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POLYMER COMPOSITE MATERIALS WITH A HIGH LEVEL OF THERMAL STABILITY BASED ON PHENOLIC RESINS AND DISPERSE SILICA FILLERS

Abstract. Development of the engineering industry is difficult without using of heat-resistant polymer composite materials for manufacturing of machines and mechanisms parts operating at temperatures up to 300°C. For this purpose it was suggested the diphenylsulfone formaldehyde resin as a polymer matrix, and different modifications of disperse silicas — white soot WS-120 and aerosol A-380 — were selected for fillers. The developed phenoplasts have high level of thermal stability (up to 370 °C), it's at 25–30°C is higher, then for initial resins. Apparently, this is a result of increasing of the interaction level on the boundary “polymer-disperse filler”, under the processing condition (at temperatures 170–190°C) due to appearing of covalent and hydrogen bonds between hydroxyl groups at the surface of the silica and methylol groups of the polymer matrix.

Keywords: polymeric composite materials, thermal stability, phenoplasts, silica fillers.

INTRODUCTION

Development of the engineering industry is difficult without using of heat-resistant polymer composite materials for manufacturing of machines and mechanisms parts operating at temperatures up to 300°C. The main factor that limits the application of well-known polymer-based materials is the significant change in the complex of physical and mechanical properties of the products during their use under enhanced temperatures. Therefore, the relevance of the problem is to create polymer composite materials (PCM) that can provide the stable performance of machines and mechanisms units at temperatures up to 300°C.

To create these, the materials selection of a polymer matrix and filler with high thermal properties is needed. The most common heat resistant polymers include — fluoropolymers, polyimides, aromatic polyamides, polyesterketones and phenolic resin [1–4]. Based on them the PCM which are filled with reinforcing fibers and disperse fillers got different morphology and nature, they can withstand temperatures up to 300°C without undergoing chemical degradation [5–19]. However, most of them are hard in processing into products; also they have the scarcity of the starting components and consequently high costs. The greatest interest among the heat-resistant polymers are phenolic, which are due to the prevalence of the initial components, together with relatively simple synthesis technology, processing into products and low cost are still promising materials for the creation of PCM with a high level of thermal stability.

MATERIALS AND METHODS

Materials. As polymer matrix was chosen a diphenylsulfone formaldehyde (DFSFR) resin,

developed and synthesized under the Department of Technologies of nature and synthetic polymers, fats and foods in SHEI “Ukrainian State University of Chemical Engineering” (Dnipro City, Ukraine). This product has a high level of thermal, physical and mechanical properties, low cost, wide distribution of the starting components and greater environmental safety than the classical phenol-formaldehyde resins [20].

The structural formula for DFSFR resin is shown in **Fig. 1**.

As fillers was chosen the next disperse silica: white soot (WS-120) of WS-120 type (GOST 18307-78), Ukraine; AEROSIL A-380 (A-380), Evonic Degussa, Germany [21; 22].

WS-120 is a silica, precipitated by reacting sodium silicate with sulfuric or hydrochloric acid, and it has the following characteristics: average particle size — 19–27 nm, the silica mass fraction — at least 87%, mass fraction of moisture — not less than 6.5%.

A-380 is silica obtained by flame hydrolysis of silicon tetrachloride, and it has the following characteristics: average particle size — 5–15 nm,

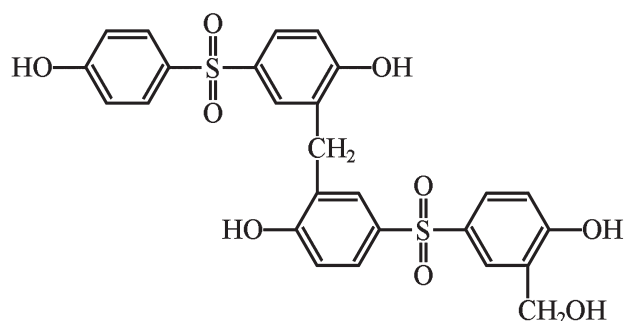


Fig. 1. The structural formula of DFSFR

the mass fraction of silicon dioxide — not less than 95%, mass fraction of moisture — not more than 1.5%.

Methods of PCM obtaining. The combination of components was conducted by impregnating an aqueous solution of the particulate filler DFSFR and further mixing them at a high-speed mechanical mixer until a suspension with uniformly distributed in the volume of the filler particles DFSFR. Drying of the mixture was carried to a constant weight in vacuum at 22–25°C. Grinding of the dried composition was performed on a high-speed paddle type mixer to a particle size of 40–70 microns. Palletization of obtained composition was done in molds at a pressure of 80 MPa. Standard test samples were prepared by compression molding at a temperature of 175±3°C with the pressure of 40 MPa and exposure material under pressure for 3 min at 1 mm thickness of the sample.

Research Methods. The morphology investigation of filler surface and PCM were performed by using electron microscopes Superprobe-733 (Jeol) and SEM-106I. Thermal stability of PCM was measured by thermogravimetric analysis in accordance with ISO-11358 using derivatograph TA Instruments TGA Q-50. Infrared spectra of fillers and developed PCM were obtained by spectrophotometer SPECORD 75-IR.

DISCUSSION OF RESEARCH RESULTS

It is well known [2] that the introducing of inorganic fillers to the phenolic resin in most cases increases of thermal properties of the PCM. However, the nature and structure of the particulate filler strongly affect the change of thermal and physical mechanical properties of PCM. To achieve a high level of complex thermal physical and mechanical properties of PCM filler must be thermally

stable at high temperatures and must have high adhesion to the polymer matrix, creating a strong bond at the interface "polymer-dispersed filler". As a fillers we used the mineral materials based on silica with high surface area (to 380 m²/g) and average particle size of 30 nm, which can ensure a high level of adhesion at the interface interaction "polymer-particulate filler" phase boundary.

The original form of the filler particles by electrostatic and Van der Waals forces are drawn, forming the agglomerates with sizes in the tens of micrometers (**Fig. 2**). Agglomeration of the filler reduces the area of contact at the interface between the phases "polymer-particulate filler", which turn reduces the level of interaction between them. The presence of such structures in the PCM will also have a negative role on the level of physical and mechanical properties as mechanical destruction will occur to these agglomerates as micro-defects. To create PCM with a high level of physical mechanical properties it is necessary to break the agglomerates of silica.

In the process of combining the components at their processing on high-speed mechanical stirrer was able to reduce and partially to destroy the silica agglomerates. As we can see from the micrographs on the surfaces studied PCM agglomerates occur fillers to 20–30 microns in size (**Fig. 3b**).

It should be noted that a further reduction in the size of the fillers agglomerates appropriate but practically difficult feasible with using the classical method of phenolic plastics processing and it is a factor in the reduction in process-ability with increased material costs while creating PCM.

It is known [1] that the quantitative characteristic of the thermal stability of polymers and PCM based on them is the temperature at which their active destruction begins. To determine the initial

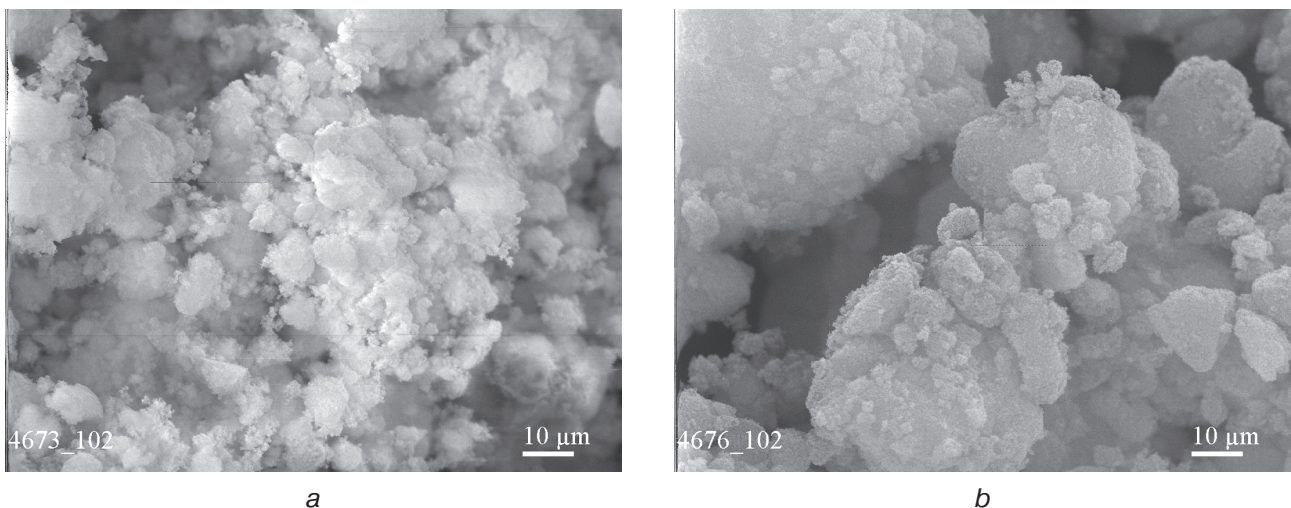


Fig. 2. Microphotographs of silica fillers: *a* — WS-120; *b* — A-380

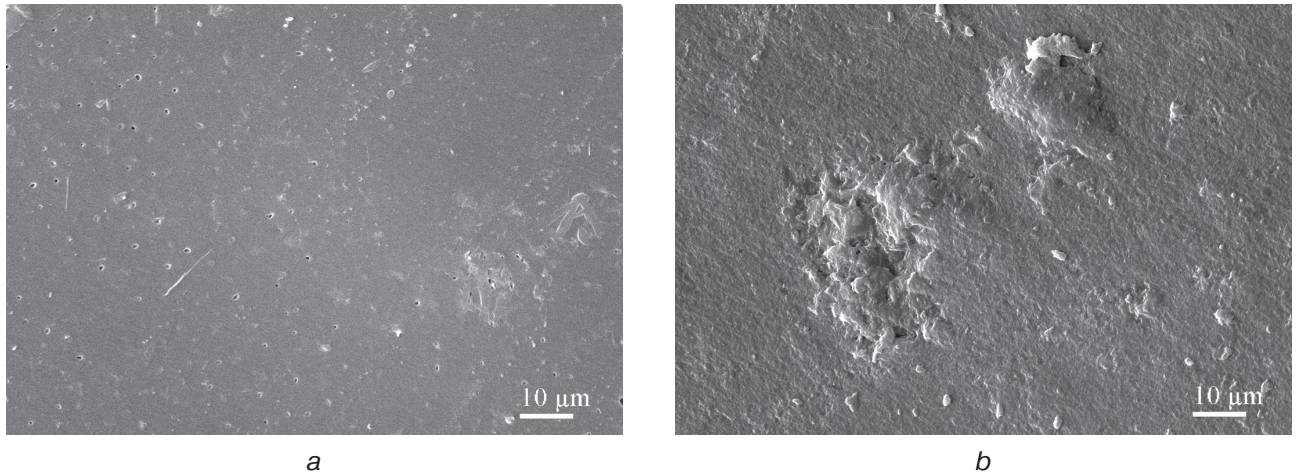


Fig. 3. Microphotographs of the surface of the original (a) and DFSFR filled by WS-120 (b)

active polymer degradation DFSFR and PCM based on it was carried out thermogravimetric analysis. The results are shown in **Fig. 4**.

From the obtained data we can see that the thermogravimetric curves of the original DFSFR and PCM based on it have a similar character. So at temperatures from 50 to 180°C there is weight loss associated with the removal of free and adhesive water. At temperatures of 180 to 340°C mass loss rate decreases. In this range the loss of weight associated with PCM phenolic residue removing unreacted components. With 340 to 370°C intensity of weight loss increases it is active phase of thermal destruction.

With increasing the filler content in DFSFR, active destruction onset temperature is shifted to higher temperatures. This phenomenon is characteristic for PCM filled with WS-120 (**Fig. 4a**), and

filled with A-380 (**Fig. 4b**). It should be noted that the heat resistance of composites filled by WS-120 at 10–15°C is higher than the composites filled by A-380.

Increased thermal stability by developed PCM may be result of physical or chemical interaction between filler and polymer matrix.

The **Table 1** presents data describing the effect of silica content in PCM on physical-mechanical properties.

It seen that, the introduction of silica dioxide to DFSFR are provide to increasing of a hardness (up to 154 MPa for the sample containing of 60 wt.% DFSFR and 40 wt.% WS-120) and compressive strength at yield (up to 154 MPa for the sample containing of 80 wt.% DFSFR and 20 wt.% WS-120). A developed materials got improved thermal stability due to operation under enhanced

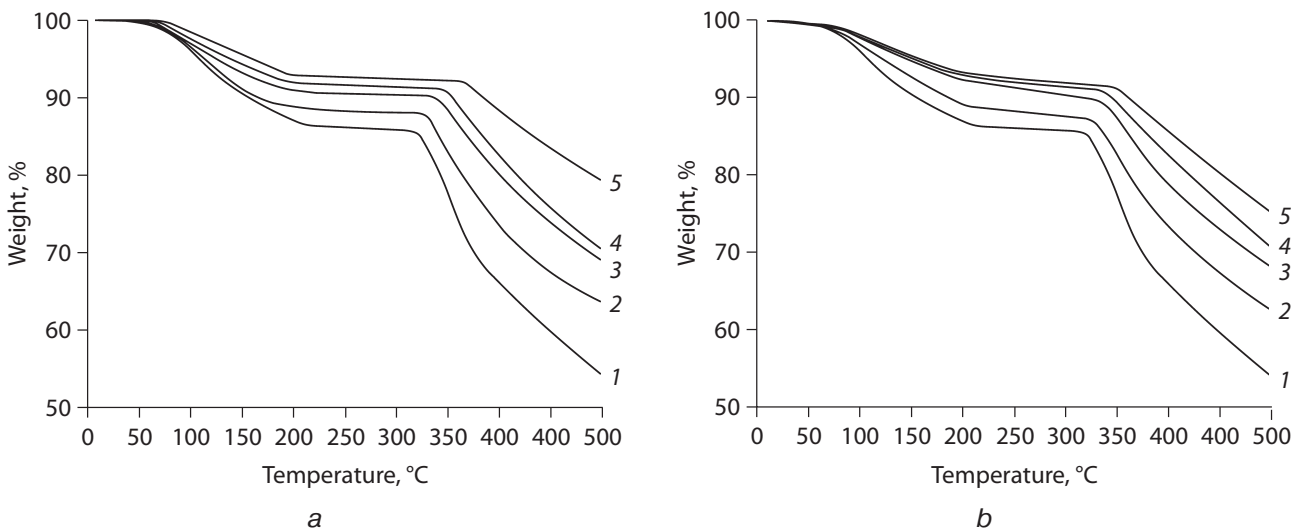


Fig. 4. Thermogravimetric curves (heat rate 10°C/min) of PCM based on DFSFR filled with (a) WS-120 and (b) A-380 (the degree of filling: 1 — 0 wt.%; 2 — 20 wt.%; 3 — 40 wt.%; 4 — 60 wt.%; 5 — 80 wt.%)

Table 1

Physical-mechanical properties of PCM based on DFSFR filled by silica

Composition	The degree of filling wt. %	The properties		
		Density kg/m ³	Compression strength at yield, MPa	Hardness, MPa
DFSFR	0	1450	171	132
DFSFR + WS-120	20	1547	179	150
	40	1650	154	154
	60	1744	89	129
	80	1840	54	110
DFSFR + A-380	20	1540	140	144
	40	1630	60	143
	60	1725	20	120
	80	1420	14	107

temperatures (from 300°C for initial DFSFR up to 350°C for PCM containing a of 60 wt.% DFSFR and 40 wt.% WS-120). Its need to note that the complex of physic-mechanical properties of developed PCM which filled by WS-120 its higher then for A-380, its can be a result of a higher content of a functional groups on the surface of a WS-120 and as a large surface area of that filler then for A-380.

