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THERMAL DESTRUCTION OF POLYDIMETHYLSILOXANE ON A PHOSPHORUS-CONTAINING SILICA SURFACE

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Abstract

Thermogravimetry, differential thermal analysis, and IR spectroscopy were used to investigate the process of thermal destruction of adsorbed polydimethylsiloxane (PDMS) in air. The disperse adsorbents were pristine fumed silica and modified fumed silica whose surface contained oxygen compounds of phosphorus.

It was shown that under the given experimental conditions the thermal destruction of PDMS on the fumed silica surface was accompanied by the complete transformation of the adsorbed PDMS to SiO_2. In the case of phosphorus-containing silica, the thermal destruction proceeded in a different way. It was found that at 140–300°C depolymerization of the siloxane chains of a certain part of the adsorbed polymer took place with the concurrent removal of volatile products of the reaction. However, the remaining part of the adsorbed PDMS interacted with the modified silica surface to form chemisorbed dimethylsilyl structures. The thermal destruction of the chemisorbed fragments of PDMS in air was initiated at 400°C or above for both types of silica investigated.

Keywords: phosphorus, polydimethylsiloxane, silica, surface, thermogravimetry

Introduction

Research into thermal transformations in layers of molecular thickness is of interest for evaluation of the processes occurring in condensed systems between adsorbed molecules and the surfaces of dispersed solids. Chemical reactions taking place through thermal transformations of molecules in an adsorption layer can have various directionalities, governed by the natures of both the adsorbate and the surface of the adsorbent.

Physicochemical properties of filled polymers are determined to a great extent by the structure and characteristics of the layers of high-molecular compounds that are in intimate contact with the surface of the filler [1]. While an adsorbed polymer is in use, the action of heat loads in its surface layers leads to chemical processes whose direction is affected by the active sites of the filler surface.

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As far as organosilicon polymeric compositions are concerned, the system polydimethylsiloxane(PDMS)/silica occupies one of the prominent positions, which is related to its importance for industry and to the fact that its components are well studied [2, 3]. It has been established in particular that silanol groups on the highly dispersed silica surface are additional sites of depolymerization of polyorganosiloxane rubbers [4]. However, the choice and applicability of the PDMS/silica system are justified not only by the practical importance of this polymeric composition. In our opinion, the molecule of PDMS is an appropriate model for research into the effects of the active surface sites of an adsorbent on the thermo-stimulated chemical reactions of adsorbed compounds. The oxidation/decomposition of methylsilyl groups accompanied by the formation of a non-volatile residue can be supplemented by the depolymerization of polysiloxane chains to form volatile products of the reaction. These factors in general, and a sufficiently high thermal stability of PDMS in particular, make this system a suitable experimental model for the techniques of differential thermal analysis (DTA) and thermogravimetry (TG).

The present paper is intended to consider the effects of chemical modification of the silica surface with oxygen compounds of phosphorus on the processes of thermal oxidation/decomposition of adsorbed PDMS.

Experimental

The components of the system under investigation were liquid organosilicon PMS-1000 (Kremniypolimer, Zaporizhzhya, Ukraine), aerosil A-300 (Khlorvinil, Kalush, Ukraine), and phosphorus-containing silica (PCS) synthesized in our laboratory.

The PCS (2.31% by mass of P) was produced by modifying fumed silica A-300 with phosphorus trichloride during heating to 600°C in air [5]. As a result of such treatment, on the SiO_2 surface, there may be formed condensed oxygen compounds of P(V) whose interaction with water vapour of the air results in the formation of surface derivatives of phosphoric acid [6].

Samples for investigation were prepared in the following way. A weighed sample of the siliceous material was placed into a glass beaker and dried in a drying oven at 107–110°C for 1.5 h. A solution of PDMS in hexane (PRA grade) of the desired concentration was then poured into the beaker up to the formation of a dispersion with a solid phase content of $\approx$10% by mass, following which the dispersion was thoroughly mixed. The suspension formed was put into an evaporating dish and maintained at room temperature for 15–17 h for the hexane to evaporate off. The samples prepared in this way were again dried in the drying oven at 107–110°C for 1.5 h.

