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MACROMOLECULAR CHEMISTRY
AND POLYMERIC MATERIALS

Thermal Degradation of Polyvinylpyrrolidone on the Surface of Pyrogenic Silica

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Abstract—Thermal degradation of polyvinylpyrrolidone was studied by thermogravimetry, IR spectroscopy, and thermal-desorption mass spectrometry.

Due to high complexing and adhesion properties, nontoxicity, and solubility in water and most organic solvents polyvinylpyrrolidone (PVP) is widely used in various branches of industry [1]. Along with common use of PVP in medicine, pharmacology, and textile industry, studies are actively pursued aimed at preparing new materials on its basis. Among them preparation of new copolymers and polymer blends including organic-inorganic hybrid materials and nanocomposites is the most promising. Such polymer–silica composites based on PVP were prepared by adsorption procedure [2, 3] or by grafting to the surface of solid particles with formation of covalent bonds between the polymer and SiO_2 [4, 5]. Previously, the PVP–silica materials were used to prepare selective membranes [6, 7], optical materials [8, 9], and chromatographic supports [10, 11].

In highly filled polymeric systems the fraction of PVP units directly contacting with the silanol surface groups of silica increases. It is known that the degree of filling and the nature of the surface active groups of dispersed filler significantly affect thermal and thermal oxidative degradation of polymeric materials [12]. Since for PVP such data are lacking, the study of thermal transformations of PVP in the adsorption layers of various thickness on the surface of finely dispersed silica is urgent.

EXPERIMENTAL

In our work we used medical-grade PVP (Sintvita, Russia) with an average molecular weight of 10 700 and A-300 Aerosil pyrogenic silica (Khlorvinil, Ukraine) with a specific surface area of 320 $m^2 g^{-1}$.

The samples were prepared as follows. First, a dispersion of silica and a 10% solution of PVP in distilled water were prepared, and the required amount of the PVP solution was added to the silica dispersion. Then the resulting mixture was thoroughly mixed and after 1-h storage deposited on glass plates as thin layers, which were dried at 80°C for 4–5 h. The product was ground in an agate mortar and additionally dried at 80°C for 1 h.

The silica samples with sorbed PVP were analyzed for the carbon content on an AN-7529 express analyzer by combustion in an oxygen flow. The specific surface area was determined by low-temperature desorption of argon according to the standard procedure. The properties of the resulting PVP–silica samples are listed in Table 1.

Thermal analysis was carried out using a Q-1500 D derivatograph. The measurement parameters were as follows: 500, 500, and 250 μV for TG, DTA, and DTG, respectively; sensitivity 200 mg, and heating rate 10 deg min^{-1}. The samples (300.16 ± 0.24 mg) were heated in a ceramic crucible.

The IR spectra were taken from pressed samples (5–6 mg cm^{-2}). The thermal transformations were studied using a heated quartz cell (CaF_2 optics). The

Table 1. Properties of PVP–silica samples

Sample no.	Carbon content, %	PVP content		S_{sp}, $m^2 g^{-1}$
		%	mmol g^{-1}	
1	3.8	5.8	0.52	258
2	8.2	12.6	1.14	217
3	11.0	16.9	1.52	183
4	15.8	24.3	2.19	128
5	19.0	29.3	2.64	65

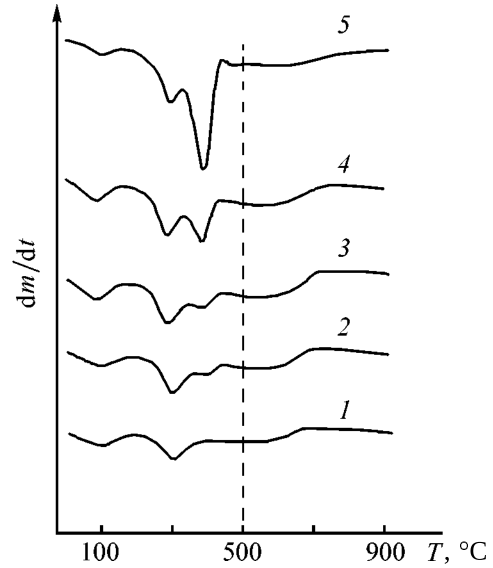
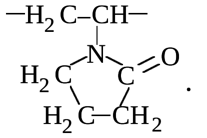


Fig. 1. DTG curves of the samples of pyrogenic silica with sorbed PVP: (d*m*/d*t*) rate of the weight loss and (*T*) temperature. The figures at the curves correspond to sample nos. in Table 1; the same for Fig. 4.

sample was heated in a spectral cell for 15 min in air and then evacuated for 1–1.5 min without cooling. The IR spectra were registered after cooling of the sealed cell to room temperature. Then the temperature of the spectral cell was increased and the measurement cycle was repeated. The IR spectra were registered on a Specord M-80 spectrophotometer.

The mass-spectrometric measurements were carried out on a vacuum thermal-desorption unit with a heated quartz cell. The mass spectra were registered on an MKh 7304 spectrometer equipped with a computer system for registration and treatment of the experimental results. The sample weight was 2.0 ± 0.3 mg.

The average molecular weight of the PVP used indicates that the polymer molecule contains about 96 monomeric units



High solubility of PVP in water allowed preparation of silica dispersions in the PVP solution in a wide concentration range of components. The presence of the silanol groups on the silica surface and the tertiary amine and carbonyl groups in the polymer molecule suggests strong adsorption interaction. However, it was found [13] that in the hybrid PVP–silica material the polymer and SiO_2 are bound only through the hydrogen bonds between the carbonyl and silanol groups.

The IR spectra of the PVP–silica samples studied exhibit the bands of stretching vibrations of the SiO–H groups (3748 cm^{-1}) that do not participate in bonding with carbonyl groups. With increasing polymer concentration the intensity of the absorption band of the C=O group (1664 cm^{-1}) increases, whereas the band at 3748 cm^{-1} decreases and finally completely disappears. With decreasing PVP concentration the fraction of the units in the polymer chain interacting with the silanol groups on the silica surface increases. These results agree with the data on the sorption of PVP on silica [3].

With increasing content of the polymer the specific surface area of the samples decreases because of the increase in the layer thickness of sorbed PVP (Table 1).

The DTG curves of the PVP–silica layers are shown in Fig. 1. The first peak with the maximal weight loss for all the samples occurs at 100–115°C and corresponds to the removal of water physically sorbed on the silica surface [14]. The DTG curves for sample nos. 2–5 exhibit three steps of the weight loss, and only in the case of sample no. 1 thermal oxidative degradation proceeds in two steps. The parameters of the weight loss during thermal degradation are given in Table 2. The weight loss in the 200–1000°C range is taken as 100%. In each sample the temperature boundary between the degradation steps was determined as the point of the minimal rate of the weight loss.

As seen from the above data, despite different width of the temperature range of the first step of oxidative degradation, the temperature maxima of all the samples occur in the narrow range: 315–325°C. Similar pattern is observed for the second step of oxidative thermolysis: T_{max} is 420–425°C, except sample no. 1.

The third stage of degradation is characterized by a lower rate of the weight loss. In this case the DTG curves exhibit a broad peak whose T_{max} increases from 570 to 660°C with increasing content of PVP in the sample.

The TG analysis reveals two stages of thermal oxidative degradation with nearly equal weight losses. The first stage proceeds in two steps, and their parameters change depending on the amount of sorbed PVP. With decreasing content of PVP in the sample the relative contribution of the weight loss in the second step decreases. As seen, in sample no. 1 the first stage of thermolysis proceeds in one step. The second stage

Table 2. Weight loss Δm in the steps of thermal oxidative degradation of the PVP–silica samples

Parameter	Sample no.					
	1	2	3	4	5	PVP_{in}
Temperature range, °C	200–415	200–390	200–380	200–370	200–340	200–395
Δm, %	43.6	41.4	38.7	23.6	23.6	13.4
Temperature range, °C	–	390–465	380–470	370–465	360–485	395–495
Δm, %	–	17.1	19.5	20.6	27.1	58.1
Temperature range, °C	415–1000	465–1000	470–1000	465–1000	485–1000	495–1000
Δm, %	56.4	41.5	41.8	55.8	49.3	20.3

of thermal oxidative degradation occurs in one step, with similar weight loss for all the samples.

For comparison, we performed the TG analysis of the initial PVP under the conditions similar to those used for the PVP–silica samples. The weight composition of the sample was comparable with that of sample no. 5: 100 mg of the polymer was mixed with 200 mg of the inert filler. As seen, the parameters of thermal oxidative degradation of this sample are significantly different. The first peak of the weight loss at T_{max} 105°C belongs to the removal of water, whose presence is manifested by a broad band at 3000–3600 cm^{-1} in the IR spectrum. The most intense weight loss is observed in a narrow temperature range (Table 2). Thermal degradation of the initial PVP powder without filler (137 mg) exhibits nearly similar results. The main weight loss (75%) occurs in the 330–430°C temperature range.

As seen from the data on the weight loss (Table 2), adsorption of PVP on the pyrogenic silica surface induces intense oxidative degradation of the polymer at lower temperatures, but hinders oxidation of the carbonized residue.

