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KINETICS STUDY OF MODIFIED COAL TAR PITCH FOAMING

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Abstract

The foaming kinetics of a modified coal tar pitch (MCTP) with a complex blowing agent (CBA) under free foaming conditions was investigated. The kinetics study showed that a rate and a foaming criterion depend on both the CBA amount and polyvinylchloride amount expended on coal tar pitch modification. Using CBA for foaming the coal tar pitch modified with polyvinylchloride, it is possible to obtain solid foams (at 150°C) with a porosity of 24 to 76% and an apparent density of 0.31 to 1.0 g/cm^3 depending on the MCTP composition. The higher the polyvinylchloride content in MCTP, the lower the density and the higher the porosity of the resulting solid foam. The research results showed the possibility of obtaining the gas-filled material based on MCTP using CBA. To obtain solid foams with a stable fine-meshed and homogeneous structure, it is necessary to optimize the conditions of MCTP foaming process. To this end, research will continue to study the effect of the pressure and the foaming temperature of MCTP on the morphological characteristics of solid foams based on it.

***Keywords**: modified coal tar pitch; complex blowing agent; foaming; kinetics; solid foams..*

1. Introduction

Coal tar pitch is widely used as a polymer matrix to produce carbon foams [1-7]. Carbon foams (solid foams) are gas filled materials in which the dispersed phase is gas, and the dispersion medium is solid. Unique properties make the solid foams effective, constructive materials and potential for use in various industries as lightweight aggregates of constructions, heat and sound insulators, materials for liquid and gas filtration and others.

Coal tar pitch (CTP) is a residue obtained during coal tar rectification, which mainly consists of high-boiling multiring aromatic and heterocyclic compounds. CTP is cheap raw material, but it cannot be used for the production of carbon foam plastics without pre-treatment since its plastic properties usually do not meet the foaming requirements [8]. Pre-treatment consists of a modification of the CTP, as a result of which its rheological properties and structure change. There are various methods of CTP modification, including the polymerization or condensation of the pitch, by heat treatment at 380-450°C [6,9] or by treatment with different chemical reagents [6,10–14] to change its viscosity and anisotropy degree.

The authors [15] proposed a low-temperature (up to 170°C) modification of a CTP with polyvinylchloride. CTP modified by polyvinylchloride (MCTP) refers to thermoplastics and has a set of properties that correspond to amorphous polymers [16]. MCTP shows viscosity anomaly, which is characteristic of high-molecular compounds and has rheological properties that can allow to use it as a precursor for solid foams obtaining [17].

MCTP is much cheaper than classical polymers, so it is economically feasible to use it as a pitch-polymeric matrix to obtain solid foams.

To form a porous structure in the gas-filled composites production, the blowing agents are used. MCTP rheological properties [18] indicate that it is advisable to use the chemical blowing agents for its foaming. MCTP has a viscosity of 55-190 Pa·s in the temperature range 125-155°C [18].

The chemical blowing agent azodicarbonamide (ADCA) was chosen as a foaming agent. At temperatures of 200-210°C, the ADCA decomposition is accompanied by chemical reactions with the mainly molecular nitrogen formation (gas number 210-220 cm^3/g) [19-21]. Such a decomposition temperature is too high for MCTP foaming due to its rheological properties changing [18].

The foaming process depends on MCTP viscosity. At temperatures 130-150°C the MCTP is in a highly elastic and viscous-flow state, that is, it has a viscosity which can provide the foam formation. At temperatures 200-210°C the MCTP shows the Newtonian flow, that is, it has destroyed structure [18], its viscosity is too low to obtain the stable foam.

To reduce the ADCA decomposition temperature, an initiator – Zn stearate ($ZnSt_2$) has been used. Previous studies have shown [22], that the addition of $ZnSt_2$ in the amount of 0.25-0.5 weight part (further wt. part) to 1 wt. part ADCA allows reducing the ADCA decomposition temperature to 140-150°C (ADCA gas number 195-220 cm^3/g).

