Transparent Polysilicone Coatings as Protecting Films for Gold Commemorative Coins

Yan Liu, Guo-Ping Yan, Hong-Wei Che, Xiao-Yan Wang, Qing-Zhong Guo

School of Material Science and Engineering, Wuhan Institute of Technology, Wuhan 430074, China

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ABSTRACT: Novel transparent organic silicone resin coatings were successfully prepared through the reaction between the alkoxy groups of methyltrimethoxy-silane (MTMS) and γ-aminopropyltriethoxysilane (APTES) and hydroxyl groups of hydroxyl terminated silicone oil (HTSO). The influences of different monomer feed mass ratio on the coating properties were investigated via measuring the hydrophobicity and hardness of coating films. The coating films were characterized with IR, UV, TG, scanning electron microscope (SEM), and automatic contact angle meter. Some properties of coating films, such as adhesion, impact resistance, and wear-resistance, were also evaluated. The results indicated that these coating films formed on the surfaces of gold commemorative coins possessed some good properties including high hydrophobicity, high water contact angles, high light transmittance, good heat-resistance, adhesion, hardness, and weatherability, etc. Moreover, the uniform, clear, transparent, and dense coating films did not cover the symphony surface patterns or affect the metallic luster. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1156–1160, 2011

Key words: organic silicone resin coating; hydrophobicity; gold commemorative coins

INTRODUCTION

When gold commemorative coins were exposed in the air during daily use and maintenance, some compounds including oxides, sulfides, carbonates, sulfites, and other substances occurred on the coin surface due to chemical and physical reactions with oxygen, water vapor, carbon dioxide, sulfur dioxide as well as some other organic matters. Subsequently, these compounds came to vulnerate the surface to form some little spots and dark veins and then were further abrased easily to cause a large area of injury because of their relative low hardness and poor abrasion resistance. Finally, these processes can destroy the structures of the fine design and gloss of gold commemorative coins.[1]

In recent years, a coating film has attracted great interest for use to protect the surface of gold commemorative coins and make them anti-oxidation and wear-resistant. Some film materials, such as acrylic paints, epoxy coatings, and polyurethane coatings, have been used for surface protection of metals and plastics. However, there are some disadvantages on these coatings to limit their wide applications, such as, (1) to react with the substrate or even change the color, (2) to be difficult and unsafe, (3) to be inconvenient and likely to have the phenomenon of sagging, or (4) to be difficult to remove from the substrate and not satisfied with abrasion-resistance and weatherability.

At present, the scratch resistant and transparent organic silicone coatings are one of the best choices to protect gold commemorative coins. These transparent polysilicone resins can adhere to the substrate tightly and form a layer of highly cross-linked, hard, wear-resistant, and water-resistant film after curing. And that the film can enhance light transmittance, improve abrasion-resistance and ultraviolet radiation resistant, prevent oxidation discoloration, and maintain

Correspondence to: G.-P. Yan (guopyan2006@163.com).

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the gloss. Therefore, these coatings have been used to protect various metals and organic polymer substrates such as polymethylmetacrylate, polycarbonate, polyethyleneterephthalate, and so on.[2–6]

It is very common to prepare the abrasion-resistance organic silicone coating by hydrolysis of organic siloxane with acids as the catalysts. Most of hard coatings were usually obtained by sol-gel process. However, the technology with an acid as a catalyst has a severe corrosion of equipment, cockamamie reprocess and other shortcomings.[7]

In this works, novel transparent polysilicone coatings were prepared through the reaction between the alkoxy groups of methyltrimethoxy-silane (MTMS) and γ-aminopropyltriethoxysilane (APTES) and hydroxyl groups of hydroxyl terminated silicone oil (HTSO) with an acid resin as the catalyst. The coating films were made from these coating solutions on iron fleet, glass fleet, and gold commemorative coin substrates. After curing, the properties of coating films were also evaluated.

EXPERIMENTAL

Instruments and reagents

MTMS and APTES were purchased from the Hubei Wuhan University Silicone New Material Co. (Wuhan, China). HTSO (1230B, hydroxyl value 8%, viscosity 20 ~ 30 mm^2/s) was purchased from the Guangzhou FuYuanGui Technology Co. (Guangzhou, China). The gold commemorative coins were the products of the Shenzhen Guobao Mint (Shenzhen, China).

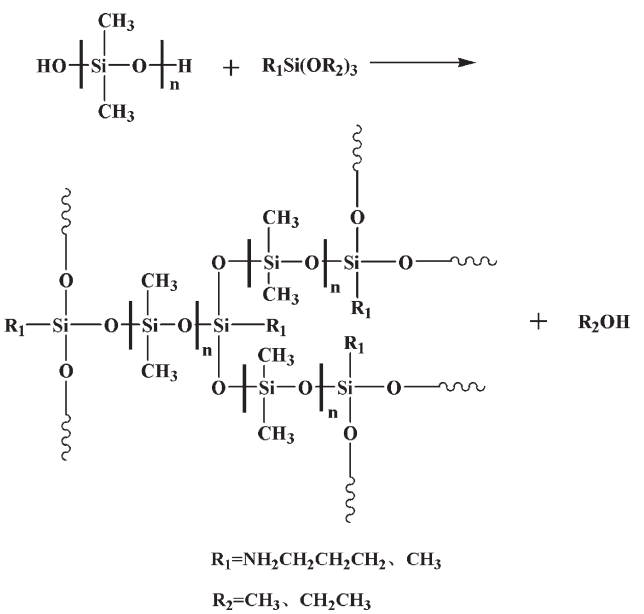

Figure 1 Preparation of polysilicone coatings.

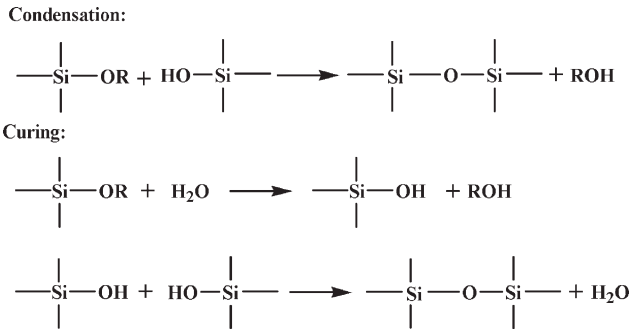

Figure 2 Formation of coating films on the substrate.

Preparation

The transparent polysilicone coatings were prepared from proper amounts of MTMS, APTES, and HTSO according to the literature.[8] The coatings were carried out on the substrates including iron fleet, glass fleet, and gold commemorative coin, and then cured at room temperature to form the films.

Characterization

The coating films were characterized with a Nicolet of 10 fourier transform-infrared (FTIR) spectrophotometer (Thermo Fisher Scientific, Madison, WI), a UV-Vis spectrophotometer (UV-2800 series, Unico, Shanghai, China), an automatic contact angle meter (SL200A/B/D Series, Solon Tech., Shanghai, China), a TG STA409-pC-uxx (Netzsch, Co. Selb/Bavaria, Germany), and a JSM-5510LV SEM (JEOL, Tokyo, Japan). Adhesion was measured by a QF2-II film adhesion test instrument (Tianjin Jingke Material Test Factory, Tianjin, China). Standard flaw cycle lines was made in the film to the substrate, and adhesion was evaluated depending on the degree of the film integrity. Impact resistance was measured with a QCJ type film impact tester (Shenzhen Litengda Machinery and Equipment Co. Ltd., Shenzhen, China). The wear-resistance of the films was represented by the hardness of the films, which was measured by a pencil hardness tester (Tianjin Central Asia Paint Test Equipment Co. Ltd., Tianjin, China).

Statistical analysis

All results were expressed as mean differences and were tested for significance by a t test, $P < 0.05$ being considered a significant difference.

RESULTS AND DISCUSSION

Preparation and characterization

The alkoxy groups Si—OR of MTMS and APTES and hydroxyl groups of HTSO were easily conjugated to prepare an appropriate degree of cross-linked

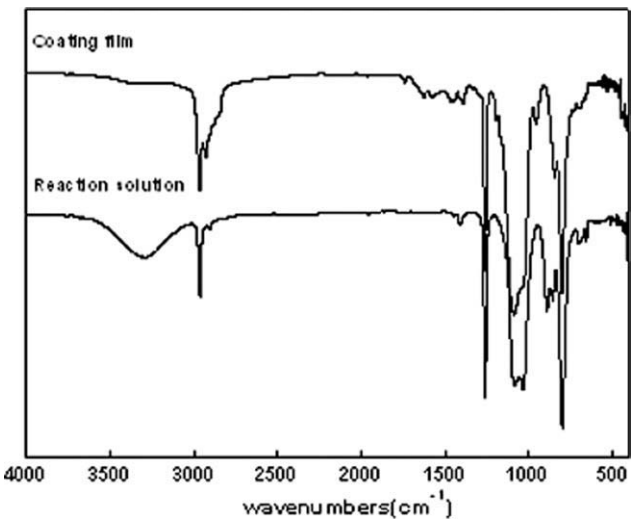

Figure 3 FTIR spectra of the coating film and reaction solution.

silicone resins and further form the coating films on the substrates at room temperature (Figs. 1 and 2). During the curing process, Si—OH was occurred through the reaction between the residual alkoxy groups and water vapor in the air. Subsequently, the condensation reactions between Si—OH and Si—OR or Si—OH took place and further improved the crosslinked degree of silicone resins to form a hard film.

The FTIR spectra of the coating films and coating solution with raw materials before reaction both showed a characteristic strong and sharp peak in 1260 cm^{-1} together with a small peak in 1416 cm^{-1}, which represents the absorption peaks of Si—CH_3 groups (Fig. 3). The single Si—O—Si stretching vibration peaks in 1088 and 1032 cm^{-1} and Si—O—Si symmetric stretching peak in 860 cm^{-1}, and the Si—C stretching vibration peak in 800 cm^{-1}, Si—OR absorption peak in 956 cm^{-1} all existed in the FTIR spectra of the coating films and reaction solution. The FTIR spectra of coating solution showed a characteristic broad peak in 3400–3200 cm^{-1} and a single peak in 896 cm^{-1}, which represented the absorption peaks of Si—O—H groups. However, the peaks of Si—O—H disappeared in the FTIR spectra of coating films after reaction. These results indicated that the dealcoholization occurred between HTSO and siloxane. Moreover, the Si—OR absorption peaks in the FTIR spectra of coating films demonstrated that there were still partly active groups for further curing reaction.

Hydrophobicity of coating films

The coating films possessed the good hydrophobicity, and their water contact angles were all higher than 90° (Figs. 4 and 5) because all Si—OR groups

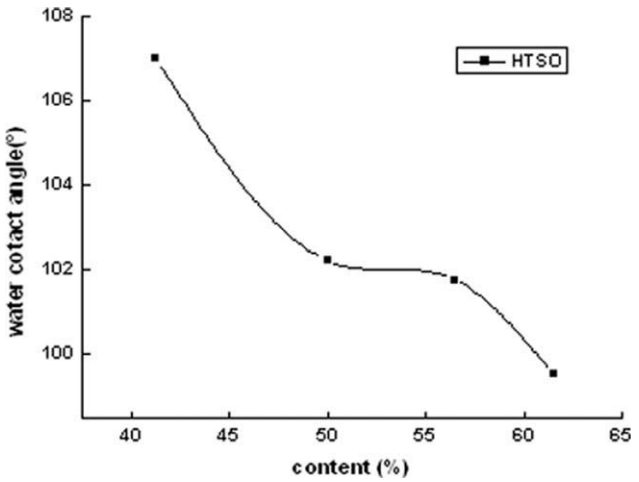

Figure 4 Influences of monomer feed mass ratio on water contact angles.

reacted with vapor in the air to generate Si—OH and then Si—OH condensed and cross-linked. Therefore, the hydrophobic end groups such as Si—O—Si and Si—CH_3 made the film significantly hydrophobic. Moreover, the water contact angles of coating films decreased and their hydrophobicity reduced when the monomer feed mass ratio of HTSO, MTMS, and APTES increased, respectively. The excess Si—OH groups in the structures of HTSO made the hydrophobicity reduced corresponding to the decline of contact angles. The excess Si—OR groups of MTMS and APTES turned into Si—OH in the drying process, and thus made the films amphiphilic enhanced.

Hardness of thin films

The coating films with different hardness ranging from HB to 4H were prepared by different monomer feed mass ratio of HTSO, MTMS, and APTES (Table I). The harness of coating films decreased with the

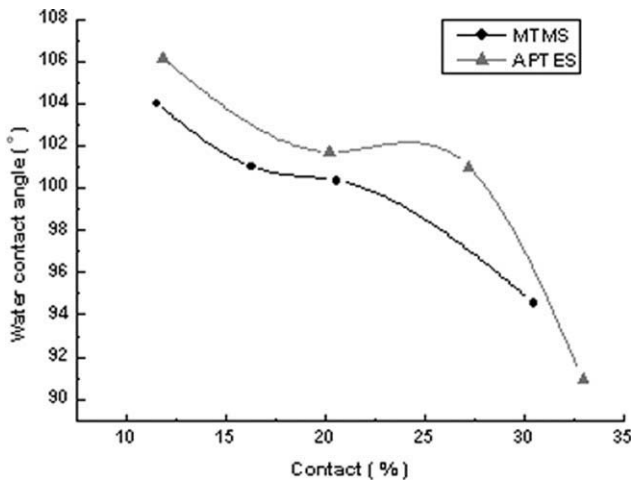

Figure 5 Influences of monomer feed mass ratio on water contact angles.

TABLE I
Pencil Hardness of Films on Substrates with Various Raw Material Contents

HTSO (%)	Hardness	MTMS (%)	Hardness	ATPES (%)	Hardness
41	4H	12	2H	12	2H
50	3H	16	3H	20	2H
57	3H	21	3H	27	3H
62	HB	30	3H	33	3H

increase of HTSO because the molecular structure of HTSO was flexible and more HTSO used caused the film more flexible. The harness of coating films enhanced slightly with the increase of MTMS and ATPES due to the increase of cross-linked degree.

Micrographs of coating films on gold commemorative coins

The SEM photographs of gold commemorative coins without and with coating films were tested by light scattering and refraction on the candy stripes of the gold commemorative coins (Fig. 6). Some depredations were observed on the uncoated coin. The candy stripes were flat on the surface of gold commemorative coins with coating films. The protective films formed on the surface of coins after painting were uniform, clear, and dense. