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Title: Synergistic effect and mechanism of platinum catalyst and nitrogen-containing silane on the thermal stability of silicone rubber

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Keywords: Silicone rubber; Platinum catalyst; Nitrogen-containing silane; TG-FTIR; Thermal stability; Degradation mechanism

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Abstract: Platinum (Pt) catalyst and nitrogen-containing silane (NS) were introduced to improve the thermal stability of silicone rubber. The effects of Pt and NS on thermal stability and degradation mechanism of silicone rubber were investigated by thermogravimetry (TG), thermogravimetry-Fourier transform infrared spectrometry (TG-FTIR), scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDXS) and Fourier transform infrared spectrometry (FTIR). A significant synergism was found between Pt and NS for improving the thermal stability of silicone rubber. When 6.67 ppm of Pt and 1.4 phr of NS were introduced, the temperature of 10% and 20% weight loss under nitrogen atmosphere were respectively increased by 36 °C and 119 °C. Meanwhile, the residue weight at 900 °C was doubled to 68% in the presence of Pt/NS. The synergistic mechanism might be that the nitrogen atom coordinated with Pt and improved the catalytic efficiency of Pt. Additionally, NS preserved the catalytic activity of Pt under air atmosphere. Hence, Pt/NS efficiently catalyzed thermal crosslinking and suppressed degradation of silicone chains. Moreover, it revealed that the presence of Pt/NS protected silicone chains from oxidation. Thus, the unzipping depolymerization by silanol groups was reduced significantly.

Feb. 8, 2016

Dear Editor:

Thank you very much for your efficient work and for your useful comments about our manuscript entitled "**Synergistic effect and mechanism of platinum catalyst and nitrogen-containing silane on the thermal stability of silicone rubber**" (ID: TCA-D-15-01075). Those comments are valuable and helpful for revising and improving our paper, as well as the important guiding significance which we hope to meet with approval. We have learned much from them. We think *Thermochimica Acta* is responsible and authoritative.

We have rechecked the manuscript carefully and revised it according to the reviewers' comments and suggestions. Revised portions are marked in red in the manuscript. The following is a point-to-point response to the reviewers' comments:

Response to Reviewer 1:

(1) **Comment:** *Authors investigated the "Synergistic effect and mechanism of platinum catalyst and nitrogen-containing silane on the thermal stability of silicone rubber". The results showed that the performance of Pt/NS filled silicon rubber is better than that of bare silicon and Pt as well as NS filled silicon rubber. The language of the article is very easy to read. In scientific point of view, the mechanism and the interpretation of the data are provided appropriately. I thus recommend the publication of this manuscript in journal of Thermochimica Acta after minor revision.*

Response: Thank you for giving positive comments on our manuscript and for giving us constructive suggestions to improve the quality of this paper. We think the comments are valuable and helpful. We have tried our best to make the corresponding revision in our manuscript and hope to meet with your approval.

(2) **Comment:** *Author should report the size of Pt particles.*

Response: Thank you very much for your comment. It is really true that the size of Pt was one of the important parameters. However, in this system, we introduced Pt by the Karstedt catalyst which was a kind of solution with platinum dissolving in it. The Karstedt catalyst is commercial products and has high solubility in polysiloxane and high catalytic efficiency, so it was better choice than Pt particles. We have mentioned this catalyst in Section 2.1.

(3) **Comment:** *The sample code PDMS and DBPMH is not well defined in the manuscript.*

Response: Thank you very much for pointing this out. We have added the abbreviations in their first use after their full names under Section 2.1.

(4) **Comment:** *The author should rationalize particular applications of the studied.*

Response: Thank you very much for your constructive suggestion. We have added applications of this study in the first paragraph. In field of aerospace, electrical equipment and automation, materials would suffer temperature as high as 900 °C and even above 1000 °C. In such conditions, high degradation temperature and residue weight of materials during different atmosphere are necessary to ensure safety. Hence,

to improve and investigate the thermal stability of silicone rubber under inert and air atmosphere was of great significance.

(5) **Comment:** *Page No. 11, line 19. 'residue ' should be 'residues'*

Response: Thank you very much for your helpful comment and suggestion. We have corrected the expression.

Response to Reviewer 2:

(1) **Comment:** *Thermal stability improvements of SR could enable its even much multifaceted applications in many important. From this point, present work represents an interesting piece of work. However, the following minor points needs to be taken into account*

Response: Thank you very much for giving positive comments on our manuscript and for giving us constructive suggestions to improve the quality of this paper. We think the comments are very valuable and helpful. We have tried our best to make the corresponding revision in our manuscript and hope to meet with your approval.

(2) **Comment:** *According to the author, "nitrogen atoms of nitrogen containing silane coordinate with Pt (6.67 ppm) through lone pair electrons and form complex and which has better dispersion in SR and also enhance catalytic activity." It is not clear how can Pt act as a catalyst when it already form such complex.*

Response: Thank you very much for your comment. Your comments are instructive to our study. We have rethought this question. It is really true that when Pt forms complex with NS, the catalytic activity of Pt was largely weakened at normal temperature. However, in this system, Pt/NS functioned at high temperature above 450 °C. Besides, in the field of organometallic chemistry and catalysis, nitrogen-containing compounds were commonly used as the ligands of Pt to obtain robust catalysts [1,2]. So it is reasonable to say that Pt/NS had enhanced catalytic activity.

[1] C. Lu, S. Gu, W. Chen, H. Qiu, Platinum (II) complexes with polydentate N-heterocyclic carbenes: synthesis, structural characterization and hydrosilylation catalysis, Dalton T. 39 (2010) 4198-4204.

[2] J. Li, C. Yang, L. Zhang, T. Ma, A novel fumed silica-supported nitrogenous platinum complex as a highly efficient catalyst for the hydrosilylation of olefins with triethoxysilane, J. Organomet. Chem. 696 (2011) 1845-1849.

(3) **Comment:** *Under 2.3.4. Fourier Transform Infrared Spectrometry (FTIR) range needs to be mentioned.*

Response: Thank you very much for your comment and suggestion. We have added this information under 2.3.4.

(4) **Comment:** *The statement addition of Pt/NS greatly reduces the degradation rate (specially first) needs more explanation.*

Response: Thank you very much for your comment and suggestion. We have added explanation in Section 3.1 and 3.2.1. Pt/NS catalyzed thermal crosslinking and facilitated formation of tight network of silicone rubber. As a result, the degradation rate was reduced significantly, since tighter network was harder to degrade. Besides,

tight network possessed less mobile chains than original network, which mainly degraded during first stage [3], thus the decrease in $R_{\max 1}$ was especially obvious. The variation of volatile products detected by TG-FTIR further revealed the thermal degradation. The cyclic oligomers were the most main products during thermal degradation. TG-FTIR result revealed that the release of cyclic oligomers was reduced after adding Pt/NS, especially during first degradation stage, which was the reason of greatly reduced degradation rate. Besides, many literatures have reported that Pt would catalyze thermal crosslinking of silicone chains [3,4].

[3] E. Delebecq, S. Hamdani-Devarennnes, J. Raeke, J.M. Lopez Cuesta, F. Ganachaud, High residue contents indebted by platinum and silica synergistic action during the pyrolysis of silicone formulations, ACS Appl. Mater. Inter. 3 (2011) 869-880.

[4] K. Hayashida, S. Tsuge, H. Ohtani, Flame retardant mechanism of polydimethylsiloxane material containing platinum compound studied by analytical pyrolysis techniques and alkaline hydrolysis gas chromatography, Polymer 44 (2003) 5611-5616.

(5) **Comment:** *In Figure 9 entitled Effect of Pt/NS on the degradation mechanism of silicone rubbers, terms: Oxygen atmosphere encapsulating Nitrogen atmosphere is not clear?*

Response: Thank you very much for pointing this out. Sorry for our unclear expression that make you confused! This paper discussed two atmosphere, namely nitrogen atmosphere and synthetic air atmosphere. To avoid ambiguity, we have added more information for synthetic air atmosphere under 2.3.1 and 2.3.2. The air atmosphere adopted was composed of nitrogen and oxygen gas. Thus, the air atmosphere mentioned in Figure 9 encapsulated nitrogen atmosphere. We didn't investigate the thermal stability under pure oxygen atmosphere, since it was relatively uncommon in practical condition.

We appreciate for your warm work earnestly, and hope that the correction will meet with approval. Once again, thank you very much for your efficient work and constructive comments.

Thank you and best wishes!

Sincerely,

Wanjuan Chen, Xingrong Zeng, Xuejun Lai,
Hongqiang Li, Weizhen Fang, Tian Liu.

- Platinum (Pt) and nitrogen-containing silane (NS) were introduced into silicone rubber.
- The thermal stability was improved by Pt/NS both under nitrogen and air atmosphere.
- The TG-FTIR of evolved gases during degradation was performed.
- The synergistic effect and mechanism of Pt and NS were proposed.

**Synergistic effect and mechanism of platinum catalyst and
nitrogen-containing silane on the thermal stability of silicone
rubber**

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ABSTRACT: Platinum (Pt) catalyst and nitrogen-containing silane (NS) were introduced to improve the thermal stability of silicone rubber. The effects of Pt and NS on thermal stability and degradation mechanism of silicone rubber were investigated by thermogravimetry (TG), thermogravimetry-Fourier transform infrared spectrometry (TG-FTIR), scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDXS) and Fourier transform infrared spectrometry (FTIR). A significant synergism was found between Pt and NS for improving the thermal stability of silicone rubber. When 6.67 ppm of Pt and 1.4 phr of NS were introduced, the temperature of 10% and 20% weight loss under nitrogen atmosphere were respectively increased by 36 °C and 119 °C. Meanwhile, the residue weight at 900 °C was doubled to 68% in the presence of Pt/NS. The synergistic mechanism might be that the nitrogen atom coordinated with Pt and improved the catalytic efficiency of Pt. Additionally, NS preserved the catalytic activity of Pt under air atmosphere. Hence, Pt/NS efficiently catalyzed thermal crosslinking and suppressed degradation of silicone chains. Moreover, it revealed that the presence of Pt/NS protected silicone chains from oxidation. Thus, the unzipping depolymerization by silanol groups was reduced significantly.

Keywords: Silicone rubber; Platinum catalyst; Nitrogen-containing silane; TG-FTIR; Thermal stability; Degradation mechanism

1. Introduction

Currently, silicone rubbers are rapidly developing to substitute traditional materials in many fields, due to their unique characteristics, such as hydrophobicity, transparency, chemical resistance, insulation properties and wide temperature adaptability [1-4]. However, as the requirement for high performance of materials enhances, how to effectively improve the thermal properties of silicone rubber has become a significant topic [5]. Especially in field of aerospace, electrical equipment and automation, materials would suffer temperature as high as 900 °C and even above 1000 °C. On such condition, high degradation temperature and residue weight of materials are necessary to ensure safety [6-8]. Traditional method to improve the thermal stability involves adding inorganic fillers. Indeed, heat conductive fillers, like BN, Al₂O₃ and MgO, facilitate heat transfer and relieve thermal degradation of silicone rubber [9-11]. Additionally, some of the calcium and aluminum-based fillers decompose at high temperature and react with silicone matrix to form barrier layer which can suppress thermal degradation of silicone rubber [12,13]. Nevertheless, high loading contents of inorganic fillers are needed to meet the requirement for thermal stability of silicone rubber, which may severely deteriorate its mechanical properties. Another way to enhance thermal stability of silicone rubber is adding metal oxides, such as Fe₂O₃, CeO₂, SnO₂ and CuO, which suppress radical decomposition [14]. However, metal oxides have poor compatibility with silicone rubber and only work for the thermal oxidative stability. Besides, the introducing of silicone compounds with specific structures [15-18], like polyhedral oligomeric silsesquioxanes and silicon resins, can also improve the thermal stability of silicone rubber. Such silicone compounds reduce the regularity of silicone chains and thus retard the random scission reaction during hydrolysis. However, those compounds are relatively complicated to prepare.

The platinum compounds are widely used in silicone rubber. The Karstedt catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethydisiloxane complex) is one of the optimal catalysts for hydrosilylation, due to its high solubility in polysiloxane and high

1 catalytic efficiency [19]. It was reported that platinum compounds were efficient in fire
2 retardancy and improvement of thermal stability [20,21]. Delebecq revealed that
3 containing over 50 ppm of Pt, silicone rubber showed increased residue at high
4 temperature; higher content of Pt would further increase the residue and degradation
5 temperature [22]. However, high content of Pt may increase the cost. Additionally, it
6 was reported that the role of platinum depended on the filler type. Pt-containing
7 silicone rubber showed high residue up to 75%, when filled with 30% vinyl-modified
8 silica. The synergistic mechanism was that platinum catalyzed crosslinking of silicone
9 chains via vinyl on the silica to form ceramic layer [22]. Despite those efforts,
10 mentioned investigations about thermal stability of Pt-containing silicone were made
11 under inert atmosphere.

12 Some patents used small contents of Pt and azo compounds to prepare fire
13 retarded silicone, in the absence of modified silica [20]. Our previous work [23] found
14 that urea-containing silane could significantly elevate the residue of silicone rubber
15 under air atmosphere and increase the thermal degradation temperature under nitrogen
16 atmosphere. However, Pt, adding as the cure catalyst in this system, had not been taken
17 into account and the synergistic effect of platinum and nitrogen compound on thermal
18 stability had not been investigated.

19 In this work, a small content of platinum catalyst (Karstedt catalyst) and
20 nitrogen-containing silane (NS, γ -aminopropyltriethoxy) were employed to improve
21 the thermal stability of silicone rubber. The thermal stability of silicone rubber under
22 nitrogen and air atmosphere was investigated by thermogravimetry (TG). The
23 combined effect of Pt and NS on the degradation mechanism was revealed by
24 thermogravimetry-Fourier transform infrared spectrometry (TG-FTIR), Fourier
25 transform infrared spectrometry (FTIR) and scanning electron microscope-energy
26 dispersive X-ray spectroscopy (SEM-EDXS).

28 **2. Experimental**

29 *2.1. Materials*

Polydimethyl/methylvinylsiloxane (PDMS, 600,000 g/mol and 0.18 mol% vinyl) gums were purchased from Nanjing Dongjue Silicone Group Co. Ltd., China. Fumed silica (SiO₂, with a specific surface area of 200 m²/g) was produced by Tokuyama Chemical Co. Ltd., China. The hydroxyl silicone oil (6 wt% hydroxyl groups) and methyl hydrogen silicone oil (1.2 wt% hydrogen groups) were provided by Shenzhen Senri Silicone Group Co. Ltd., China. 2,5-Bis(tert-butylperoxy)- 2,5-dimethylhexane (DBPMH) was the product of Shin-Etsu Chemical Corporation, China. The Karstedt catalyst, namely platinum(0)-1,1,3,3-tetramethyldisiloxane (3000ppm of Pt) was provided by Guangzhou Tinci Silicon Technology Co. Ltd., China. γ -aminopropyltriethoxysilane was supplied by Dongguan Bettely New Materials Technology Co. Ltd., China.

2.2. Preparation of silicone vulcanizates

According to ISO 2393, hydroxyl silicone oil, SiO₂ and methyl hydrogen silicone oil were blended into polydimethyl/methylvinylsiloxanes in a two-roll mill (XK-168, Dongguan Lina Machinery Industrial Co., Ltd., China) to obtain a transparent compound. Then, the compound went through heat treatment in a ventilated oven at 150 °C for 2 hours. After that, γ -aminopropyltriethoxysilane, Karstedt catalyst and DBPMH, were introduced into the compound via the two-roll mill. The obtained mixture was vulcanized under compression (8 MPa, 165 °C) for an optimal cure time, which was tested by the UR-2030 rheometer. The secondary vulcanization was conducted at 200 °C for 4 hours [24]. Formulations of the silicone vulcanizates are showed in Table 1.

Table 1

Formulations of silicone rubbers.

Sample codes	PDMS gums (g)	SiO ₂ (g)	Hydroxyl silicone oil (g)	Methyl hydrogen silicone oil (g)	Pt (ppm)	NS (g)	DBPMH (g)
PDMS	100	40	8	0.5	0	0	2
PDMS/Pt	100	40	8	0.5	6.67	0	2
PDMS/NS	100	40	8	0.5	0	1.4	2
PDMS/Pt/NS	100	40	8	0.5	6.67	1.4	2

2.3. Testing and Characterization

2.3.1. Thermogravimetry (TG)

Thermogravimetric analysis was conducted on TG209 (Netzsch Instruments Co., Germany) from 30 °C to 900 °C. The heating rate was 20 °C /min. 5~10 mg of samples was measured in an alumina crucible under a nitrogen flow or a synthetic air flow of 40 mL/min. The synthetic air flow consisted of 21% oxygen gas and 79% nitrogen gas.

2.3.2. Thermogravimetry-Fourier Transform Infrared Spectrometry (TG-FTIR)

The thermogravimetry-Fourier transform infrared spectrometry (TG-FTIR) was applied to investigate the volatile products of silicone rubber during thermal degradation, which was composed of a thermogravimeter (TG209, Netzsch Instruments Co., Germany), a Fourier transform infrared spectrometer (Tensor 27, Bruker Optics, Germany) and a transfer tuber with inner diameter of 1 mm connecting them. About 15 mg samples were heated from 30 °C to 900 °C at a heating rate of 20 °C/min, under nitrogen or synthetic air atmosphere. The synthetic air atmosphere was composed of 21% oxygen gas and 79% nitrogen gas. During the process, the volatile products were continuously transferred to Tensor 27 for IR testing through the connected tube with a temperature of 230 °C.

2.3.3. Scanning electron microscopy-energy dispersive X-ray spectrometer (SEM-EDXS)

The morphology of silicone rubber residues heated from room temperature to certain temperature in a furnace under nitrogen atmosphere was characterized by scanning electron microscopy (SEM, EVO18, Carl Zeiss Jena, Co., Germany). The surface of residue was coated with a gold layer (several nanometers in thickness) for observation. The elemental analysis of residues was conducted by energy-dispersive X-ray spectrometer (EDXS, Oxford Inca250, Oxford Instruments Co., Britain), an integrated tool in SEM.

2.3.4. Fourier Transform Infrared Spectrometry (FTIR)

The spectra of silicone rubber residues heated from room temperature to certain temperature in a furnace under air atmosphere were measured by Fourier transform infrared spectroscopy (FTIR, Tensor 27, Bruker Optics, Germany), after mixing the samples with spectroscopy grade potassium bromide powder. The recorded ranges were from 4000 cm^{-1} to 400 cm^{-1} . Only the spectra of silicone rubbers were obtained by attenuated total reflection method in the range from 4000 cm^{-1} to 600 cm^{-1} .

3. Results and discussion

3.1. Thermal stability

The thermal stability of silicone rubbers under nitrogen atmosphere was investigated by TG. The TG curves and their derivative (DTG) curves are shown in Fig. 1. The characteristic parameters are displayed in Table 2. As demonstrated, the characteristic temperatures of 10% weight loss (T_{10}) were delayed for only $5\text{ }^{\circ}\text{C}$ and $16\text{ }^{\circ}\text{C}$, after adding Pt or NS, respectively. However, the combined addition of Pt and NS (Pt/NS) improved T_{10} and temperature of 20% weight loss (T_{20}) for $36\text{ }^{\circ}\text{C}$ and $119\text{ }^{\circ}\text{C}$, respectively. Additionally, the residue of PDMS/Pt/NS at $900\text{ }^{\circ}\text{C}$ was 68%, which was much higher than 30% for PDMS. Fig. 1b shows that the addition of Pt/NS greatly reduces the degradation rate. The maximum degradation rate during the first stage ($R_{\max 1}$) was decreased from $6.98\text{ wt\%/min}$ to $2.13\text{ wt\%/min}$, when Pt/NS was introduced to PDMS. Besides, the $R_{\max 1}$ of PDMS/Pt was $3.90\text{ wt\%/min}$, which was also lower than $R_{\max 1}$ of PDMS. It might be that Pt catalyzed thermal crosslinking of silicone chains, so tightly crosslinked network was formed to resist degradation of silicone chains. [21] Besides, the formation of tight network reduced mobile chains which tended to degrade in first stage [22], thus $R_{\max 1}$ was decreased significantly. Moreover, nitrogen atoms were easy to coordinate with Pt through lone pair electrons. Those Pt-NS coordination complexes were stable at high temperature and contributed to better dispersion [25] and enhanced catalytic activity [26] of Pt. Hence, the thermal degradation was further suppressed.

Fig. 1. TG (a) and DTG (b) curves of silicone rubbers under nitrogen atmosphere.

Table 2

Characteristic parameters of TG and DTG for silicone rubbers.

Sample codes	Degradation under nitrogen atmosphere					Degradation under air atmosphere			
	T ₁₀ (°C)	T ₂₀ (°C)	R _{max1} (wt %/min)	R _{max2} (wt %/min)	Residue at 900°C (wt%)	T ₁₀ (°C)	T ₂₀ (°C)	R _{max} (wt %/min)	Residue at 900°C (wt%)
<i>PDMS</i>	526	562	6.98	8.26	30	461	499	12.3	44
<i>PDMS/Pt</i>	531	594	3.90	8.60	47	453	495	14.4	48
<i>PDMS/NS</i>	542	581	5.86	9.29	34	459	486	11.8	49
<i>PDMS/Pt/NS</i>	562	681	2.13	4.25	68	472	527	5.24	68

Fig. 2 shows the TG and DTG curves of silicone rubbers under air atmosphere. And the characteristic parameters are exhibited in Table 2. As demonstrated, neither Pt nor NS increased the degradation temperatures. However, the addition of Pt/NS delayed T₂₀ for 28 °C. Besides, R_{max} was reduced from 12.3 wt%/min to 5.24 wt%/min in the presence of Pt/NS. As a result, the final residue of PDMS/Pt/NS reached 68%, which was higher than 44% for PDMS. Nevertheless, the increase in residue by adding Pt or NS alone was insignificant. The failure of Pt affecting thermal stability under air atmosphere might be due to the oxidation of Pt. However, with the existence of NS, Pt seemed to preserve its influence, which might be due to the coordination of Pt and NS [26].

Fig. 2. TG (a) and DTG (b) curves of silicone rubbers under air atmosphere.

3.2. Thermal degradation under nitrogen atmosphere

3.2.1. TG-FTIR analysis

To further investigate the degradation process of silicone rubber during nitrogen atmosphere, TG-FTIR was used to detect the volatile products released during thermal degradation. The 3D FTIR spectra and accumulated spectra of volatile products are shown in Fig. 3. As demonstrated, the cyclic oligomers (814 cm^{-1} , 1026 cm^{-1} , 1084 cm^{-1} , 1265 cm^{-1} and 2968 cm^{-1}) were the main products for all the samples [27]. However, the FTIR spectra for PDMS/Pt/NS showed peaks assigned to methane (3018 cm^{-1} and 1306 cm^{-1}) [22]. Moreover, the new peak at 1356 cm^{-1} for PDMS/Pt/NS was attributed to stretching vibration of Si-CH₂-Si [28,29]. Those products were attributed to two competing mechanism during thermal degradation. Molecular mechanism occurred by random scission to produce cyclic oligomers (Scheme 1a) [30]. Radical mechanism happened through homolytic cleavage of Si-CH₃ which further induced crosslinking reaction and volatilization of methane (Scheme 1b) [30]. It was reported that Pt would catalyze the mentioned radical mechanism [21]. The radical mechanism would suppress the molecular mechanism, since random scission was easier to occur in highly mobile chains than in crosslinked chains. The obvious peaks assigned to methane for PDMS/Pt/NS indicated an enhanced radical mechanism. Besides, the band at 1356 cm^{-1} (Si-CH₂-Si), which represented the crosslinking points, further indicated the formation of a tight crosslinking network for PDMS/Pt/NS at high temperature.

Fig. 3. The 3D FTIR spectra and accumulated spectra of volatile products of silicone rubbers during pyrolysis under nitrogen atmosphere.

Scheme 1. The mechanism for the formation of cyclic oligomers (a), methane and Si-CH₂-Si (b).

Fig. 4 presents the evolution of mentioned volatile products versus temperature, according to characteristic absorbance at 3018 cm⁻¹, 1356 cm⁻¹ and 1026 cm⁻¹, respectively. NS had small effect on volatile products. However, the release of methane for PDMS/Pt was larger than that for PDMS and the release of cyclic oligomers was smaller. It suggested that Pt promoted radical mechanism and suppressed molecular mechanism. Furthermore, PDMS/Pt/NS showed the largest release of methane and the smallest release of cyclic oligomers. It meant the role of Pt was enhanced in the

presence of NS. The decreased release of cyclic oligomers, the main products, explained reduced degradation rate for PDMS/Pt and PDMS/Pt/NS, as shown in Fig. 1. During the first stage, the degradation by random scission mainly occurred in highly mobile chains, which were loosely crosslinked and out of the silica-restrained domains [22]. The significantly decreased release of cyclic oligomers for PDMS/Pt/NS indicated a low fraction of highly mobile chains in residue, due to radical crosslinking catalyzed by Pt/NS. Entering the second stage, the absorbance peak assigned to Si-CH₂-Si for PDMS/Pt/NS indicated a tightly crosslinked residue. Besides, the release of cyclic oligomers for PDMS/Pt/NS was also lower than that of other samples during the second stage. It indicated that the majority of remaining silicone chains for PDMS/Pt/NS had involved in a firm network to generate the final residue.

Fig. 4. The FTIR absorbance of volatile products versus temperature under nitrogen atmosphere.

3.2.2. Morphology and element analysis

The residue of PDMS at 900 °C was a grayish powder, while the residue of PDMS/Pt/NS was a hard black solid. Actually, PDMS/Pt/NS residue had better strength and shape retention than PDMS residue. The SEM images of PDMS and PDMS/Pt/NS residues at 900 °C are displayed in Fig. 5. It showed that PDMS was loose and porous, while PDMS/Pt/NS looked dense. EDXS (Fig. 5) revealed that at 540 °C, PDMS/Pt/NS had lower carbon content than PDMS, due to the larger release of methane. However, above 540 °C, carbon content of PDMS was sharply decreased

and lower than that of PDMS/Pt/NS. It indicated that enhanced radical crosslinking of PDMS/Pt/NS promoted more silicone chains to constitute the firm three-dimensional network of residue. Thus, the loss of carbon through volatilization of oligomers was significantly suppressed. Such three-dimensional network accounted for the strength retention of PDMS/Pt/NS residue. Besides, the ratios of Si/O for PDMS were close to 1/2 at 900 °C, due to the SiO₂-dominant residue. However, the ratio of Si/O for PDMS/Pt/NS were higher, implying more silicone chains (which had higher ratio of Si/O than silica) had involved in residue network.

Fig. 5. The SEM images and element analysis of PDMS and PDMS/Pt/NS residues after pyrolysis under nitrogen atmosphere.

3.3. Thermal degradation under air atmosphere

3.3.1. TG-FTIR analysis

Fig. 6 shows the FTIR spectra of volatile products released under air atmosphere. It revealed that the volatile products were different from those under nitrogen atmosphere. CH₂O (1745 cm⁻¹), CO₂ (2359 cm⁻¹ and 2314 cm⁻¹), CO (2179 cm⁻¹ and 2114 cm⁻¹) and H₂O (3500-3700 cm⁻¹) were detectable in the volatile products besides cyclic oligomers (814 cm⁻¹, 1026 cm⁻¹, 1084 cm⁻¹, 1265 cm⁻¹ and 2968 cm⁻¹) and methane (1306 cm⁻¹ and 3018 cm⁻¹). Under air atmosphere, oxidation occurred in alkyl of the silicone chains, which resulted in the release of CH₂O and formation of silanol groups (Si-OH), as showed in Scheme 2a [27]. The silanol groups induced unzipping depolymerization (Scheme 2b) and produced cyclic oligomers more easily than random scission [5]. Additionally, the oxidation of methane would produce gases of

1 might be that the silanol groups generated by oxidation of silicone chains not only
2 induced depolymerization of silicone chains through unzipping reaction (Scheme 2b)
3 [5], but also facilitated cleavage of Si-CH₃ bond to produce methane. This could be
4 supported by much larger release of methane below 600 °C under air atmosphere than
5 under nitrogen atmosphere. Besides, dehydration condensation occurred among silanol
6 groups to yield H₂O and formed crosslinking points of Si-O-Si (Scheme 2c). Such
7 additional crosslinking points contributed to higher residue of silicone rubbers under
8 air atmosphere than under nitrogen atmosphere.

9 It revealed that incorporating Pt alone would not reduce the release of CH₂O and
10 cyclic oligomers. Instead, the existence of Pt/NS markedly decreased the release of
11 CH₂O and cyclic oligomers. This indicated that the oxidation of silicone chains and
12 unzipping depolymerization were significantly suppressed. Besides, the release of
13 methane for PDMS/Pt/NS during 440~500 °C was much lower than that for PDMS,
14 which might be also due to the suppressed oxidation and reduced silanol groups.
15 Nevertheless, much large release of methane for PDMS/Pt/NS was observed above 500
16 °C, like that under nitrogen atmosphere. This indicated that tight crosslinking was
17 developing and high stability of residue could be expected, owing to the catalytic
18 action of Pt/NS. However, platinum alone couldn't increase the release of methane
19 above 500 °C, implying the loss of catalytic activity. CO and CO₂ were the incomplete
20 and complete oxidation products of methane, respectively. It could be seen that after
21 adding Pt/NS, the release of CO decreased while CO₂ increased. This further indicated
22 that the oxidation in silicone chains was suppressed, since suppressed silicone
23 oxidation could spare more oxygen to support complete oxidation of methane.

Fig. 7. The FTIR absorbance of volatile products versus temperature for silicone rubbers under air atmosphere.

3.3.2 FTIR analysis

Fig. 8 presents the FTIR spectra of residues taken out at various temperatures under air atmosphere. It showed that the characteristic absorptions of Si-CH₃ (2964 cm⁻¹, 1262 cm⁻¹ and 800 cm⁻¹) existed from 30 °C to 450 °C, but disappeared from 530 °C to 900 °C for PDMS. However, there still existed weak characteristic absorptions of Si-CH₃ at 530 °C for PDMS/Pt/NS. This supported that suppressed oxidation contributed to slow loss of -CH₃ in silicone chains, due to the combined action of Pt/NS. Nevertheless, characteristic absorptions of Si-CH₃ disappeared at 600 °C, since maximum release of methane for PDMS/Pt/NS occurred at 570 °C (Fig. 7). The peaks at 1021 cm⁻¹ and 1094 cm⁻¹ corresponded to linear and three-dimensional Si-O, respectively [31]. It showed that the relative intensity of peaks at 1021 cm⁻¹ versus 1094 cm⁻¹ decreased as temperature rose, especially for PDMS. This suggested slower volatilization of linear Si-O in PDMS/Pt/NS than that in PDMS, which was attributed to the reduced unzipping depolymerization. The peaks at 478 cm⁻¹ and 810 cm⁻¹ were assigned to the three-dimensional Si-O-Si and Si-C [32,33], respectively. It revealed that PDMS/Pt/NS exhibited higher relative intensity of Si-C peak than PDMS above

530 °C. This indicated higher fraction of Si-C network and lower fraction of Si-O network, due to the enhanced thermal crosslinking and suppressed oxidation of PDMS/Pt/NS.

Fig. 8. The FTIR spectra of PDMS (a) and PDMS/Pt/NS (b) after pyrolysis under air atmosphere.

3.4. Possible mechanism

Based on analysis mentioned above, the possible mechanism could be that platinum could catalyze radical crosslinking of silicone chains to form tight crosslinking network, thus the degradation of silicone chains by molecular mechanism was suppressed. The presence of NS improved the catalytic efficiency and avoided the oxidation of platinum by coordinating with platinum. Besides, Pt/NS suppressed the oxidation of silicone chains; hence the destructive unzipping depolymerization was significantly decreased. The combined effect of Pt/NS on degradation mechanism of silicone rubber was showed in Fig. 9. Due to the catalytic action and antioxidation, Pt/NS contributed to a dense and high residue with high fraction of Si-C network.

3

4. Conclusions

A small amount of platinum catalyst and γ -aminopropyltriethoxysilane (NS) were introduced to improve the thermal stability of silicone rubber. It revealed that Pt and NS exhibited a synergistic effect on thermal stability of silicone rubber. After adding Pt/NS, silicone rubber showed 36 °C and 119 °C increase in T_{10} and T_{20} , under nitrogen atmosphere, respectively. The residue weight at 900 °C under nitrogen and air atmosphere was elevated from 30% to 68% and from 44% to 68%, respectively. It was found that there were two degradation stages under nitrogen atmosphere, which corresponded to the volatilization of highly mobile chains and constrained chains. The presence of Pt/NS facilitated tight crosslinking and promoted silicone chains to form firm network. Thus the random degradation was largely reduced. Under air atmosphere, the degradation happened at lower temperature due to the oxidation of silicone chains. This was because the generated Si-OH from oxidation induced unzipping depolymerization. The existence of NS preserved the catalytic activity of Pt under air atmosphere. Furthermore, the combined action of Pt/NS significantly suppressed the oxidation in silicone chains and thus retarded unzipping depolymerization remarkably. Therefore, the introduction of platinum and nitrogen-containing silane was an efficient way to improve thermal stability of silicone rubber.

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Table 1 Formulations of silicone rubbers

Table 1							
Formulations of silicone rubbers.							
Sample codes	PDMS gums (g)	SiO ₂ (g)	Hydroxyl silicone oil (g)	Methyl hydrogen silicone oil (g)	Pt (ppm)	NS (g)	DBPMH (g)
PDMS	100	40	8	0.5	0	0	2
PDMS/Pt	100	40	8	0.5	6.67	0	2
PDMS/NS	100	40	8	0.5	0	1.4	2
PDMS/Pt/NS	100	40	8	0.5	6.67	1.4	2

Table 2 Characteristic parameters of TG and DTG

Table 2

Characteristic parameters of TG and DTG for silicone rubbers.

Sample codes	Degradation under nitrogen atmosphere					Degradation under air atmosphere			
	T ₁₀ (°C)	T ₂₀ (°C)	R _{max1} (wt %/min)	R _{max2} (wt %/min)	Residue at 900°C (wt%)	T ₁₀ (°C)	T ₂₀ (°C)	R _{max} (wt %/min)	Residue at 900°C (wt%)
PDMS	526	562	6.98	8.26	30	461	499	12.3	44
PDMS/Pt	531	594	3.90	8.60	47	453	495	14.4	48
PDMS/NS	542	581	5.86	9.29	34	459	486	11.8	49
PDMS/Pt/NS	562	681	2.13	4.25	68	472	527	5.24	68

Fig.1 TG N2

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Fig.2 TG and DTG air
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Fig.3 3D N2
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Fig.4 TG-IR N2

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Scheme 1 degradation in N2
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Fig.5 SEM
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Fig.6 3D AIR

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Scheme 2. Si Oxidation
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a

b

c

Fig 7 air TGIR.tif
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Fig 8 air IR

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Fig.9a

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Fig.9b

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