Currently, there is no information in literature sources about foaming of CTP modified by polyvinylchloride with the chemical blowing agents using. Therefore, the topic of the presented work is the investigation of complex blowing agent ADCA-$ZnSt_2$ influence on the kinetics of CTP foaming modified by polyvinylchloride. To this end, the relevant experiments were carried out, where the amount of used complex blowing agent ADCA-$ZnSt_2$ was varied from 1 to 5 weight part per 100 weight part of MCTP (weight part per 100 weight part further wt. p./100 wt. p.).

2. Experimental

2.1. Materials

For the study, CTP granules (6-8 mm) grade B (DSTU 8389:2015) were used: the METTLER softening point – 108°C; density 1.314 g/cm^3; content of substances insoluble in toluene - 31%, in quinoline - 9%, coke residue 56%; viscosity at 140°C – 9.3 Pa·s, at 160°C – 1.34 Pa·s; water content - 0.1%.

Polyvinylchloride C-6370-G (PVC) in accordance with the requirements of GOST 14332 - powder with a particle size of 100-200 microns; density 1.35 g/cm^3; bulk density 0.55 g/cm^3; K_F=63; melting point 150-220°C (with destruction).

Azodicarbonamide $NH_2CON{=}NCONH_2$ (CAS: 123-77-3). ADCA is yellow-orange crystalline substance odorless; decomposition temperature 210°C; gas number 218 cm^3/g; the content of the basic substance 95%. Optimal decomposition temperature –210 °C and higher, decomposition reaction is exothermic and autocatalytic.

Zn stearate ($(C_{17}H_{35}COO)_2Zn$) (CAS:1592-23-0)–white powder; melting point 130°C; Zn content 10.1%; powder bulk density 0.5 g/cm^3. Complex blowing agent (CBA) was prepared by mixing of ADCA and $ZnSt_2$ in the ratio of ADCA:$ZnSt_2$=1:0.25 (wt. part).

2.2. Foaming method

First, a mixture of CTP with different amount of PVC (3-20 wt. p./ 100 wt. p. of CTP) was subjected to low temperature modification for 2 hours at T = 170°C. After modification, the mixture was cooled and crushed to a powdered state.

The MCTP powder was mixed with a given amount of CBA (1 to 5 wt. p./ 100 wt. p. of MCTP) to a homogeneous state. The resulting mixture was filled into form by 2/3 of the volume, was compacted and closed a lid. The form was a cylindrical container (diameter - 3.5 cm, height - 2 cm, volume - 19.2 cm^3) with a lid.

The foaming process was carried out at atmospheric pressure in the closed form in a thermostat at T= 150°C for 60 minutes. At the end of the foaming, the form was quickly cooled to room temperature under a stream of cold water for τ = 2 min. Solid foam tablet was removed from the form, and its volume was measured.

Under the experimental conditions, a method based on the separation (condensation) of the gas phase in the volume of the MCTP (under free foaming conditions) was implemented. At atmospheric pressure, the powdered mixture melted upon heating foamed because of CBA decomposition, and the form was filled with foam under the pressure of the resulting gases. Fixation of the formed macrostructure of the foamed pitch occurred as a result of cooling. At cooling the viscosity of liquid matrix increased up to a loss of fluidity, i.e., the liquid matrix was transformed into a rigid material.

To estimate the efficiency of MCTP foaming by the CBA, the value of the foaming criterion (C_f) was used:

$$C_f = \frac{V_f}{V_0},$$

where: V_0 MCTP volume after foaming without of CBA; V_F–MCTP volume after foaming with CBA addition.

2.3. Research methods

To estimate the thermochemical transformations occurring in the system CTP-PVC under the action of ADCA and CBA, the thermogravimetric analysis and FTIR-spectroscopy have been used. The thermogravimetric analysis was carried out with Netzsch TG 409 PC Luxx in a dynamic heating mode up to 600°C in a nitrogen flow (80 mL/min) with a rate of oven temperature rises 10°C/min. Infrared investigations of the samples were performed on a Fourier IR-spectrometer Nicolet iZ10 Spectrometer in the range of 500-4500 cm^{-1}.

3. Result and discussion

First, the thermogravimetric analysis of dry mixtures of CTP, PVC, and ADCA was performed to determine the temperature of intense gas evolution.

Thermogravimetric analysis of dry mixtures of CTP, PVC and ADCA showed that ADCA (5. wt. p./100 wt. p. of CTP) decreases the weight loss temperature (5 and 10%) and increases the rate of decomposition comparing to CTP without a blowing agent (Table 1). In addition, in the presence of PVC, a further increase in the rate of the components mixtures decomposition is observed. From this, we can conclude that PVC initiates thermal decomposition reactions, accompanied by the release of volatile substances.

Table 1 The results of thermogravimetric analysis of CTP mixtures with PVC and ADCA

№	Mixture composition, wt. part			5% weight loss		10% weight loss	
	CTP	PVC	ADCA	T, °C	Weight loss rate ν, %/min	T, °C	Weight loss rate ν, %/min
1	100	0	0	266	1.1	301	1.7
2	100	0	5	248	1.6	278	2.5
3	100	5	5	255	2.8	268	5.5
4	100	10	5	255	2.1	280	2.8
5	100	20	5	255	2.8	275	3.5

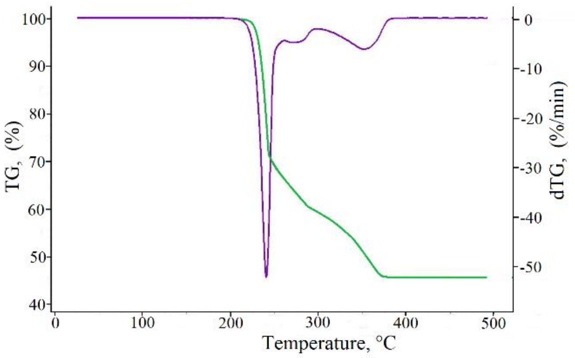

Fig. 1. Thermogravimetric curves of ADCA

From the analysis of the thermogravimetric curves of the samples (Fig. 1, 2) it can be seen that the change in the character of the DTG curves is mainly due to the presence of ADCA in mixtures. For ADCA (Fig. 1), the maximum weight loss rate of 52%/min is observed at 238°C; weight loss is 34%. The maximum weight loss rate for mixtures with a PVC content of 5 - 20 wt. part is in the range of 2.8 - 5.5%/min, while the weight loss is about 10% (Table 1)

The shift of the temperature of the maximum weight loss rate of the mixtures compared to ADCA to the region of higher temperatures of 268-280°C (Fig. 2) is explained by the decrease in the chemical reactions rate of the blowing agent decomposition in the viscous medium of CTP and PVC. Thus, thermogravimetric analysis of dry mixtures of CTP, PVC, and ADCA showed that the use of ADCA without an initiator would require a temperature above the ADCA decomposition temperature to foam the mixture of CTP and PVC. However, the undesirable processes of CTP and PVC destruction are accelerated at such temperatures. In addition, the low viscosity of CTP and the products of its interaction with PVC will not allow obtaining the stable foam.

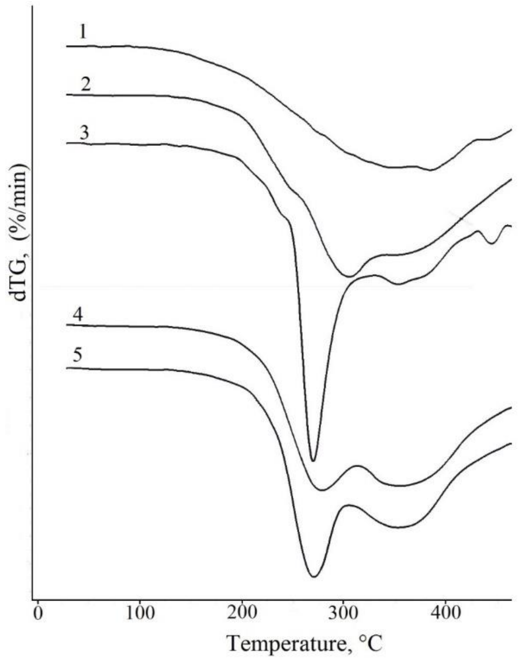

Fig. 2 Thermogravimetric curves of CTP (1) and mixtures of CTP with PVC and ADCA. Ratio CTP: PVC: ADCA (wt. part): 2)–100:0:5; 3)– 100:5:5; 4)– 00:10:5; 5)– 100:20:5

To investigate the foaming kinetics of CTP modified with PVC, the experiments were conducted in which a complex blowing agent (ADCA-$ZnSt_2$) was used in an amount from 1 to 5 wt. p./100 wt. p. of MCTP.

The foaming kinetics of CTP modified with different amounts of PVC (3 - 20 wt. p./100 wt. p. of CTP), depending on the amount of CBA at 150°C is shown in Fig. 3-5.

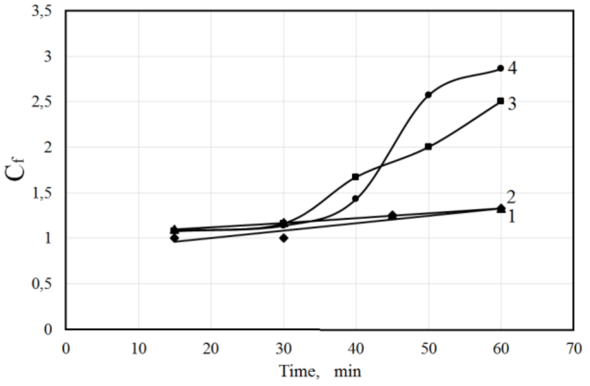

Fig. 3 Kinetics of the MCTP foaming at the ratio MCTP:CBA = 100:1 (wt. part) at T = 150°C depending on the modifier PVC amount (wt. p./100 wt. p. of CTP): 1) – 3; 2) – 7; 3) – 10; 4) – 20

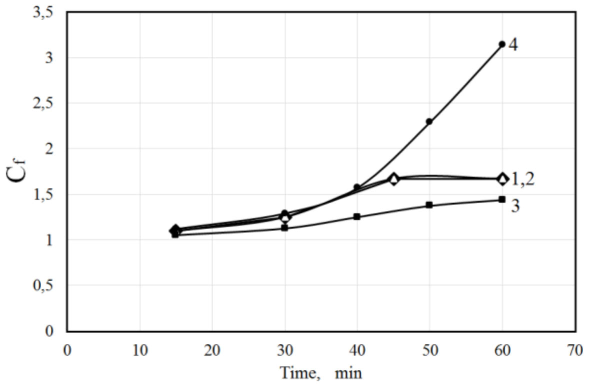

Fig. 4 Kinetics of MCTP foaming at the ratio MCTP:CBA = 100:5 (wt. part) at T = 150°C depending on the modifier PVC amount (wt. p./100 wt. p. of CTP): 1) – 3; 2) – 7; 3) – 10; 4) – 20

During the experiments, it was found that the necessary condition for the foaming process is the transfer of the powder composition into the melt, which takes about 15 minutes. Chemical reactions, leading to the release of gaseous substances, begin to activate only in the melt.

Kinetic curves (Fig. 3, 4) of the MCTP foaming at CBA amount of 1 and 5 wt. p./100 wt. p. of MCTP show the presence of the induction period from the 15th to the 30th minute, at which foaming is practically not observed. After the induction period, the chemical reactions of the CBA decomposition are activated, which is confirmed by the increase in the rate and in the foaming criterion. The rate and the foaming criterion depend on PVC amount expended on the modification of the CTP.

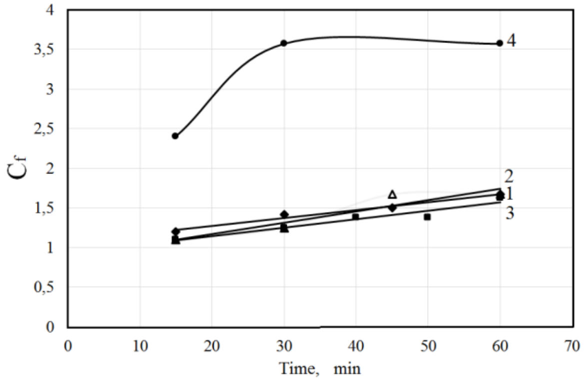

Fig. 5 Kinetics of the MCTP foaming at the ratio MCTP:CBA = 100:3 (wt. part) at T = 150°C depending on the modifier PVC amount (wt. p./100 wt. p. of CTP): 1) – 3; 2) – 7; 3) – 10; 4) – 20.

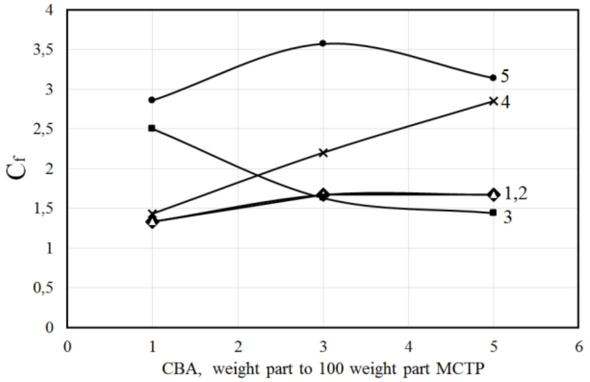

Fig.6 Dependence of the maximum foaming criterion value (C_{max}) for the MCTP on the CBA amount at T=150°C and the holding time of 60 minutes. MCTP with PVC content (wt. p./100 wt. p. of CTP): 1) - 3; 2) - 7; 3) - 10; 4) - 15; 5) - 20.

The kinetic curves of the MCTP foaming at CBA amount of 3 wt. p./100 wt. p. of MCTP have a slightly different character (Fig.5). When foaming CTP, modified by 3 - 10 wt. part of PVC, the rate and foaming criterion is not high and practically do not depend on the amount of PVC. However, the high content of PVC (20 wt. p./100 wt. p. of CTP) in the MCTP leads to the fact that already at the stage of melting an intensive gas evolution begins, which is confirmed by a high foaming rate, which ends in the 30th minute.

Calculations of MCTP averaged foaming rate (υ_f) up to reaching the maximum value of C_f at a temperature of 150°C showed that υ_f depends on the amount of PVC in the MCTP, and on the amount of CBA (Table 2).

$$\vartheta_f = \frac{\Delta C_{max}}{t_{max} - t_{ind}}$$

where: υ_f – averaged foaming rate, min^{-1}; ΔC_{max} – the change of foaming criterion C_f up to reach its maximum value; t_{ind} – induction period time, min; t_{max} – a time of maximum C_f reaching, min.

Table 2 Averaged foaming rates of MCTP up to reach the maximum C_f value at a temperature of 150°C, depending on the content of PVC and CBA

№	MCTP composition		CBA amount, wt. p./100 wt. p. of MCTP	C_{max}	$\upsilon_f \cdot 10^2$, min^{-1}
	CTP, wt. part	PVC, wt. part			
1	100	3	1	1.3	1.1
2	100	3	3	1.7	0.8
3	100	3	5	1.7	1.4
4	100	7	1	1.3	0.5
5	100	7	3	1.7	1.4
6	100	7	5	1.7	1.4
7	100	10	1	2.5	4.5
8	100	10	2	2.1	2.5
9	100	10	3	1.3	1.3
10	100	10	5	1.4	1.1
11	100	20	1	2.9	5.7
12	100	20	3	3.6	7.8
13	100	20	5	3.1	6.2

An increase in the foaming rate is observed with an increase in the PVC content in the composition of the MCTP to 10–20 wt. p./100 wt. p. of CTP. At 20 wt. p./100 wt. p. of PVC in the MCTP the foaming rate is maximum and is $5{,}7\cdot10^{-2}$ – $7{,}8\cdot10^{-2}$ min^{-1}, depending on CBA amount (Table 2, exp.11-13).

It should be noted that the maximum foaming rate value is $4.5\ 10^{-2}$ min^{-1} for MCTP with a PVC content of 10 wt. p./100 wt. p. of CTP was observed only at CBA amount of 1 wt. p./100 wt. p. of MCTP. For such an MCTP composition, the foaming rate decreases with an increase in the CBA amount to 5 wt. p./100 wt. p. of MCTP (Table 2, exp.7-10).

For MCTP with low PVC content (3–7 wt. parts on 100 wt. parts CTP), the foaming rate is low and ranges from $0.5\cdot10^{-2}$ to $1.4\cdot10^{-2}$ min^{-1} (Table 2, exp.1-6).

The dependence of the foaming criterion C_{max} on the PVC content and the CBA amount at T=150°C and the holding time of 60 min is presented in Fig.6. Analysis of the curves in Fig. 6 showed that for different compositions of the MCTP, the effect of CBA manifests itself in different ways. The maximum foaming criterion 2.9-3.6 is observed for MCTP modified by 20 wt. part of PVC at CBA amount 1-5 wt. p./100 wt. p. of MCTP. When foaming MCTP containing PVC 15 wt. part with an increase of CBA amount from 1 to 5 wt. part the foaming criterion increases from 1.4 to 2.85. For MCTP modified with 3-7 wt. part of PVC, with an increase in the CBA amount (1-5 wt. p./100 wt. p. of MCTP), there is a slight increase in C_{max} from 1.3 to 1.7. Only for MCTP modified with 10 wt. part of PVC, with an increase in CBA amount from 1 to 5 wt. part a decrease in the foaming criterion from 2.5 to 1.4 is observed.

From Table 3 it can be seen the properties of solid foam depend on both the CBA amount and the PVC content in the MCTP. When foaming MCTP with a high PVC content, (10 -20 wt. p./100 wt. p. of CTP) solid foams with the highest porosity (up to 76%) and low apparent density (up to 0.31 g/cm3) are obtained. The solid foam properties depend on the PVC and CBA amount (Table 3, exp.7-13).

Table 3 Characterization of solid foams obtained by foaming the MCTP with a CBA at T=150 °C and P_{atm}

№	MCTP composition CTP, wt. part	PVC, wt. part	CBA amount, wt. p./100 wt. p. of MCTP	Apparent density ρ, g/cm^3	Porosity, %
1	100	3	1	0.99	25
2	100	3	3	0.81	38
3	100	3	5	0.80	39
4	100	7	1	1.00	24
5	100	7	3	0.81	38
6	100	7	5	0.81	38
7	100	10	1	0.53	60
8	100	10	2	0.65	51
9	100	10	3	0.62	53
10	100	10	5	0.69	48
11	100	20	1	0.40	70
12	100	20	3	0.31	76
13	100	20	5	0.36	73

With a low PVC content (3-7 wt. part) in the MCTP, the solid foam properties are mainly influenced by the CBA amount, the higher its consumption, the lower the apparent density and the higher the porosity (Table 3, exp.1-6). With an increase in CBA amount from 1 to 5 wt. part the apparent density decreases from 0.99 to 0.81 g/cm3, and the porosity increases from 24 to 39%.

In the process of research, it was found that for samples of solid foams containing 3, 7, 15, 20 wt. parts PVC, the optimal CBA amount is 3 wt. p/100 wt. p. of MCTP, and for solid foam containing 10 wt. parts PVC, the optimal CBA amount is 1 wt. p./100 wt. p. of MCTP.

As can be seen (Fig. 7), all foam samples have a porous structure. The pore size ranges from 200-500 μm to 1 mm. The study of the obtained samples structure of solid foams showed that the gas-filled material is characterized by large pore size and heterogeneity. This is most likely due to the mismatch of the gas evolution kinetics and cell growth with a change in the MCTP viscosity. MCTP foaming at atmospheric pressure and T=150°C leads to asynchrony of these processes, which makes it difficult to obtain a foam with a stable and homogeneous cellular structure. When CBA decomposes, gas bubbles are formed, which coalesce due to their merging, forming large cells or cavities inside the sample. It can be assumed that with the rapid CBA decomposition and low viscosity of the MCP at 150°C, the destruction of the cell walls is observed, and a material with a heterogeneous large-cell structure is obtained.

Infrared spectroscopy allowed determining the basic changes in chemical bonds and functional groups observed during MCTP foaming.

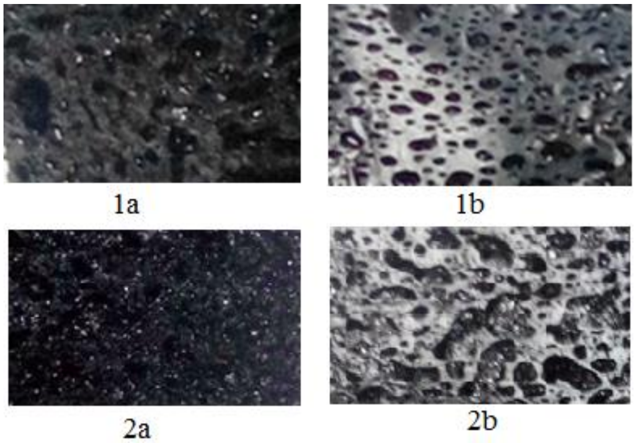
1a 1b
2a 2b

Fig.7 Photographs of gas-filled MCTP samples (3 wt. part of CBA per 100 wt. part MCTP): a - pores inside the sample; b - pores on the surface of the sample. MCTP samples (wt. part of PVC per 100 wt. part of CTP): 1) 10; 2) 20

It is known that the absorption band at 3040 cm^{-1} corresponds to the stretching vibrations of the aromatic CH bond, and the band at 1600 cm^{-1} corresponds to the stretching vibrations of the C=C double bond [23]. The peaks of 2700 - 2980 cm^{-1} and 1480 to 1370 cm^{-1} are related to the aliphatic hydrogen stretching absorption in CH_2 and CH_3 structures [24]. The peaks of 2920 cm^{-1} and about 2860 cm^{-1} are characteristic of CH_2, and a peak of about 2960 cm^{-1} is characteristic of the methyl CH_3-group. The absorption band 1690 - 1730 cm^{-1} characterizes the vibrations of the carbonyl group C=O in the CTP [25-26].

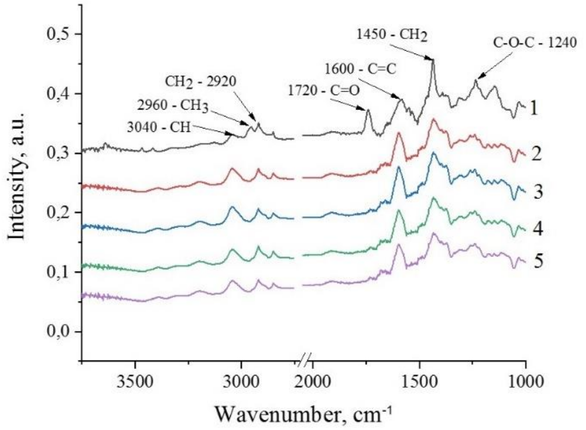

Fig.8. FTIR-spectra of the initial CTP (1), foamed CTP (2) and MCTP solid foams (CBA amount 5 wt. p./100 wt. p. of MCTP). The composition of solid foams based on the MCTP (PVC amount, wt. p./100 wt. p. of CTP): 3) - 5; 4) - 10; 5) - 20

From the presented spectra (Fig. 8) it can be seen that all solid foams are characterized by an increase in aromaticity compared to the initial pitch, which is confirmed by an increase in the intensity of the absorption bands at 3040 cm^{-1}–stretching vibrations of CH aromatic bond, and also in the region of 1600 cm^{-1} –stretching vibrations of the double bond C=C.

In solid foams, absorption bands of 2920, 2860 and 1450 cm^{-1} are observed that characterize the methylene groups of CH_2, which are most likely to be in the form of methylene bridges between the aromatic rings system. The absence of an absorption band of 2860 cm^{-1}, which is typical of the methyl group CH_3, indicates on its removal when the foam is obtained.

The oxygen containing components of CTP are manifested in the form of absorption bands of C-O-C aromatic esters stretching vibrations at 1240 cm^{-1}-asymmetric vibrations, and carbonyl groups C=O at a wavenumber of 1720 cm^{-1}. In the process of MCTP foaming, destruction of the oxygen bonds with the removal of oxygen is observed, resulting in the disappearance of the absorption band C=O 1720 cm^{-1} and decreasing the intensity of the absorption band of C-O-C aromatic esters at 1240 cm^{-1}.

4. Conclusion

Thermogravimetric analysis of dry mixtures of CTP, PVC, and ADCA showed that the use of ADKA without an initiator would require a temperature above the decomposition temperature of ADCA to foam a mixture of CTP and PVC. However, at such temperatures, undesirable processes of CTP and PVC destruction are accelerated. In addition, the low viscosity of CTP and the products of its interaction with PVC will not allow obtaining the stable foam.

The use of the ADCA-$ZnSt_2$ complex blowing agent (in the amount of 1 to 5 wt. p./100 wt. p. of MCTP) allowed foaming the MCTP at a temperature of 150°C, which is significantly lower than the ADCA decomposition temperature. The research of the MCTP foaming kinetics showed that the rate and the foaming criterion depend on both the CBA amount and the amount of PVC expended on the CTP modification. With increasing PVC content in MCTP from 3-7 to 10-20 wt. p./100 wt. p. of CTP, depending on the CBA amount, the rate increases by 3 to 9 times, and the foaming criterion increases by 2 to 3 times. The maximum foaming criterion of 3.6 and the maximum foaming rate of $7.8 \cdot 10^{-2}$ min^{-1} were observed for gas-filled compositions obtained by foaming MCTP with PVC content of 20 wt. p./100 wt. p. of CTP.

Using Fourier method of IR-spectroscopy, it was found that during the MCTP foaming, physicochemical transformations occur, in particular, destruction of oxygen-containing functional groups and elimination of methyl groups, which leads to an increase in the aromaticity of solid pitch foams.

Studies have shown that using CBA for foaming a CTP modified with PVC, it is possible to obtain solid foams (at 150°C) with a porosity of 24 to 76% and an apparent density of 0.31 to 1.0 g/cm^3 depending on the composition of the MCTP. The higher the PVC content in MCTP, the lower the density and the higher the porosity of the resulting solid foam.

The study of obtained solid foams structures showed that the gas-filled material is characterized by large pore size and heterogeneity. This is most likely due to the mismatch of the gas releasing kinetics and cell growth with a change in MCTP viscosity. MCTP foaming at atmospheric pressure and T = 150°C leads to asynchrony of these processes, which makes it difficult to obtain a foam with a stable and homogeneous cellular structure.

The investigation's results showed the possibility of obtaining the gas-filled material based on MCTP using CBA. To obtain solid foams with a stable fine-meshed and homogeneous structure, it is necessary to optimize the conditions of MCTP foaming process. To this end, research will continue to study the effect of the pressure and the foaming temperature of MCTP on the morphological characteristics of solid foams based on it.

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