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Thermal degradation of amino-group-modified polydimethylsiloxane

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Abstract Degradation behaviors of amino-group-modified polydimethylsiloxane (APS) under nitrogen and air atmosphere were studied by thermogravimetric analysis, pyrolysis–gas chromatography-mass spectrometry, and infrared spectroscopy, and the effect of amino-group content on the thermal stability of the tested APS was investigated. Results showed that the existence of amino-group in APS molecule decreased its thermal stability, and the degradation behavior and mechanism of APS in nitrogen and air atmosphere were different.

Keywords Amino-group-modified polydimethylsiloxane · Thermal degradation

Introduction

Amino-group-modified polydimethylsiloxane (PDMS) is a kind of important silicone oil commonly used on chemical fiber and textile industry. Especially, in the production process of commercial carbon fibers, amino-group-modified PDMS (APS) is commonly used as a protective finish for polyacrylonitrile (PAN) precursor fibers [1–3]. To convert into carbon filaments, the PAN precursor need to be heated under an oxidative atmosphere of a temperature of 200–400 °C first, and then heated under an inert atmosphere of a temperature of at least 1000 °C. In order to obtain high performance product, it is tried to set to a high tension or to a high draw ratio in these processes. However, at that time, the monofilaments may fusion-bond with each other to impair the quality and appearance. The APS oil agent can effectively prevent this problem, and this results in a significantly improve of the tensile strength of the final product. Since APS plays an important role in this high temperature processes, it seemed pertinent to clarify its thermal properties.

The high temperature stability and the degradation mechanism of polysilocaxanes have been widely investigated in the past decades. Thermal property of PDMS has attracted much attention due to its basic position in this group of material [4–8]. It is well known that thermal degradation of PDMS in inert atmosphere results in depolymerization at 400–650 °C to produce cyclic oligomers [4, 5], while in oxidative atmosphere the depolymerization products are silica and small molecule like carbon monoxide, water, carbon dioxide, formaldehyde, and methanol [7]. Thermal properties of PDMS with different substituent groups, such as aromatic rings, carbonhydrates, and some other groups, were also studied [9–12]. Dvornic [13] reported a systematic review of the studies about this subject. However, literature about thermal properties of PDMS modified by amino-group was not founded.

Thus, this article aims to investigate the thermal properties of APS. In this study, the studies of the effects of amino-group content and the degradation behavior and mechanisms under different atmospheres are presented.

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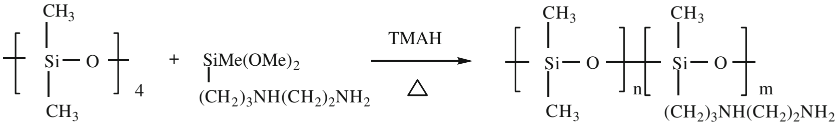


Fig. 1 Equilibration reaction scheme for the preparation of APS

Experimental

Materials

PDMS (analysis purity, molecular mass: 12000–15000), *N*-(2-aminoethy)-3-aminopropylmethy-dimethoxysilane (98%), hexamethyldisiloxane (98%), and octamethylcyclotetrasiloxane (98%) were all obtained from Alfa Aesar, China. Tetramethylammonium hydroxide (TMAH) (analysis purity) as catalyst was purchased from Tianda chemical reagent factory. All of them were used as-received.

Preparation of APS

The polymerization reaction was carried out in a three-necked flask equipped with a thermometer, a reflux condenser, and a stirrer. Octamethylcyclotetrasiloxane, hexamethyldisiloxane, and *N*-(2-aminoethy)-3-aminopropylmethy-dimethoxysilane were placed into the flask and thermostated in an oil bath until constant temperature was set up. Then the catalyst, TMAH solution was introduced. After the reaction was over, the small molecule substances including residual reactants and water were eliminated through vacuum distillation. The scheme of the polymerization is shown in Fig. 1.

Characterization of APS

The intrinsic viscosity ($[\eta]$) was measured with a ubbelohde viscometer. The viscosity-average molecular mass (M_v) of the polymer was calculated using the following equation:

$$[\eta] = K(M_v)^\alpha \tag{1}$$

where K and α has a value of 2×10^{-4} and 0.66, respectively [14].

The APS amino value was estimated by chemical titration, of which the details are available elsewhere [15]. Some necessary information of the APS sample was shown in Table 1.

Table 1 Some details of APS sample

Sample no.	Amine value/mmol g^{-1}	Mean yield/%	M_v
S_1	0.19	96	11986
S_2	0.31	92	10264
S_3	0.43	91	12247

Thermal analysis

Thermogravimetry (TG) analysis for the APS samples was performed on a NETZSCH STA 409 PC/PG thermoanalyzer with a heating rate of 5 °C min^{-1} and continuously flowing nitrogen or air (60 mL min^{-1}).

Infrared measurement

The residues from 200, 400, and 600 °C in both air and nitrogen were finely grounded with KBr, pellets were pressed for infrared (IR) studies on a Nicolet Magna 550 II Fourier transform IR spectrometer.

Pyrolysis–gas chromatography–mass spectrometry measurement

The pyrolysis–gas chromatography–mass spectrometry (PY–GC–MS) measurement system was used to analyze the volatile degradation products of APS. In this system, a CDS-5000 pyrolyser was directly coupled with a Agilent 6890N/5975GC-MS instrument. The sample was introduced into the pyrolyser and heated at 10 °C min^{-1} to 500 °C and kept at this temperature for 10 min, with the flow of helium or air gas (50 mL min^{-1}).

Elemental analysis

The composition of the solid degradation residues of APS was analyzed by Vario EL III elemental analyzer. The contents of carbon, hydrogen, and oxygen can be directly determined, and the residual mass was assumed to be silicon.

Results and discussion

Effect of amino-group content in APS molecule on its thermal degradation

The effect of amino-group content in the APS molecule on its thermal degradation behavior was studied, as shown in Fig. 2 and Table 2. It can be seen that the temperature of APS on every characteristic mass loss point is lower than PDMS, especially at the early stage of the degradation. For example, the onset degradation temperature of PDMS is about 361 °C, and it is lower than 265 °C of APS; while the temperature for 20% mass loss (°C) are 430 °C and lower than 390 °C, respectively. Furthermore, there is an obvious

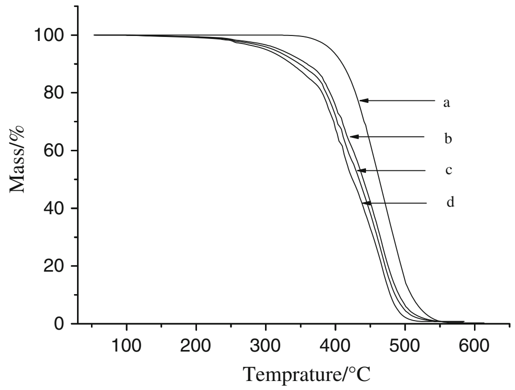


Fig. 2 TG curves of APS sample with different amino value: (*a*) PDMS; (*b*) S_1; (*c*) S_2; (*d*) S_3

Table 2 TG data of APS with different amino-group content

Sample	Temperature of degradation onset/°C	Temperature for 5% mass loss/°C	Temperature for 20% mass loss/°C	Final residue/%
PDMS	361	393	430	0.25
S_1	263	319	390	0.20
S_2	254	308	376	0.21
S_3	249	299	359	0.28

change tendency that characteristic mass loss temperature decreased with increasing amino value. The final mass loss of both PDMS and APS was close to 100%. This means that the existence of amino-group significantly decreased the thermal stability of APS, compared with PDMS.

Thermal degradation behavior of APS

Figure 3 shows TG curves obtained in nitrogen and air atmosphere for APS S_1 sample. As can be seen, there is an obvious difference between the two curves on the final mass loss. The residue left at 650 °C in air atmosphere is fine white powder which is around the average 18%, varying by ±5%, while in nitrogen condition, the sample almost lost all of its mass, the residue is less than 0.2% and there is no infusible residue left.

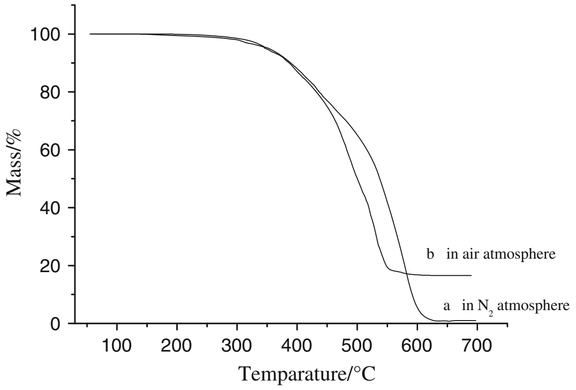


Fig. 3 TG curves of APS S_1 sample

The mass percentage of elements contained in the final white residue under air atmosphere was analyzed. The result and the calculated empirical formula were shown in Table 3. There is neither N nor C element in the residue, and according to the empirical formula, it seems reasonable to consider the residue as silica with some Si–OH group.

Figure 4 shows the IR spectra of sample of APS and its degradation residues at different conditions. It shows four groups of middle and strong absorption bands at 2963–2905 cm^{-1} ($\nu_{C\text{–}H}$), 1261 cm^{-1} ($\delta_{C\text{–}H}$,),

Table 3 Elemental analysis of the final thermo-oxidative degradation residue of APS

H/%	O/%	Si/%	Empirical formula
0.18	53.68	46.16	$H_{0.055}SiO_{2.035}$

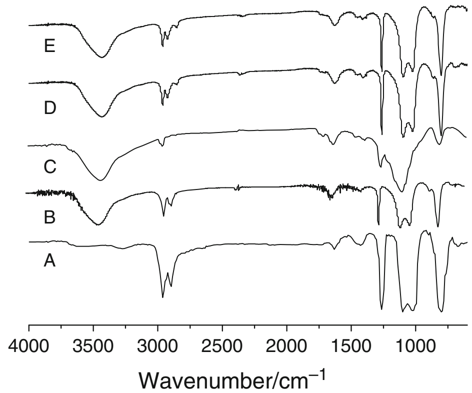


Fig. 4 IR spectra of APS sample (*A*) and its degradation residues at 200 °C in air (*B*), 500 °C in air (*C*), 200 °C in nitrogen (*D*), 500 °C in nitrogen (*E*)

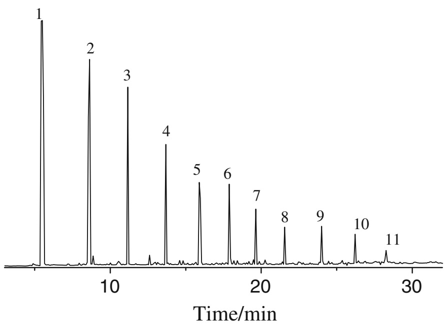


Fig. 5 Pyrograms of the S_1 sample obtained at 500 °C(He)

Table 4 Assignment of GC main peaks of S_1 thermal degradation products of Fig. 5

Peak no.	Compound
1	Cyclotrisiloxane, hexamethyl
2	Cyclotetrasiloxane, octamethyl
3	Cyclopentasiloxane, decamethyl
4	Cyclohexasiloxane, dodecamethyl
5	Cycloheptasiloxane, tetradecamethy
6	Cyclooctasiloxane, hexadecamethyl
7	Cyclononasiloxane, octadecamethyl
8	Cyclodecasiloxane, eicosamethyl
9	Cycloundecasiloxane, docosamethyl
10	Cyclododecasiloxane, tetracosamethyl
11	Cyclotresdecasiloxane, esacosamethyl

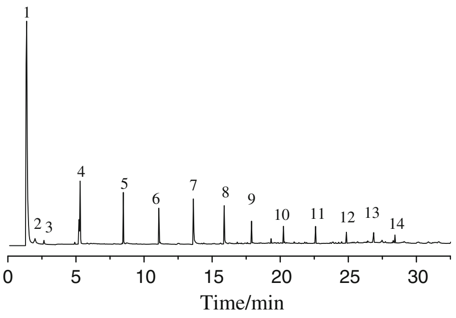


Fig. 6 Pyrograms of the S_1 sample obtained at 500 °C (air)

Table 5 Assignment of GC main peaks of S_1 thermal degradation products of Fig. 6

Peak no.	compound
1	Nitrogen
	Carbon monoxide
2	1,2-Ethanediamine, *N*-methyl
3	Triethylamine
	1-Propanamine, *N*-(1-methylethyl)
4	Cyclotrisiloxane, hexamethyl
5	Cyclotetrasiloxane, octamethyl
6	Cyclopentasiloxane, decamethyl
7	Cyclohexasiloxane, dodecamethyl
8	Cycloheptasiloxane, tetradecamethy
9	Cyclooctasiloxane, hexadecamethyl
10	Cyclononasiloxane, octadecamethyl
11	Cyclodecasiloxane, eicosamethyl
12	Cycloundecasiloxane, docosamethyl
13	Cyclododecasiloxane, tetracosamethyl
14	Cyclotresdecasiloxane, esacosamethyl

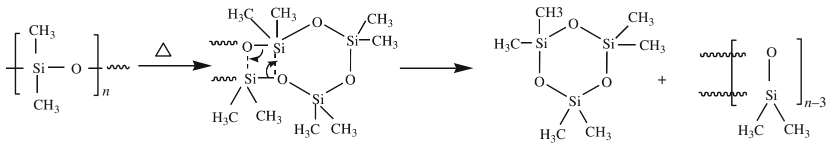
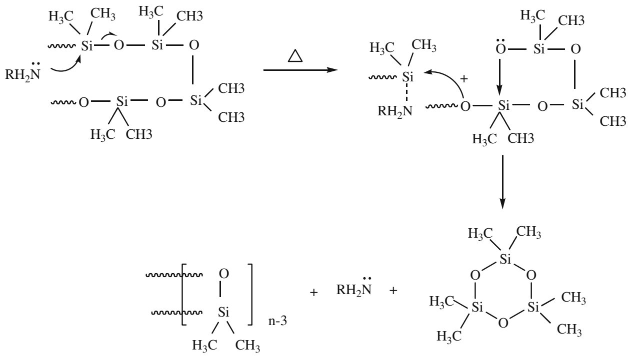


Fig. 7 Thermal degradation mechanism of PDMS in nitrogen



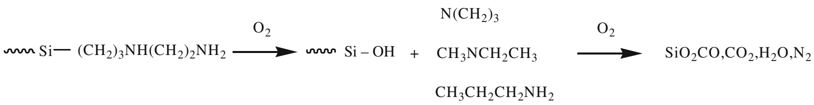
* RH_2N is the amino-group in APS

Fig. 8 A thermal degradation mechanism of APS in nitrogen

1104–1010 cm^{-1} (s, $\nu_{Si–O}$), and 799 cm^{-1}(s, $\nu_{Si–C}$) in the spectra of APS, indicating Si–CH_3, Si–O, –CH_3 functional groups in the molecule of APS [16]. The band from CH_3 located at 2963–2905 and 1261 cm^{-1} became much weaker after treated at 500 °C than at 200 °C in air, while there was almost no change in nitrogen atmosphere. This implies that when the decomposition reaction of APS happens in air, CH_3 group on the side chain takes part in the reaction; whereas in nitrogen, CH_3 group is almost not involved in the reaction. In other words, the mechanism of APS degradation in air and nitrogen is different.

Figure 5 and Table 4 show the results of PY–GC–MS test of the S_1 sample at 500 °C in high purity helium atmosphere. The products are cyclic oligomers arrange from D_3 to D_{13}, whose yield tends to decrease as the degree of polymerization increase. Compound with amino-group is not detected; this may be due to the small amine value of the sample. This result is very close to that obtained from the test of PDMS [8].

Figure 6 and Table 5 show the results of PY–GC test of the S_1 sample at 500 °C in air atmosphere. It is noticeable that all the products of APS thermal degradation shown in Table 4 are also appeared in Table 5, but besides these cyclic oligomers, the products in air also include nitrogen, carbon monoxide (peak no. 1), and small amount of amine (peak no. 2 and 3). These products indicate that the oxidation takes place in the side chain when APS decomposes in air. According to literature, oxidation takes place by reaction in the gas phase between oxygen and volatile oligomers formed by thermal degradation; this may explain that why thermal degradation products also appear when the sample decomposes in air atmosphere.



$$\sim Si-(CH_2)_3NH(CH_2)_2NH_2 \xrightarrow{O_2} \sim Si-OH + \begin{matrix} N(CH_2)_3 \\ CH_3NCH_2CH_3 \\ CH_3CH_2CH_2NH_2 \end{matrix} \xrightarrow{O_2} SiO_2CO,CO_2,H_2O,N_2$$

Fig. 9 Thermal oxidative degradation of amino-group in APS

Mechanism of APS degradation

In early studies, it has been found that the degradation process of PDMS under inert and oxidative atmosphere was quite different [4–8]. For APS studied in this article, as discussed above, the differences between intermediate and final product of the degradation under nitrogen and air atmosphere suggest that the mechanisms in the two conditions are different too.

Mechanism of APS thermal degradation in nitrogen

Many earlier works have studied the mechanism of thermal degradation of PDMS. Theoretically, the thermally weakest bond in PDMS is the C–Si bond (with bond energy of 78 kcal mol^{-1}). However, the decomposition of PDMS under no air atmosphere firstly occurred at Si–O bond (with bond energy of 108 kcal mol^{-1}) instead. A widely accepted thermal degradation of PDMS proceeds by the depolymerization reaction shown in Fig. 7. In the scheme, the small ring has a polymerization degree of 3, actually, it may up to 13 or even higher [8]. The driving force is the higher thermodynamic stability of the small rings relative to that of the long open-chain linear macromolecules at degradation temperatures. Because of the pronounced polarity of the Si–O linkage and flexibility of the $-(Si-O)_n-$ segments, this reaction can take place either intramolecularly within a single polymer molecule, or intermolecularly between two adjacent macromolecules [13].

As mentioned above, comparing with PDMS, the thermal stability of APS is weaker than PDMS, this implies that the amino-group can promote or catalyze the degradation process of APS. Therefore, there must be another mechanism besides the one showed in Fig. 7. According to the study of Lweis [6], the ionic or polar impurities in PDMS may induce nucleophilic cleavage of Si–O bonds, initiating the degradation of PDMS at relative lower temperature. As for APS with amino-group in side chain, a mechanism shown in Fig. 8 is proposed. In this process, the splitting of the main chain Si–O bonds is initiated by the electron transfer between nitrogen atom in the amino-group and Si–O bond in the main chain. In other words, the amino-group acts as catalyst in the degradation of APS. This result in lower activation energy of degradation than non-catalyzed reaction, and this is why the degradation of APS begins at a much lower temperature than PDMS. The products in the degradation process are mixture of cyclic oligomers from trimer upwards, so there were few infusible residues in the experiment.

Mechanism of APS thermal degradation in air

It has been studied that when subjected to heat in the presence of air, PDMS exhibits a marked tendency toward oxidation which eventually leads to the formation of pure silica [7, 13]. The PDMS degrades and forms volatile oligomers at first, then these oligomers react with oxygen, results in complete oxidation to H_2O, CO_2, and SiO_2 [8].

According to our results in this study, PY–GC test shows the existence of cyclic oligomers and amine, IR test implies that oxidation takes place in side-chain and element analysis proves the producing of silica, it seems reasonable to deduce that the thermo-oxidative degradation process of APS is similar to that of PDMS. The amino-group part in the side-chain may react as shown in Fig. 9.

Conclusions

Degradation of APS in nitrogen and air atmosphere is a different process. In nitrogen, the decomposition occurs at Si–O bond, forms cyclic oligomers and leaves no infusible residues, whereas in air the decomposition occurs mainly at side-chain, produces residue of silica with a mass ratio of about 18%. The existence of amino group decreases the thermal stability of APS compared to PDMS.

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