DTA and TG were performed with a Q-1500 D (MOM, Hungary) derivatograph. The measurements were made in corundum crucibles. The average sample mass was 100.6±0.6 mg. The heating rate was 5°C min^{-1}. The parameters of the derivatograph used were as follows: DTA: 100 μV; TG: 500 μV; DTG: 500 μV; sensitivity: 20 or 50 mg.

The samples for IR spectroscopy were pressed (200 MPa) into thin plates with a specific mass of 15–18 mg cm^{-2}. The measurements were carried out on an IKS-29 IR spectrometer (LOMO, Russia).

Table 1 Characteristics of samples

Sample	S_{sp}/m^2 g^{-1}	Carbon content	PDMS content
		mass%	
System A-300/PDMS			
1	240	1.72±0.07	5.30
2	150	2.84±0.07	8.76
3	150	3.32±0.05	10.24
4	120	5.41±0.14	16.68
5	100	6.85±0.03	21.17
6	50	12.54±0.07	38.11
System PCS/PDMS			
1P	135	2.35±0.05	7.24
2P	120	3.06±0.03	9.43
3P	115	4.61±0.12	14.21
4P	90	6.83±0.12	21.06
5P	60	10.74±0.10	33.12

The elementary analysis for the carbon content of the samples was made by calcination in oxygen [7]. The specific surface area was determined by the standard method of the thermal desorption of argon. The sample characteristics obtained are listed in Table 1. The amount of PDMS adsorbed was chosen so that the lowest content of the polymer would be close to that of a monolayer on the assumption of the interaction of every silicon atom in the polymer chains with a silanol group of the silica surface (Table 1, sample 1).

Results and discussion

Under atmospheric conditions, the thermal decomposition of PDMS adsorbed on the surface of fumed silica A-300 is accompanied by an exothermal effect in the DTA curve (Fig. 1a). Here, a certain correlation may be observed between the amount of PDMS in the sample, the intensity of the peaks, the surface area under them, and the temperature of onset of the exothermal effect. As the content of the adsorbed substance increases, the low-temperature shoulder of the peak is shifted towards lower temperatures, with a concurrent increase in the intensity of the exothermal effect.

The DTG curves exhibit two well-defined regions of mass loss (Fig. 1b). The first region is attributed to the removal of the physically sorbed water (T_{max}: 60–70°C), while the second is related to the temperature interval of the exothermal effect (Q) and is due to the thermal decomposition of the adsorbed PDMS. The measurement results are listed in Table 2.

The thermal decomposition of PDMS adsorbed on PCS proceeds in a different way. The DTA curves (Fig. 2a) do not exhibit any pronounced thermal effects for the samples under investigation. The smooth trend and domed shape of the curves are

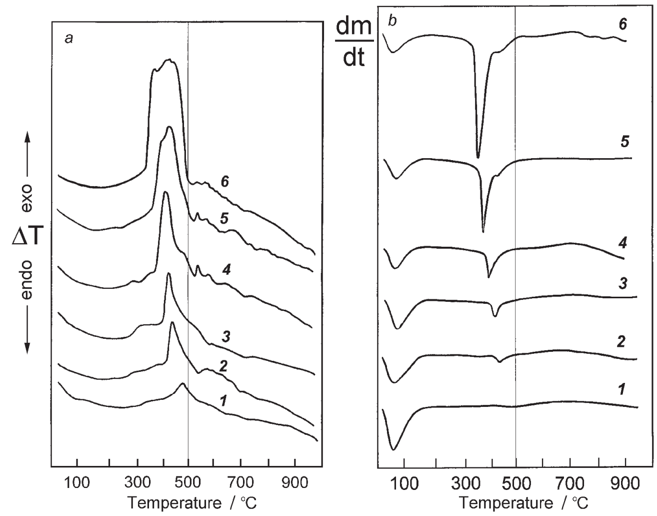


Fig. 1 a – DTA; and b – DTG curves for a series of A-300/PDMS samples

due to the corresponding chemical processes and are revealed through the use of a highly sensitive DTA parameter, which is necessary for a rigorous evaluation of small amounts of the adsorbed polymer.