It is known that due to processing of phenolic resin which are filled with dispersed materials, was observed an interaction between the functional groups on the surface of filler and polymer matrix [23]. In our case, on the surface of the silica, are large numbers of hydroxyl groups chemically bonded to silicon atoms [24], which can form chemical bonds with the polymer matrix during the process-

ing. To confirm this assumption, was conducted a study by infrared spectroscopy (Fig. 5).

In the infrared spectra of the materials an absorption rate is presented which is specific for silicas in: 1050–1210 cm⁻¹ area, which is responsible for antisymmetric fluctuations Si-O bonds in Si-O-Si of tetrahedron; 800–810 cm⁻¹, which characterizes the symmetric vibrations of tetrahedron SiO₂; 965–974 cm⁻¹, and responding to the wobble Si-O bonds in Si-OH; 3430–3440 and 1620–1640 cm⁻¹, which describes the stretching and deformation vibrations of bound and free hydroxyl groups.

It is known [25] that the presence of hydroxyl groups on the filler surface promotes the formation of hydrogen bonds with the polymer matrix more electronegative atoms due to PCM processing.

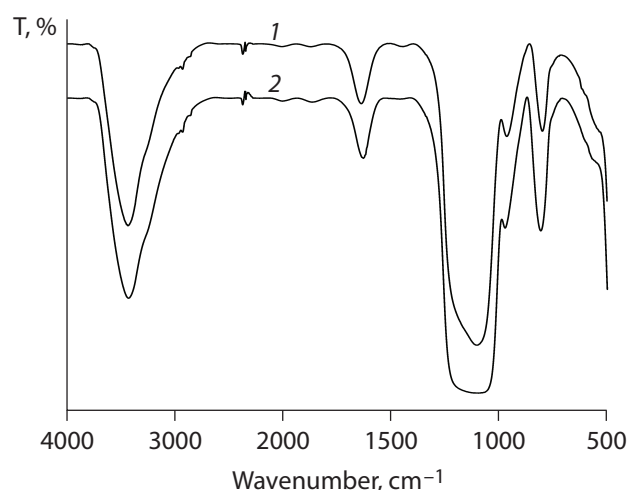


Fig. 5. IR spectra of silica oxide: 1 — WS-120; 2 — A-380

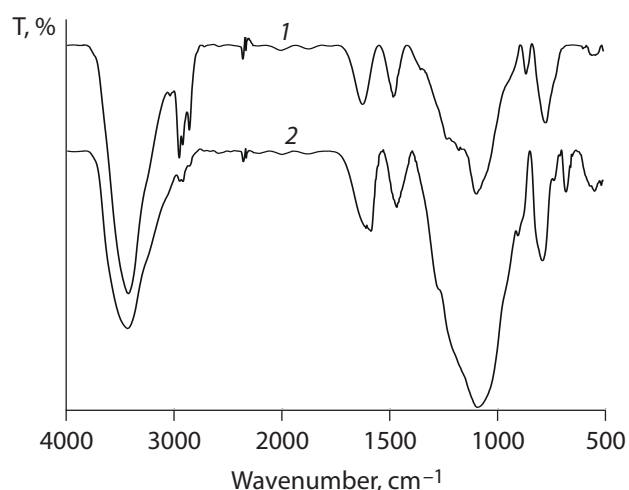


Fig. 6. IR spectra of PCM (60% DFSFR + 40% filler) filled with silica: 1 — WS-120; 2 — A-380

To confirm the characteristics of the chemical formation of bonds between the polymer matrix and filler we carried out the spectroscopic study of PCM based DFSFR filled with silica (**Fig. 6**).

In the IR spectra of the PCM, there are intense absorption peaks in the 3430–3450 and 1610–1640 cm^{-1} , they describe the stretching and deformation vibrations of free and associated groups (–OH).

It should be noted that the intensity of absorption peaks in the region 3430–3450 from PCM with WS-120 and A-380 is different. More intensive absorption peak observed for PCM filled by WS-120, it indicates the formation of a larger number of hydrogen bonds between the filler surface and polymer matrix. Such a hypothesis is correlated with the results of thermogravimetric analysis and it is likely the result of more intensive interaction at the interface “polymer – disperse filler”.

CONCLUSION

It was established that the PCM based on DFSFR and silica got the high level of thermal stability. It was found that the content in DFSFR of silicas shifts the temperature of the active destruction of PCM toward higher temperatures. Since the heat resistance of developed polymer composites 25–30°C is more than for the initial polymer has and it achieves 370°C. Apparently, this is result of increasing the level of interaction on the boundary “polymer-disperse filler”, at the processing condition (temperature 170–190°C) due to appearing of covalent and hydrogen bonds between hydroxyl groups on the surface of silica and methylol groups of the polymer matrix.

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ПОЛИМЕРНІ КОМПОЗИЦІЙНІ МАТЕРІАЛИ З ВИСОКИМ РІВНЕМ ТЕРМІЧНОЇ СТАБІЛЬНОСТІ НА ОСНОВІ ФЕНОЛЬНОЇ СМОЛИ І ДИСПЕРСНИХ ДІОКСИДІВ КРЕМНІЮ

Резюме. Розвиток машинобудівної галузі ускладнився без використання термостійких полімерних композиційних матеріалів для деталей машин і механізмів, що працюють при температурах до 300°C. Запропоновано як полімерну матрицю обрати діфенілолсульфон-формальдегідну смолу, а в якості наповнювачів використати дисперсні кремнеземи — білу сажу марки БС-120 та аеросил марки А-380. Розроблені матеріали мають високу термічну стабільність (до 370°C), що на 25-30°C вище, ніж для ненаповненого полімеру. Такий результат проявився при збільшенні рівня взаємодії в процесі переробки на межі розподілу фаз “полімер — дисперсний наповнювач” в умовах переробки (при температурах 170–190°C) за рахунок утворення ковалентних і водневих зв’язків між гідроксильними групами на поверхні наповнювача та метилольними групами полімерної матриці.

Ключові слова: полімерні композиційні матеріали, термічна стабільність, фенопласти, наповнювачі з кремнезема.

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ПОЛИМЕРНЫЕ КОМПОЗИЦИОННЫЕ МАТЕРИАЛЫ С ВЫСОКИМ УРОВНЕМ ТЕРМИЧЕСКОЙ СТАБИЛЬНОСТИ НА ОСНОВЕ ФЕНОЛЬНОЙ СМОЛЫ И ДИСПЕРСНЫХ ДИОКСИДОВ КРЕМНИЯ

Резюме. Развитие машиностроительной отрасли затруднено без использования термостойких полимерных композиционных материалов для изготовления деталей машин и механизмов, работающих при температурах до 300°C. Предложено в качестве полимерной матрицы использовать дифенилолсульфон-формальдегидную смолу, а в качестве наполнителей — дисперсные кремнеземы — белую сажу марки БС-120 и аеросил марки А-380. Разработанные материалы имеют высокую термическую стабильность (до 370°C), что на 25-30°C выше, чем для ненаполненного полимера. Такой результат может быть следствием увеличения уровня взаимодействия на границе раздела фаз “полимер — дисперсный наполнитель” в условиях переработки (при температуре 170–190°C) за счет образования ковалентных и водородных связей между гидроксильными группами на поверхности наполнителя и метилольными группами полимерной матрицы.

Ключевые слова: полимерные композиционные материалы, термическая стабильность, фенопласты, наполнители из кремнезема.

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