eta 0$ – the initial viscosity (Pa s); $k\eta$ – the coefficient of the viscosity increase (min-1).

This allows to determine the activation energy of the curing process $(E\eta)$ in two ways [8]:

- to determine $k\eta$ from the graphical dependence $ln\eta = f(t)$ and then to calculate $E\eta$ from the tangent of the slope of the dependence $k\eta = f(1/T)$ (1 mode);

- to calculate Eq from the tangent of the slope of the dependence ln(1/tg) = f(1/T), since $1/tg \sim k\eta$ (2 mode).

The results of the calculations are shown in Table 2.

Table 2. Activation energy values.					
	E_{η} , kJ/mol				
	Mode 1	Mode 2			
КМ-9К	21.4	22.8			
Binder	16.7	15.8			

Regardless of the method (mode) to calculate $E\eta$, the values of this parameter are close to each other for every system. It should be noted that $E\eta$ is lower for the Binder in comparison with KM-9K, that means higher speed of curing of the Binder.

Using thermomechanical analysis (TMA), it is possible to calculate the parameters of the network structure of the cured systems [9]: the viscoelastic modulus (E), the molecular weight of the chain segment between crosslinking nodes (Mc) and the crosslinking density (nc). The systems were cured for 2 h at 120 °C. The obtained results are given in Table 3.

Table 3. Results of TMA.							
	<i>E</i> , MPa	M_c , g/mol	$n_c \cdot 10^{-3}$, mol/cm ³				
КМ-9К	3.8	3780	0.31				
Binder	5.4	1040	0.16				

It is seen from Table 3 that the developed Binder forms a network structure with higher density than KM-9K, which should contribute to the production of stronger and less porous PMC.

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The developed binder was filled with nanosized Al_2O_3 , obtained by the plasma-chemical method. All samples were subjected to thermal treatment for 2 h at 1200 °C. Mechanical and technological properties of PCM are presented in Table 4.

Tuble 1. Meenamear and teenmorogrear properties of Tenn.							
	$\sigma_{\rm fs}$, MPa	$\sigma_{\rm cs}$, MPa	$Sh_{\rm v}$, %	$\pi_{\mathrm{a}}, \%$			
KM-9K + 75 mas. % Al ₂ O ₃	34	116	2,2	4,3			
Binder + 75 mas. % Al_2O_3	42	144	1,0	1,8			

 Table 4. Mechanical and technological properties of PCM

It is obvious that the developed binder makes it possible to obtain PCM with improved mechanical and technological properties. This is due to a more complete completion of the curing process and the formation of a denser network structure due to the use of the selected modifiers.

4. Conclusions

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The specific features of the curing of polymethylsiloxane resin (KM-9K) have been investigated by Soxhlet extraction and rotational viscometry. The influence of modifiers on the rheokinetics of the curing process is shown. The optimal amounts of modifiers were chosen. Thermomechanical studies have established that the developed Binder has a higher modulus of elasticity and forms a denser network structure upon curing. Polymer-ceramic materials were obtained by filling the developed Binder with nanoscale plasma-chemical Al₂O₃, obtained by the plasma-chemical method. Mechanical tests have shown that after heat treatment at 1200 °C PCM, based on the Binder, have higher mechanical properties, lower shrinkage and porosity in comparison with materials with KM-9K.

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