Table 2 TG data on mass loss from samples of A-300/PDMS

Sample	Mass loss/% in temperature intervals			Q
	20–180°C	180–300°C	300–1000°C	
1	3.60	0.32	0.80	0.32
2	2.72	0.32	1.36	0.56
3	2.96	0.64	3.12	1.44
4	1.92	0.48	3.44	1.99
5	1.92	0.72	6.13	4.38
6	1.28	0.48	7.60	6.71

The greatest rate of mass loss falls within the interval 170–260°C, and the onset of polymer decomposition is observed at 115–140°C. With increasing amount of PDMS, the temperature intervals of the termination of water desorption and the beginning removal of the polymer decomposition products overlap one another by 10–30°C. In view of this fact, it was decided that, during the processing of the experimental data, the temperature of onset of the thermal destruction of the adsorbed polysiloxane should be taken as 140°C, since the DTG results on a control sample of PCS indicate that the removal of the physically sorbed water is practically completed at this temperature. The measurement results are presented in Table 3.

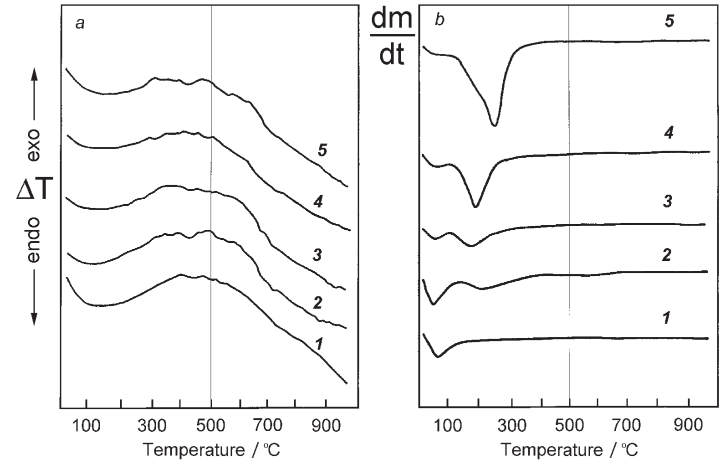


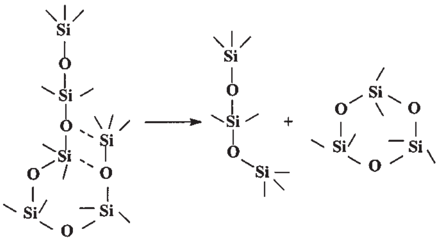
Fig. 2 a – DTA; and b – DTG curves for a series of PCS/PDMS samples

Table 3 TG data on mass loss from samples of PCS/PDMS

Sample	Mass loss/% in temperature intervals		
	20–140°C	140–300°C	300–1000°C
PCS	3.32	1.03	0.40
1P	2.63	0.88	0.48
2P	2.79	2.58	1.36
3P	3.10	6.17	1.59
4P	3.58	12.99	1.19
5P	4.51	24.72	1.99

From the results achieved, it is evident that the main difference between the thermal decomposition of PDMS on the surfaces of the starting and the modified silicas consists in the absence of a profound exothermal effect and in a substantially larger amount of volatile products of the destruction which are removed at temperatures up to 300°C.

It is known that there are two major directions of the thermal decomposition of PDMS [8]. In an inert atmosphere or under vacuum, depolymerization of the siloxane chains proceeds, with the formation of cyclic oligomers according to the following scheme:



(1)

This reaction leads to the formation of predominantly three- or four-membered cycles with the elementary unit $–Si(CH_3)_2O–$. During the depolymerization, organopolysiloxane can undergo a complete transformation into volatile products. The TG method registers this phenomenon as a complete loss of the sample mass.

In air, the thermal decomposition proceeds via the oxidation of methylsilyl groups. The final product of the oxidation/thermolysis of PDMS in a medium of oxygen is SiO_2:

$$–Si(CH_3)_2O^- + 4O_2 \rightarrow SiO_2 + 2CO_2 + 3H_2O \qquad (2)$$

It should be noted that, side by side with carbon dioxide, at different stages of the oxidation/thermolysis the formation and release of formaldehyde, formic acid, methanol and carbon monoxide may be observed [8, 9]. The oxidation of Si–CH_3 groups in the solid residue is accompanied by the formation of Si–OH groups, which immediately begin to interact with each other to form siloxane bonds Si–O–Si [8].