Adsorption of the PVP molecules on the silica surface decreases the flexibility of the molecular chains, causing the nonequilibrium strained state of the polymer chain [15]. As a result, the strained sections that appeared in macromolecule more readily undergo thermal oxidation, and thus the volatile products can appear under milder conditions. According to [16], the volatile products of PVP oxidation at 300–400°C are carbon dioxide and pyrrolidone. We assume that the TG peak at T_{max} 320°C belongs specifically to the stage of thermal oxidative degradation of the strained sections of the polymer chain. The relative weight loss in this stage decreases with decreasing weight fraction of silica and thus with decreasing surface area of silica in the sample.

The stage of oxidative degradation at T_{max} 420°C was observed for all the samples containing more than 12% PVP. This stage involves thermal degradation of the polymer chains occurring in the adsorption layer at a larger distance from the silica surface. The relative weight loss in this step increases with increasing content of PVP in the sample.

The IR spectroscopic study of thermal oxidative degradation of the PVP–silica samples in air was performed by heating in steps according to the procedure given above. The IR spectra of sample no. 1 registered in the 20–600°C range are shown in Fig. 2a. As seen, a new absorption band appears at 1600–1800 cm^{-1}.

The dependences of the intensity of the selected absorption bands on the temperatures of thermal degradation are shown in Fig. 2b. Above 200°C a new absorption band appears at 1712 cm^{-1} and reaches the highest intensity at 300°C. At this temperature the majority of the C–H groups is broken down (Fig. 2b, curves *1*, *4*) and the sample becomes brown. The IR spectrum of sample no. 5 with the highest content of PVP exhibits an absorption band at 1770 cm^{-1} after heating to 300–350°C (Fig. 2c).

Appearance of new absorption bands in the course of thermal degradation is probably due to the change in the environment of the carbonyl groups of the sorbed polymer, with formation of double bonds. The stretching vibration band of the C=O groups conjugated with these double bonds is observed at 1720 cm^{-1} [17]. With increasing layer thickness of the adsorbed polymer more complex cyclic structures involving carbonyl groups and oxygen atoms in the polymer chain can appear. The frequencies of the C=O groups in such structures are 1740–1800 cm^{-1} [17].

The thermal degradation of the adsorbed polymer in vacuum was monitored by the composition of the

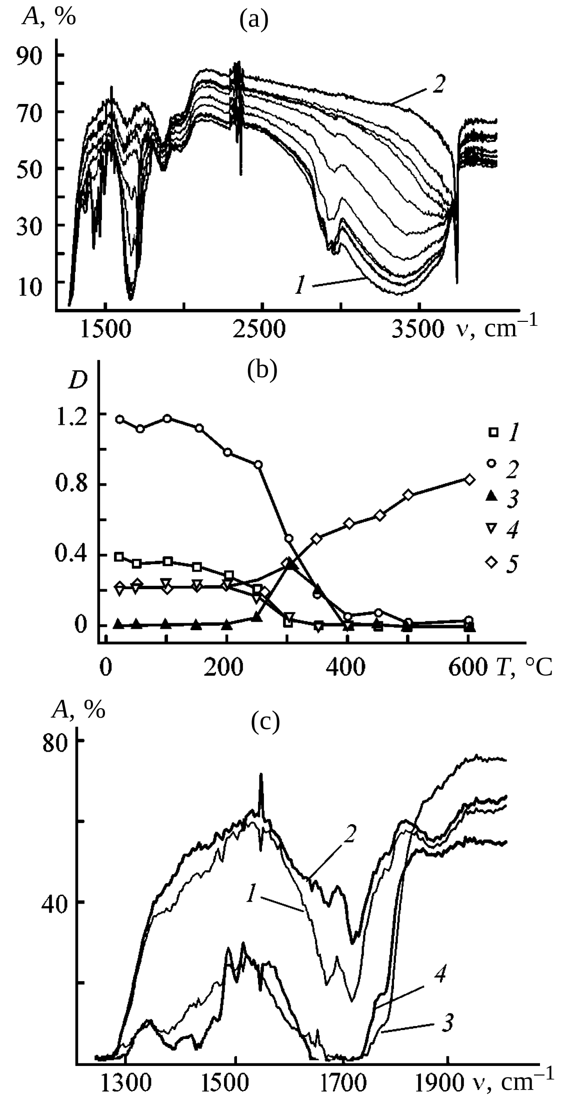


Fig. 2. (a) IR spectra of sample no. 1 (*1*) at room temperature and (*2*) after heating for 15 min to 600°C in air and evacuation for 1 min (intermediate spectra correspond to intermediate heating temperatures); (b) optical density $D = \log I_0/I$ at (*1*) 1428, (*2*) 1660, (*3*) 1712, (*4*) 2924, and (*5*) 3748 cm^{-1} as influenced by the temperature of thermal treatment *T*, and (c) IR spectra of sample nos. (*1, 2*) 1 and (*3, 4*) 5 after heating for 15 min in air at 300 and 350°C and evacuation for 1 min. (*A*) Transmission and (ν) wave number.

