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# Ambient-curable polysiloxane coatings: structure and mechanical properties

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Abstract Ambient-curable polysiloxane coatings were prepared by hydrolysis and condensation of 3-methacryloxypropylmethyldimethoxysilane (MPDS) and methyltriethoxysilane (MTES) and subsequently mixing with 3-aminopropyltriethoxysilane (APS). The structures of the as-obtained polysiloxane oligomers as well as the dried polysiloxane coatings on tinplate substrates were analyzed by FTIR and <sup>29</sup>Si NMR. The mechanical properties of the coatings were thoroughly examined at both macro-level and micro-level using a pendulum hardness rocker, an impact tester, and a nanoindentation/nanoscratch instrument. Effects of the molar ratio of MPDS/MTES, the dosage of aqueous ammonia solution, and the catalytic condition on the structure of polysiloxane oligomers as well as the structure and mechanical properties of the polysiloxane coatings were investigated. The dried coatings with thickness of 15-26 µm are highly elastic. The hardness (Koenig hardness and microhardness), impact resistance and scratch resistance are mainly dependent on the condensation degree of polysiloxane coatings rather than on the organic component of the coatings. A proper pre-hydrolysis process or more APS is benefit for enhancing the mechanical strength of the polysiloxane coatings. Polysiloxane coatings with high hardness and excellent scratch resistance can be prepared preferentially at low molar ratio of MPDS/MTES.

**Keywords** Alkoxysilane · Sol–gel · Polysiloxane coatings · Mechanical properties

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#### **1** Introduction

A variety of polysiloxane coatings have been developed by a sol-gel process of organofunctional alkoxysilane since these coatings can provide corrosion protection [1-8], scratch resistance [9–12], and various surface wettabilities (i.e., hydrophobicity [8], superhydrophobicity [13]) for the coated substrates. The general strategy for fabrication of polysiloxane coatings is based on the hydrolysis and condensation of alkoxysilanes in the presence of water and catalysts (acid or alkali) first and then casting on substrates to form dried coatings, baking at high temperatures is usually necessary during drying step to achieve high condensation degree and thus better performance of coatings [14]. Because of the intrinsic coating stresses at higher condensation degree, crack-free coatings can be obtained only with thickness no more than 10 µm. In addition, the high-temperature treatment restricts the application of polysiloxane coatings on some relatively soft substrates such as plastics or immobile articles. To solve the problem, room-temperature (RT) curing process was exploited for the sol-gel derived polysiloxane coatings. For examples, Wang et al. [15] mixed the epoxy-hybrid silica sol, pro-hydrolyzed from tetraethoxysilane and 3-glycidoxypropyltrimethoxysilane, with cerium nitrate-doped alumina sol to fabricate a RT-curable anticorrosion coating. Xing et al. [16, 17] successfully prepared RT-dried polysilsesquioxane coatings using special catalysts, such as phytic acid. Huang et al. [18] employed 3-aminopropyltriethoxysilane (APS) to cure the mixture of pre-hydrolyzed methyltriethoxysilane (MTES) and polymethylhydrosiloxane. RT curing can also be realized using UV-irradiation radical polymerization [19] for the alkoxysilanes bearing carbon-carbon double bonds or organic amine curing agents (i.e. Jaffamine [20], diethylenetriamine [21]) for the alkoxysilanes bearing epoxy groups. Nevertheless, the backbones of these coatings are not purely composed of Si–O bonds, unavoidably deteriorating the thermal stability, weatherability, chemical resistance of the polysiloxane coatings. As far, most of researches on RT-cured polysiloxane coatings are focused on the anticorrosion [15–17] but seldom on the mechanical properties, which severely hinders the application of sol–gel derived polysiloxane coatings as the durable topcoats for vehicles, steel constructions, outdoor equipments and so on.

In this article, polysiloxane oligomers were first prepared by pre-hydrolysis of MTES with 3-methacryloxypropylmethyldimethoxysilane (MPDS) using deficient amount of water, and further mixing with APS to fabricate polysiloxane coatings. The coatings can be quickly cured at an ambient temperature with the help of the moisture in the air and the dried films can reach around twenty micrometers in thickness. Effects of the molar ratio of MPDS/ MTES, the dosage of aqueous ammonia solution and the catalytic condition on the structures of the pre-hydrolyzed polysiloxane oligomers and the corresponding polysiloxane coatings were investigated. The mechanical properties of the coatings were thoroughly examined at both macro-level and micro-level. The relationship between the structure and mechanical properties of the RT-cured polysiloxane coatings was discussed.

# 2 Experimental

#### 2.1 Materials

3-Methacryloxypropylmethyldimethoxysilane (MPDS, 98%) and methyltriethoxysilane (MTES, 98%) were purchased from Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd. of China. 3-Aminopropyltriethoxysilane (APS, 98%), hydrochloric acid (HCl 38–40%), aqueous ammonia solution (28 wt%), absolute ethanol (AR) and acetone (AR) were all purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received. Deionized water was used throughout the experiments.

## 2.2 Preparation of polysiloxane oligomers and coatings

Polysiloxane oligomers were prepared by co-hydrolysis/ condensation of MPDS and MTES. The typical process was conducted as follows: A 50 mL round-bottom flask equipped with a condenser was put in an oil bath. Then, a certain amount of MPDS and MTES were charged into the flask and magnetically stirred, followed by dropwise addition of aqueous ammonia (or hydrochloric acid)/ethanol solution within 15 min at room temperature. After that, the oil bath was heated to 90 °C and the reaction mixture was refluxed at that temperature for 3 h to obtain polysiloxane oligomers. The dosages of raw materials for different Runs are listed in Table 1.

Polysiloxane coatings were prepared by mixing the asobtained polysiloxane oligomer solution with a certain amount of APS (usually 30% based on the weight of the polysiloxane oligomer solution). The coatings can be quickly cured at an ambient temperature with the help of the moisture in the air. If APS was not used, all polysiloxane coatings were always in liquid state even after 1 week. Herein, APS, on one side, acts an alkaline catalyst for the further condensation of polysiloxane oligomers, and on the other side, participates in the co-hydrolysis/condensation with polysiloxane oligomers [22]. The coatings were cast on tinplates by a drawdown rod and dried at room temperature for 1 week. The samples were then used for further structure characterization and mechanical tests. All tinplate sheets were aforehand polished with 20# metallographic abrasive papers, and then cleaned with acetone.

 Table 1
 The formulations for preparation of polysiloxane oligomers and coatings

Runs	MPDS (mol)	MTES (mol)	NH <sub>3</sub> /H <sub>2</sub> O solution <sup>a</sup> (g)	Ethanol (g)	APS <sup>t</sup> (%)
PT91	0.045	0.005	0.9	1	30
PT82	0.04	0.01	0.9	1	30
PT64	0.03	0.02	0.9	1	30
PT55	0.025	0.025	0.9	1	30
PT46	0.02	0.03	0.9	1	30
PT28	0.01	0.04	0.9	1	30
PT19	0.005	0.045	0.9	1	30
PT010	0	0.05	0.9	1	30
PT46-0.25	0.02	0.03	0.225	1	30
PT46-0.5	0.02	0.03	0.45	1	30
PT46-1.5	0.02	0.03	1.35	1	30
PT46-2	0.02	0.03	1.8	1	30
PT46-N <sup>e</sup>	0.02	0.03	0	0	30
РТ46-Н	0.02	0.03	0.9 <sup>c</sup>	1	30
PT46-A	0.02	0.03	0.9 <sup>d</sup>	1	30
PT46-10%	0.02	0.03	0.9	1	10
PT46-20%	0.02	0.03	0.9	1	20
PT19-N <sup>e</sup>	0.05	0.045	0	0	30

<sup>a</sup> The concentration of aqueous ammonia solution is 0.1 mol/kg

<sup>b</sup> The percentage of APS (based on the mass of the as-obtained polysiloxane oligomer solution) was used in the fabrication of moisture-cured coatings

 $^{\rm c}\,$  Hydrochloric acid solution with a concentration of 0.1 mol/kg was used

<sup>d</sup> The concentration of the aqueous ammonia solution is 1.0 mol/kg <sup>e</sup> MPDS and MTES were directly blended with APS without prehydrolysis

#### 2.3 Characterization

Fourier transform infrared (FTIR) spectra were recorded using a Nicolet Nexus 470 spectrometer (ThermoFisher, USA) in the wavenumber range of 650–4,000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and accumulation of 32 scans. Liquid polysiloxane oligomer solution was dropped onto the surface of NaCl plate and quickly dried by infrared irradiation for direct characterization. The dried polysiloxane coatings were blended with KBr to form sample plates.

Liquid-state <sup>29</sup>Si-NMR spectra were obtained on Avance DMX500 (Bruker Biospin Gmbh, Germany) using 10 mm probe at 59.6 MHz. Polysiloxane oligomer solution was first dissolved in deuterated acetone before measurement. Solid-state <sup>29</sup>Si CP MAS NMR were carried out on a Bruker DSX300 spectrometer using standard Bruker 7 mm double-resonance H–X MAS probe at a spinning frequency of 4.2 kHz. The spectra were recorded with a crosspolarization time of 5 ms, and composite pulse <sup>1</sup>H decoupling was applied during the acquisition. The spectra were referenced externally to tetramethylsilane.

The pendulum hardness (Koenig hardness) of polysiloxane coating was measured with 707 KP pendulum hardness rocker (Sheen Instrument Ltd., UK). The time of the Koenig pendulum swinging from 6° to 3° was automatically recorded at room temperature. The average value from three measurements on different sites of the same sample was adopted.

The impact resistance of the coatings was determined by a QCJ impact tester (Height range: 0–50 cm, Shanghai XianDai Environment Engineering Technique Co., Ltd, China). The hammer (1 kg) freely falls on the sample from a certain height. The highest height that does not cause film failure is regarded as the impact resistance.

The nanoindentation tests were carried out using an ultra nanoindentation tester (CSM Instruments, Switzerland) with a Berkovich diamond indenter. After contacting with the surface, the indenter was approached into the coatings with a constant strain rate of  $0.05 \text{ s}^{-1}$  until 2,000 nm of depth was reached, held at the maximum load for 50 s, and then withdrawn from the surface with the same rate as loading. At least 5 indents were performed on each sample and average values were finally adopted. The hardness and elastic modulus were calculated by the Oliver and Pharr method [23].

Nanoscratch tests were conducted with a nanoscratch tester (CSM Instruments, Switzerland) using a Rockwell indenter (conical, die angle 90°, tip radius 10  $\mu$ m). A prescan procedure with a load of 3 mN was first conducted. The tip was then pushed into the sample with increasing load from 3 mN to the preset maximum load, and meanwhile moved with a constant velocity to attain 0.5 mm of scratch length within 30 s. The surface profile was

recorded by a depth sensor. After the tip was removed, a post-scan with a load of 3 mN was performed to determine the residual depth of the scratch. An optical microscope was employed to observe the appearance of the scratch tracks. The maximum load in the scratch tests for acquiring critical load was set as 100 mN for PT91 and PT64 coatings, 250 mN/s for PT28 and PT19 coatings, and 150 mN for all other coatings. The critical load was an average of three parallel measurements. A maximum load of 40 mN was used in the other scratch tests.

#### 3 Results and discussion

# 3.1 Synthesis and structure of polysiloxane oligomers

Polysiloxane oligomers were prepared by the sol-gel reaction of MPDS and MTES. Based on the molecular structures of the precursors, it can be deduced that the asobtained polysiloxane oligomers were possibly constituted by linear, branch and/or network silicon-oxo units, as shown in Scheme 1. FTIR and liquid-state <sup>29</sup>Si-NMR analysis were conducted to illustrate the actual structure of the polysiloxane oligomers prepared at various molar ratios of MPDS/MTES, various dosages of aqueous ammonia solution, or different catalytic conditions.

#### 3.1.1 FTIR analysis

The FTIR spectra of the polysiloxane oligomers prepared at various molar ratios of MPDS/MTES are shown in Fig. 1. The peaks at 1,720 and 1,640  $\text{cm}^{-1}$  are attributed to the stretching vibrations of C = O and C = C, respectively. These two peaks decline as the molar ratio of MPDS/MTES reduces, clearly indicating the different compositions of polysiloxane oligomers. A broad absorption band at 3,140-3,720 cm<sup>-1</sup> due to the stretching vibration of -OH is observed. Since the peak at around  $1,630 \text{ cm}^{-1}$  due to the bending of water molecules is not discernible, this band should be mainly assigned to the silanol groups, demonstrating the hydrolysis of MPDS/ MTES in the pro-hydrolysis step. More interestingly, the intensity of this band decreases as the molar ratio of MPDS/MTES decreases. This implies the higher condensation degree of the polysiloxane oligomer at higher amount of MTES, which is resulted from the lower steric hindrance of methyl substituent in contrast to methacryloxypropyl substituent for the condensation of silanol groups [24]. A small sharp peak at  $2,836 \text{ cm}^{-1}$  due to the symmetrical stretching vibration of C-H in -OCH3 [5] occurs for samples PT91, PT82, and PT64, while a strong peak centered at 2.926  $\text{cm}^{-1}$  due to the asymmetrical vibration

Scheme 1 The possible siliconoxo units formed from the cohydrolysis/condensation of MPDS and MTES





Fig. 1 The FTIR spectra of polysiloxane oligomers prepared with different molar ratios of MPDS/MTES

of  $-CH_2$ - in  $-OCH_2CH_3$  [4, 6] exists for all samples. These peaks suggest that the hydrolysis of alkoxyl group is incomplete for all Runs, due to the deficient amount of water in the sol-gel process. Unfortunately, the stretching vibration of Si-O-Si at around 1,000–1,100 cm<sup>-1</sup> overlaps with that of Si–O–C, thus the condensation can not be directly evidenced from the strong peak at this band.

The FTIR spectra of the polysiloxane oligomers prepared with different contents of aqueous ammonia solution are presented in Fig. 2. For the sake of comparison, the FTIR spectrum of PT46-N (i.e. the mixture of MPDS and MTES) is also given in Fig. 2. With increasing dosage of ammonia solution, the intensity of the small peak at  $2,836 \text{ cm}^{-1}$  due to  $-\text{OCH}_3$  group obviously decreases, apparently indicating that more alkoxyl groups are hydrolyzed. To distinguish the hydrolysis and condensation degree of these samples, the area ratios of the bands at  $3,140-3,720 \text{ cm}^{-1}$  (due to -SiOH) and  $2,750-3,140 \text{ cm}^{-1}$ (due to C-H) to the peak at 1,640 cm<sup>-1</sup> (due to C = C) were quantitatively calculated, as shown in Table 2. It can be seen from samples PT46-0.25, PT46-0.5 and PT46 that the area ratio,  $A_{2750-3140}/A_{1640}$ , considerably decreases as the amount of ammonia solution increases, suggesting more alkoxyl groups were hydrolyzed. Nevertheless, A<sub>2750-3140</sub>/A<sub>1640</sub> slightly changes for samples PT46, PT46-1.5 and PT46-2. This means that only a little alkoxyl groups were further hydrolyzed when the dosage of ammonia solution exceeded 0.9 g (i.e. Run PT46, corresponding to 2.6:1 of the alkoxyl groups-to-water molar



Fig. 2 The FTIR spectra of polysiloxane oligomers prepared at different dosages of aqueous ammonia solution

ratio). The area ratio,  $A_{3140-3720}/A_{1640}$ , has a similar trend with increasing water dosage in the sol-gel process. For samples PT46-0.25, PT46-0.5 and PT46, higher ratio of  $A_{3140-3720}/A_{1640}$  at higher dosage of ammonia solution means the hydrolysis of more alkoxyl groups, being consistent with the ratio of  $A_{2750-3140}/A_{1640}$ . Since both the hydrolysis and condensation have impact on the intensity of the band at 3,140–3,720 cm<sup>-1</sup>, the evolution of the condensation degree of the as-obtained polysiloxane oligomers can not be deduced from the ratio of  $A_{3140-3720}/A_{1640}$ .

The polysiloxane oligomer prepared using diluted hydrochloric acid (sample PT46-H) or concentrated ammonia solution (PT46-A) was also characterized by FTIR. The area ratios,  $A_{2750-3140}/A_{1640}$  and  $A_{3140-3720}/A_{1640}$ , were calculated and given in Table 2. It can be clearly seen that much lower hydrolysis and condensation degree is exhibited at acidic condition (comparing PT46-H with PT46). Concentrated ammonia solution can not increase the hydrolysis but can slightly promote the condensation reaction (Comparing PT46-A and PT46).

# 3.1.2 <sup>29</sup>Si NMR analysis

The <sup>29</sup>Si NMR spectra of some typical polysiloxane oligomers are shown in Fig. 3. The peaks at -8.5, -14.1, and



Fig. 3 <sup>29</sup>Si NMR spectra of polysiloxane oligomer

-22.1 ppm correspond to  $D^0$ ,  $D^1$ , and  $D^2$  species [25, 26], and the peaks at -43.0, -47.5, -56.0, -65.6 ppm to  $T^0$ ,  $T^1$ ,  $T^2$ , and  $T^3$  species [27, 28], respectively. The peaks due to  $T^i$  (i = 1-3) species are invisible for the samples prepared at high molar ratio of MPDS/MTES (i.e., PT91 and PT64) or low dosage of ammonia solution (i.e., PT46-0.5). As the amount of aqueous ammonia solution increases, the peaks attributing to  $D^2$  and  $T^i$  (i = 1-3) species rise and the peak for  $T^0$  specie declines, suggesting more ammonia solution favor the condensation reaction.

The percentages of  $D^i$  and  $T^i$  species  $(D_i, T_i)$  as well as the condensation degree  $(D_c)$  are quantitatively calculated according to the following equations [19, 27, 29]:

$$D_i(\%)$$

$$=\frac{A_{D^{i}}}{A_{D^{0}}+A_{D^{1}}+A_{D^{2}}+A_{T^{0}}+A_{T^{1}}+A_{T^{2}}+A_{T^{3}}}\times 100$$
(1)

 $T_i(\%)$ 

$$=\frac{A_{T^{i}}}{A_{D^{0}}+A_{D^{1}}+A_{D^{2}}+A_{T^{0}}+A_{T^{1}}+A_{T^{2}}+A_{T^{3}}}\times 100$$
(2)

$$D_{c}(\%) = \left[\frac{D_{1} + 2D_{2}}{2} + \frac{T_{1} + 2T_{2} + 3T_{3}}{3}\right] \times 100$$
(3)

**Table 2** The area ratios of the bands at 2,750–3,140 cm<sup>-1</sup> (C–H) and 3,140–3,720 cm<sup>-1</sup> (O–H) to the peak at 1,640 cm<sup>-1</sup> (C = C)

Samples	A <sub>2750-3140</sub> /A <sub>1640</sub>	A <sub>3140-3720</sub> /A <sub>1640</sub>	Samples	A <sub>2750-3140</sub> /A <sub>1640</sub>	A <sub>3140-3720</sub> /A <sub>1640</sub>
PT46-N	14.8	1.8	PT46-1.5	7.9	15.2
PT46-0.25	12.2	6.1	PT46-2	7.3	16.2
PT46-0.5	10.1	11.0	РТ46-Н	12.2	16.1
PT46	8.0	15.6	PT46-A	7.9	14.0

Sample name	Percenta	Percentage of silicon-oxo species, %							The remained active
	$\overline{D_0}$	$D_1$	$D_2$	T <sub>0</sub>	$T_1$	T <sub>2</sub>	T <sub>3</sub>		group (mol) <sup>a</sup>
PT91	20.2	60.2	17.6	0	1.9	0.0	0.0	48.4	0.41
PT64	12.1	56.1	17.6	9.2	0.0	5.0	0.0	49.0	0.49
PT46	8.0	35.0	12.6	10.1	7.6	16.3	10.4	53.9	0.50
PT19	0	4.6	5.1	6.6	5.0	31.7	47.0	77.2	0.30
PT46-0.5	18.2	37.9	14.6	21.6	0.0	7.7	0.0	38.6	0.70
PT46-1.5	6.0	27.7	14.9	2.9	6.9	26.5	15.2	63.9	0.38

Table 3 The percentage of various silicon-oxo species and D<sub>c</sub> of the polysiloxane oligomer

<sup>a</sup> The molar amount of -Si-OH, -Si-OC<sub>2</sub>H<sub>5</sub>, and -Si-OCH<sub>3</sub> in 100 g of as-obtained polysiloxane oligomer solution

where  $A_{D}^{i}$  and  $A_{T}^{i}$  are the peak areas of the D<sup>i</sup> and T<sup>i</sup> species, respectively. The results are summarized in Table 3. As we know,  $D^2$  and  $T^2$  species constitute the linear structure, and T<sup>3</sup> species form branch/network structure. Thus, it can be inferred from these data that PT91, PT64, and PT46-0.5 are composed of linear polysiloxane oligomer with low molecular weight (for example, dimer and trimer) while PT46, PT19 and PT46-1.5 are the mixture of linear and branch/network oligomers with relatively high molecular weight. Besides the polysiloxane oligomer, however, monomers (hydrolyzed or un-hydrolyzed) exists in all the as-obtained polysiloxane oligomer solutions, as indicated by  $D_0$  and  $T_0$ . Table 3 also shows that the D<sub>c</sub> steadily increases with increasing molar ratio of MPDS/MTES, agreeing with the FTIR results as shown in Fig. 1. Higher D<sub>c</sub> was also manifested at higher dosage of ammonia solution. Contrarily, the amount of the remained active groups (-Si-OH, -Si-OC<sub>2</sub>H<sub>5</sub>, -Si-OCH<sub>3</sub>) in the unit mass of polysiloxane oligomer solution displays inverse trends with molar ratio of MPDS/MTES (except for PT91) and ammonia solution dosage. These active groups will further contribute to the cross-linking in the drying step of polysiloxane coatings.

#### 3.2 Preparation and structure of polysiloxane coatings

Figure 4 shows the FTIR spectra of the dried coatings prepared with various molar ratios of MPDS/MTES. Similar to the FTIR spectra of polysiloxane oligomers, the absorption peaks at  $1,720 \text{ cm}^{-1}$  due to C = O and  $1,640 \text{ cm}^{-1}$  due to C = C clearly demonstrate the various fractions of methacryloxypropyl groups in the coatings. The small peak at 2,836 cm<sup>-1</sup> due to  $-\text{SiOCH}_3$  disappears in the FTIR spectrum of PT91 coatings, indicating the further hydrolysis of polysiloxane oligomer during drying step. Big change appears in the absorption band of -OH at a wavenumber of  $3,140-3,720 \text{ cm}^{-1}$ . Compared to the spectra of oligomers, the intensity of the absorption band greatly decreases for all coatings, demonstrating the further



Fig. 4 The FTIR spectra of polysiloxane coatings prepared at different molar ratios of MPDS/MTES

condensation of the silanol groups of polysiloxane oligomers. The remained weak peak at this band may be resulted from the low quantities of the residual free silanol groups and the amino group of APS. In addition, a new peak at the wavenumber of 1,570 cm<sup>-1</sup> occurs for most of the spectra. This peak is assigned to the bending vibration of  $-NH_2$ group. When the amount of MPDS increases, the peak weakens even disappears for PT91 coatings, which is owed to the aza-Michael reaction between  $-NH_2$  group and C = C bond [30]. Deducing from the intensity of the new peak at 1,570 cm<sup>-1</sup>, the weak band at 3,140–3,720 cm<sup>-1</sup> much possibly comes from the residual free silanol groups for PT91 and PT64 coatings and from  $-NH_2$  groups for PT19 and PT28 coatings.

FTIR analysis was also carried out for the coatings fabricated from the polysiloxane oligomers of PT46-0.25, PT46-0.5, PT46-1.5, PT46-2, PT46-H, and PT46-A. In comparison with the FTIR spectra of PT46, these coatings display a stronger peak at 3,140–3,720 cm<sup>-1</sup>,suggesting that the condensation degree is relatively lower for the



Fig. 5 The FTIR spectra of polysiloxane coatings prepared with different amounts of APS

coatings. Nevertheless, no obvious difference of the other peaks can be distinguished.

Figure 5 shows the FTIR spectra of polysiloxane coatings prepared with different APS contents. The peak at  $1,570 \text{ cm}^{-1}$  due to  $-\text{NH}_2$  declines with decreasing APS dosage and even disappears for PT46-10% coatings, which further demonstrates the occurrence of aza-Michael reaction between  $-\text{NH}_2$  group and C = C group in the coatings. In addition, the intensity band at  $3,140-3,720 \text{ cm}^{-1}$  remarkably increases as the amount of APS decreases, indicating that lower APS amount will lead to lower condensation degree of polysiloxane coatings.

Figure 6 displays the <sup>29</sup>Si CP MAS NMR spectra of PT91, PT64, PT46 and PT19 coatings. It can be found that



Fig. 6 The solid-state <sup>29</sup>Si CP MAS NMR spectra of the dried polysiloxane coatings prepared with different molar ratios of MPDS/ MTES

the dried polysiloxane coatings are mainly composed of  $D^2$  (21.2 ppm) and  $T^3$  (66.6 ppm) structures. Whatever,  $D^2$  structure dominates in the MPDS-rich coatings (PT91 and PT64) and  $T^3$  structure in the MTES-rich coatings (PT46 and PT19). Little quantities of  $D^1$  (14.2 ppm) or  $T^2$  (57.8 ppm) structures are observed for the coatings prepared with high amount of MPDS or MTES. This fact indicates that some Si–OR/Si–OH groups are still remained in the cured polysiloxane films. The incomplete condensation is caused by the immobility of the function groups at solid state.

#### 3.3 Macro-mechanical properties

The Koenig hardness and impact resistance of polysiloxane coatings are summarized in Table 4. Clearly, higher pendulum hardness of the coating can be obtained at higher MTES content, because of the higher condensation degree and higher fraction of inorganic silicon-oxo component in the coatings. To our surprise, the impact resistance of the coatings steadily increases with increasing MTES content, despite of the reduced organic component in the coatings. This indicates that the impact resistance depends on the cross-linking degree rather than on the fraction of the flexible organic component (i.e. methacryloxypropyl group) in the coatings. However, when the polysiloxane oligomer was merely pre-hydrolyzed from MTES, the polysiloxane coating (PT010) severely cracked and exfoliated from the substrate after ambient-curing.

Among the coatings prepared with various contents of aqueous ammonia solution, PT46 and PT46-1.5 possess higher Koenig hardness and better impact resistance while PT46-2 has slightly weaker mechanical properties. PT46-N and PT46-0.25 have the lowest Koenig hardness and the worst impact resistance. Additionally, PT19-N coating has similar excellent impact resistance (50 cm kg) to PT19 coating but much lower Koenig hardness. Comparing PT46-H, PT46-A with PT46 coatings, it is found that the Koenig hardness of polysiloxane coatings is less influenced by the catalytic condition, but obviously poor impact resistance was exhibited at high ammonia concentration. Consequently, a proper pre-hydrolysis process of MPDS/ MTES is rather important to ameliorate the mechanical properties of polysiloxane coatings. In addition, Table 4 shows that more APS in the coatings can efficiently improve the mechanical properties due to the enhanced cross-linking degree.

## 3.4 Nanoindentation tests

Figure 7 shows the typical loading-hold-unloading curves of the polysiloxane coatings prepared with various molar

**Table 4** The macro-mechanical properties of polysiloxane coatings

Run	Coating thickness (µm)	Koenig hardness (s)	Impact resistance (cm kg)	Run	Coating thickness (µm)	Koenig hardness (s)	Impact resistance (cm kg)
PT91	26	80	11	PT19-N	16	93	50
PT82	25	81	15	PT46-0.25	22	55	20
PT64	24	90	21	PT46-0.5	20	104	27
PT55	24	102	27	PT46-1.5	23	111	33
PT46	20	110	31	PT46-2	23	99	30
PT28	19	134	42	РТ46-Н	22	98	27
PT19	15	151	50	PT46-A	21	104	18
PT010	15	Cracking		PT46-10%	17	100	22
PT46-N	22	63	15	PT46-20%	21	104	25



Fig. 7 The loading-hold-unloading curves of polysiloxane coatings prepared with different MPDS/MTES ratios

ratios of MPDS/MTES. On loading, the force increases with increasing depth. The curve steadily shifts upwards with increasing MTES content, indicating that the composites' resistance to indentation gradually increases. Creep behavior is observed for all coatings during a period of holding time. Interestingly, the deformation almost completely recovers after unloading for all coatings, indicating the high elasticity of the polysiloxane coatings. The microhardness (H) and elastic modulus (E) are also presented in the figure. Both of them notably increases with increasing MTES content, which is consistent with the macro-mechanical properties as discussed above. This result further confirms that low molar ratio of MPDS/ MTES is benefit for creating hard and tough polysiloxane coatings.

Indentation load-depth curves of the coatings with various contents of ammonia solution (samples PT46-N, PT46-0.5, PT46, PT46-1.5 and PT46-2) are displayed in Fig. 8. Similarly, all coatings exhibit excellent elasticity. The microhardness and elastic modulus correspondingly



Fig. 8 The loading-hold-unloading curves of polysiloxane coatings prepared using different dosages of aqueous ammonia solution

increase from 70 to 204 MPa and 0.29 to 0.65 GPa when the mass of aqueous ammonia solution changes from 0 to 1.5 g in the pro-hydrolysis step. Further increase of the ammonia solution to 2.0 g causes slight deterioration of the hardness and elastic modulus. This trend is completely the same as that of macro-mechanical properties, and can be well explained by the evolution of the structure of polysiloxane oligomers as revealed by the FTIR and <sup>29</sup>Si NMR spectra. That is, the higher the cross-linking degree of the polysiloxane oligomer is, the higher the microhardness and elastic modulus of the polysiloxane coatings are.

The load-depth curves of polysiloxane coatings prepared at various catalytic conditions or different APS dosages are shown in Fig. 9. The highest microhardness and elastic modulus are obtained for PT46 coating while relatively low microhardness and elastic modulus were acquired for PT46-H and PT46-A coatings. It is well known that the hydrolysis and condensation of alkoxysilanes are equilibrium reactions. The acid catalyst is



Fig. 9 The loading-hold-unloading curves of polysiloxane coatings prepared at different catalytic conditions and APS dosages

more effective for hydrolysis than condensation, resulting in more unreacted Si-OH groups. However, the alkali catalyst is effective for both hydrolysis and condensation. Higher condensation degree of polysiloxane oligomer and hence denser coatings are reached under alkaline condition in contrast to acidic condition, which is confirmed from FTIR analysis. As for the coating prepared using the concentrated ammonia solution, higher condensation degree tends to form network polysiloxane cluster rather than linear polysiloxane chain. Part of the remaining -SiOH/-SiOR groups are encapsulated in the interior of the cluster and are difficult to condense with APS, leading to a reduced condensation degree of the coating. Figure 9 also shows that the microhardness and elastic modulus of the polysiloxane coatings remarkably increase as the APS dosage increases. Because APS is a kind of trialkoxysilane, it tends to form network structures during a sol-gel process [22]. More APS implies higher cross-linking degree of the dried coatings and thus superior mechanical properties.

150 0 120 Residual depth Coating thickness -4000 **Depth** (nm) Penetration depth -8000 60 ritical load -12000 30 Load -16000 0.1 0.2 0.3 0.4 0.5 Scratch distance (mm)

Fig. 10 Typical profiles of penetration depth and residual depth of PT46-1.5 coating

#### 3.5 Nanoscratch tests

Nanoscratch tests were employed to evaluate the scratch resistance of the polysiloxane coatings. Figure 10 shows the penetration depth and residual depth profiles for PT46-1.5 coating in a typical scratch test with a maximum load of 150 mN. An obvious jump of penetration depth profile is observed at a load of 96 mN. By comparing the appearance of the film along scratch track, it is found that 96 mN is just the critical load for film failure. Below the critical load, the polysiloxane coating was only pressed without damage. When the applied load was high enough, the buckling and chipping of the coating took place off, being responsible for the drastic fluctuation of the curve. The highest depth can be attained during scratch tests, which can be regarded as the coating thickness.

Table 5 summarizes the critical loads and coating thicknesses of the polysiloxane coatings. As the molar ratio of MPDS/MTES increases, the critical load considerably increases and then decreases. The highest critical load of 129 mN is obtained for PT28 coating. PT19 coating has a relatively low critical load although it has the highest

Table 5 Critical load and thickness of polysiloxane coatings

Sample name	Thickness <sup>a</sup> (μm)	Critical load (mN)	Sample name	Thickness <sup>a</sup> (μm)	Critical load (mN)
PT91	30(26)	$39 \pm 5$	PT46-1.5	20(23)	$96 \pm 4$
PT64	27(24)	$55 \pm 2$	PT46-2.0	19(23)	$78 \pm 2$
PT46	19(20)	$78 \pm 6$	PT46-N	21(22)	$68 \pm 9$
PT28	18(19)	$129 \pm 2$	РТ46-Н	24(22)	$76\pm7$
PT19	15(15)	$91 \pm 2$	PT46-A	20(21)	$71 \pm 6$
PT46-0.25	26(22)	$57 \pm 3$	PT46-10%	17(17)	$46 \pm 3$
PT46-0.5	19(20)	$60 \pm 1$	PT46-20%	22(21)	$72 \pm 15$

The data in the bracket are gotten from a thickness gauge

hardness (Koenig hardness and microhardness) and impact resistance. This may be caused by the poorer adhesive strength of PT19 coating with substrate because PT19 coating has lower fraction of methacryloxypropyl groups relative to PT28 coating. Table 5 also shows that the critical load for film failure increases with the increasing amount of aqueous ammonia solution and, however, reduces at excessive amount of aqueous ammonia solution (PT46-2). Higher critical load was obtained for the coating using diluted ammonia solution (PT46) in comparison with the coating using diluted hydrochloric acid (PT46-H) or concentrated ammonia solution (PT46-A). Additionally, the higher the APS dosage is, the better the scratch resistance of the coating is. These critical load results well match the trends of macro-mechanical properties and microhardness. It seems that the critical load is mainly dependent on the mechanical strength of the coating.

Scratch tests at a low maximum load of 40 mN were also carried out to evaluate the reflow capability of polysiloxane coatings. Film failure was not observed in all scratch tests. The penetration depth as well as the residual depth is typically presented in Fig. 11 for the coatings prepared with different molar ratios of MPDS/MTES. It can be seen that the penetration depth become shallower with lower molar ratio of MPDS/MTES. This result well matches the microhardness of the coatings. Interestingly, except for PT64 at the load beyond around 18 mN (namely, penetration depth of around 5,800 nm), very low residual depth exists for all other scratch tracks, indicating the high reflow capability of polysiloxane coatings. This implies that the polysiloxane coatings have excellent scratch resistance.

The depth profiles of the coatings prepared with different dosages of ammonia solution are plotted in Fig. 12. The penetration depth increases and then decreases at the same load as the dosage of ammonia solution increases, being



Fig. 11 Profiles of penetration depth and residual depth of polysiloxane coatings prepared with different MPDS/MTES ratios in scratch tests using a maximum load of 40 mN



Fig. 12 Profiles of penetration depth and residual depth of polysiloxane coatings prepared with different water dosages in scratch tests using a maximum load of 40 mN

similar to the variation of microhardness. Low residual depth is exhibited for all coatings except PT46-N, further demonstrating the high reflow capability of the coatings. PT46-N has shallower penetration depth than PT46-0.25 and PT46-0.5, but displays an poorer reflow capability in comparison with other coatings, especially at the load beyond 21 mN (corresponding to the penetration depth of 4.4  $\mu$ m).

The scratch tests using a maximum load of 40 mN were also conducted for the coatings prepared at various catalytic conditions (PT46-H and PT46-A) or various APS dosages (PT46-10%, PT46-20%). It was found that the penetration depth varied in a similar way to the critical load. High reflow capability after scratch was observed for all these coatings.

#### 4 Conclusions

Thick polysiloxane coatings with total silicon-oxo backbone were prepared by co-hydrolysis/condensation of MPDS and MTES in the presence of deficient water dosage and subsequently ambient-curing using APS as the catalyst and curing agent. The pro-hydrolyzed product is a solution of linear or a mixture of linear, branch, and network polysiloxane oligomers, depending on the composition of precursors, the dosage of ammonia solution as well as the catalytic condition. Higher condensation degree of polysiloxane oligomers and thus of the cured polysiloxane coatings were obtained at lower molar ratio of MPDS/ MTES. However, at the same molar ratio of MPDS/MTES, appropriate condensation degree of polysiloxane oligomer using a proper pro-hydrolysis process avails the formation of dense polysiloxane coatings. In addition, more APS can efficiently enhance the condensation degree of polysiloxane coatings in the range of the APS dosage involved.

Both the hardness (Koenig hardness and microhardness) and impact resistance are dependent on the condensation degree of polysiloxane coatings rather than on the composition of the coatings. Generally, the higher the hardness of the coatings is, the higher the critical load for film failure is. A little deviation of the critical load was observed for the coatings prepared with low molar ratio of MPDS/ MTES, presumably due to the poor adhesive force with substrate. High elasticity was exhibited in both nanoindentation and scratch tests, indicating the excellent scratch resistance of the ambient-cured polysiloxane coatings. Particularly, those polysiloxane coatings prepared at low molar ratio of MPDS/MTES (i.e. 2:8-1:9) are extremely prominent in mechanical properties, and should have great potentials as the scratch- and weather-resistant topcoats for vehicles, steel constructions, outdoor equipments and so on.

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