With allowance for the content of PDMS in the studied samples, we calculated the final results of the changes in sample mass during the reactions proceeding according to schemes 1 and 2. When determining experimental values of the mass loss in terms of the TG data, we took account of the fact that, in the case of the samples of the A-300/PDMS system, the main destruction process occurs in a temperature interval governed by the extent of the exothermal effect. The mass losses from samples of PCS/PDMS were determined in the interval 140–300°C.

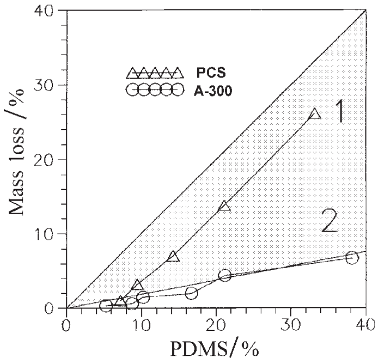


Fig. 3 Comparison of experimental and calculated dependences of mass loss on content of PDMS in samples (according to TG data)

The calculated and experimental data are presented for comparison in a diagram (Fig. 3). The lower line of the darkened region illustrates the reaction proceeding according to scheme 2. The upper line represents the reaction proceeding according to scheme 1. It is quite obvious that the corresponding curves illustrating the course of possible intermediate variants of the reaction will be within the region defined by these limiting lines. The experimental data showed that in the samples of A-300/PDMS the practically complete oxidation of dimethylsilyl groups proceeded according to reaction 2. The presence of phosphorus compounds on the silica surface leads to depolymerization of the adsorbed PDMS according to reaction 1.

The fact that the calculated curve (reaction 1) and the experimental curve for the series of samples of PCS/PDMS are almost parallel indicates that all these samples contain a constant fraction of adsorbed polysiloxane, whose thermal decomposition proceeds according to a different scheme.

The process of the thermal decomposition of PDMS on A-300 was the subject of an earlier detailed inquiry [10]. It was established that the thermolysis involved chemisorption processes with the participation of the PDMS decomposition products and the fumed silica surface. It was assumed that, in the case of the PCS, a proportion of the PDMS might also undergo chemisorption and then destruction according to reaction 2. However, the absence of specific exothermal effects did not permit us to corroborate such an assumption by means of the thermal analysis method. In order to verify the validity of the assumption, use was made of IR spectroscopy, which is a most informative method for the identification of chemical surface compounds on dispersed silica [11, 12]. The experiment was carried out with a standard vacuum apparatus and involved step-by-step heating. To detect the possible effects, a series of tests was conducted on sample 5P with the maximum content of PDMS. The sample, made in the shape of pressed plate, was put into the quartz call with a spectroscopic cell having optical windows of CaF_2. The quartz cell was exposed to air at the desired temperature for 25 min, evacuated for 1.0–1.5 h and cooled, following which spectra were recorded. The furnace temperature was then raised, and the whole cycle described was repeated.

The results achieved are presented in Fig. 4. It is seen that on the PCS surface there are chemisorbed $Si–CH_3$ groups which are stable in air at 400°C. As the temper-

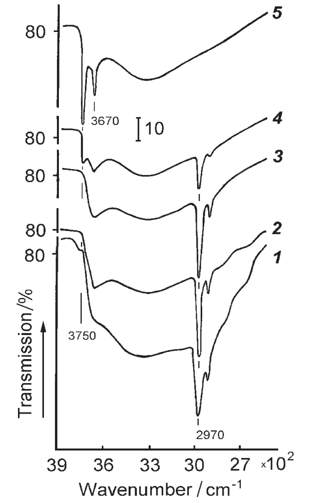


Fig. 4 IR spectra of sample 5P after heating in air for 25 min at a temperature of 1 – 120; 2 – 300; 3 – 400; 4 – 500 or 5 – 600°C

ature is increased to 500°C and above, the methylsilyl groups are oxidized, and the IR spectra begin to exhibit absorption bands at 3670 and 3750 cm^{-1}, characteristic of P–OH and Si–OH groups, respectively, on the PCS surface.

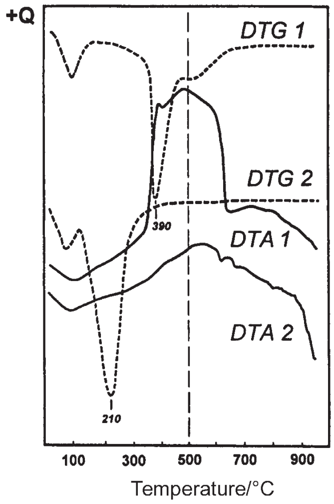


Fig. 5 DTA and DTG curves for preliminary pressed samples at a heating rate of 5°C min^{-1}: 1 – sample 6 (270.1 mg; TG-500; DTG-250; DTA-100); 2 – sample 5P (275.7 mg; TG-500; DTG-500; DTA-100)

However, this IR experiment differs from the previous one not only in the heating conditions, but also in that the sample is in the pressed state. In order to elucidate any possible influence of factors associated with diffusion, the series of PCS/PDMS samples for tests on the derivatograph was extended by addition of pressed sample 5P. The powdered plates of the pressed sample which were used for the IR spectroscopy were put into the derivatograph crucible, with the sample mass increased to 275.7 mg. The general pattern of the thermal decomposition, however, remained practically unchanged and did not show any additional signs of oxidation of the chemisorbed methylsilyl groups, only slight shifts in the peak temperatures in the DTA and DTG curves being observed (Fig. 5).

The fact that the calculated and experimental curves for the PCS/PDMS samples are parallel (Fig. 3) implies the presence for chemisorbed groups on the surface of all the samples after removal of the depolymerization products. To verify this assumption, the IR spectroscopy experiment was conducted in a somewhat different way. A pressed plate of the sample (29–38 mg) was fixed in a quartz holder, put into the furnace chamber, heated to 400°C, and maintained there for 15 min. (The additional experiment allowed us to establish that heating for 30 min did not decrease the amount of the chemisorbed groups.) The sample was then quickly transferred into the spectroscopic cell. The cell was evacuated for 1–2 min and cooled, following which the IR spectral characteristics were measured. The results achieved are listed in Table 4.

The data indicate that on the surface of all the samples there is an absorption band for the valence vibrations at 2979 cm^{-1} characteristic of chemisorbed methylsilyl groups.

Table 4 Optical density of the absorption band at 2979 cm^{-1} for C–H vibrations ($D_{C–H}$) in the case of PCS/PDMS samples calcined at 400°C in air

Sample	Plate mass/ mg	$D_{C–H}=\log I_0/I$	$D_{C–H}$ reduced to mass of 30 mg	PDMS content/ mass%
1P	37.0	0.38	0.30	7.24
2P	38.0	0.45	0.36	9.43
3P	29.5	0.43	0.44	14.21
4P	36.0	0.54	0.45	21.06
5P*	30.5	0.33	0.32	33.12

*Experiment performed under conditions of step-by-step heating

Let us consider $D_{C–H}$ in the above-mentioned interval of values as a quantity that is proportional to the concentration of sorbed polysiloxane. In such a case, after heating at 400°C, the difference in the content of chemisorbed groups for all the samples comprises ±25%, whereas the difference in the starting contents of PDMS in samples 5P and 1P is 4.5-fold.

The results considered allow us to infer that the formation of a layer of chemisorbed derivatives of phosphoric acid on the fumed silica surface facilitates depolymerization of the siloxane chains and the removal of volatile reaction products. However, in this situation there remains a possibility of formation of chemisorbed PDMS structures whose thermal stability in air corresponds to that of analogous surface compounds on the starting fumed silica A-300 [13]. According to the IR spectroscopic data, on the surface of the studied PCS there are no silanol groups. Their absence gives ground to the assumption that the chemisorption of fragments of PDMS proceeds through active sites with the participation of phosphorus atoms and the formation Si–O–P bonds. In the case of silicon phosphates, such bonds are stable at 1000°C and above [14].

The outlined scheme of the destruction of the PCS/PDMS system does not offer any explanation for the absence of a profound exothermal effect during the oxidation/thermolysis of methylsilyl groups, such as is observed for the A-300/PDMS system. The modification of the silica surface with oxygen-containing compounds of phosphorus does not affect the thermal stability of the attached dimethylsilyl groups, although to all appearances it varies the character of the intermediate chemical reactions occurring during the overall thermal oxidation process.

Conclusions

The general conclusion is made that, upon heating on the surface of PCS+PDMS, one may observe first the process of depolymerization of polysiloxane, accompanied by the release of volatile products and then, at temperatures over 200°C, the formation of chemisorbed PDMS structures.

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