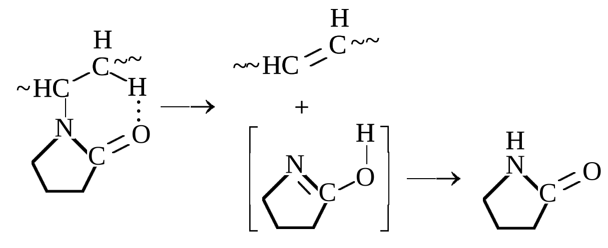
volatile degradation products using mass spectrometry. It was found that the degradation of PVP with liberation of pyrrolidone begins at approximately 100°C in all the samples studied. This low-temperature step in the PVP degradation suggests that similar process occurs in air simultaneously with removal of water from the samples. We failed to separate the contributions of these processes to the weight loss using IR and DTG data.

The degradation of the PVP–silica and initial PVP samples involves different number of stages (Fig. 3). The low- and high-temperature stages proceed at $T_{\max}$ 90–105 and 350–390°C, respectively. Additional step is observed for the initial PVP at 280–300°C. To confirm that this intermediate step involves thermal degradation of the initial polymer, we studied the PVP samples with an average molecular weight of 10 000. For this purposed we used another PVP sample from Sintvita (Russia), K-15 PVP (Fluka), and PVP after dissolution in water and drying in air at 75°C. In all the cases the intermediate stage of thermal degradation was observed. Simultaneous appearance of various ions in the mass spectra (Fig. 3) indicates degradation of the polymer with formation of volatile products and their further fragmentation in the ionization source of a mass spectrometer.

As seen from the mass spectra registered at $T_{\max}$ for low- and high-temperature degradation stages, the difference in the yields of the molecular ions of pyrrolidone (85^+) and vinylpyrrolidone (111^+) is the most significant. These two ions can be used to analyze thermal degradation of PVP, because the relative intensity of the ion 85^+ in the mass spectra of vilylpyrrolidone is lower than 8.1% [18], whereas in the spectrum of pyrrolidone the vinypyrrolidone molecular ion (111^+) is absent.

The mass thermograms for the ions 85^+ and 111^+, taken in the course of degradation of the samples with adsorbed polymer, are shown in Fig. 4. As seen, pyrrolidone is released in two stages, whereas vinylpyrrolidone appears only in one stage; the ratio of the release of pyrrolidone in both stages was determined. For sample nos. 1, 3, 5 the ratio I_{85^+}(2nd stage)/I_{85^+}(1st stage) is 6.56, 2.75, and 1.66, respectively; in the case of the initial PVP it is 1.04.

The degradation of vinyl polymers (polyvinyl alcohol, polyvinyl acetate, polyvinyl chloride) starts with breakdown of the side groups [19] with formation of the corresponding double bonds. Similar scheme of breakdown of the pyrrolidone ring with formation of the intermediate cyclic complex was suggested for PVP in [16].



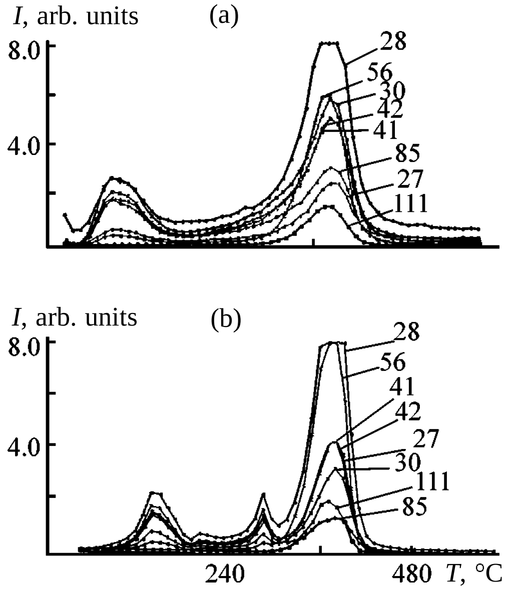


Fig. 3. Mass thermograms of (a) sample no. 5 and (b) initial PVP. (*I*) Relative intensity and (*T*) temperature; the same for Fig. 4. The numbers at the curves are the weights of the positive ions.

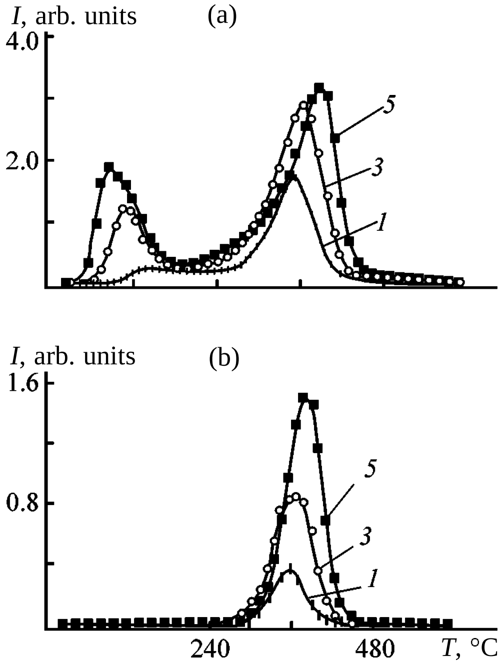


Fig. 4. Mass thermograms for the ions (a) 85^+ (pyrrolidone) and (b) 111^+ (vinylpyrrolidone).

The hydrogen bond between the C=O group in PVP and the silanol group of the SiO_2 surface can block formation of such cyclic complex and thus hinder elimination of pyrrolidone from the polymer chain. This phenomenon is observed in the low-temperature stage of thermolysis. With decreasing amount of adsorbed polymer the fraction of the carbonyl groups bound by hydrogen bonds decreases, which, in turn, decreases pyrrolidone release. Restricted flexibility of the polymer molecules sorbed on the support can also decrease the yield of the intermediate complexes.

Vinylpyrrolidone is released only in the high-temperature stage of PVP degradation. We found certain correlation between the ratio I_{85^+}/I_{111^+} and the content of PVP in the sample. This ratio changes from 4.35 to 2.03 for sample nos. 2 and 5, respectively. In the case of various initial PVP samples I_{85+}/I_{111+} varies within the range 0.53–0.68.

Thermal degradation of the polymer macromolecule is accompanied by breakdown of both side and main chains. This process involves elimination of the monomer units from the ends of the main chain and with increasing number of the breaks in the main chain the polymerization rate increases. Variation of the ratio of the degradation products (ions 85^+ and 111^+) suggests changes in the thermal degradation mechanism.

In all the PVP–silica samples a pronounced dependence is observed between the amount of the adsorbed polymer and degradation with release of pyrrolidone and depolymerization with formation of vinylpyrrolidone. In the samples with a lower content of PVP, i.e., with a higher content of the units of adsorbed macromolecule directly bound to the silica surface, thermal degradation in the high-temperature stage is characterized by a greater contribution of elimination of the pendant rings and smaller contribution of depolymerization. Thermal treatment in a vacuum at 700°C gives a carbonized residue on the silica surface. After vacuum thermolysis in the course of mass spectrometric studies the samples studied became black.

Our experimental results give the following qualitative pattern of PVP degradation. At temperatures of up to 200°C certain fraction of pyrrolidone rings is removed and double bonds in the chains appear. As a result, cross-links in the polymer are formed, which hinder the flexibility of macromolecule. With increasing temperature, separate units of the initial PVP molecules acquire the mobility required to form intramolecular complexes promoting elimination of the pyrrolidone rings (T_{max} 280–300°C). In contrast, in the case of PVP–silica samples the solid matrix significantly affects macromolecules occurring in the adsorption layer, which additionally hinders flexibility of macromolecules and thus elimination of the pendant groups. As a result, the stage with T_{max} 280–300°C in the PVP–silica samples is absent.

Further heating causes the homolytic cleavage of the polymer chains in both initial and adsorbed polymer (T_{max} 360–400°C). In this degradation stage sorbed polymer hinders cleavage of the main chain and thus promotes carbonization of the silica surface.

CONCLUSIONS

Thermal and thermal oxidative degradation of polyvinylpyrrolidone sorbed on the pyrogenic silica surface and of that occurring in the initial state differs in the number of degradation stages and amount of the volatile products appearing in these stages. In both cases adsorption of polyvinylpyrrolidone shifts the processes completing the polymer degradation toward higher temperatures. The increased fraction of the polymer units directly bound with the silanol groups on the silica surface hinders release of pyrrolidone in the low-temperature degradation stage and depolymerization of polyvinylpyrrolidone at high temperatures.

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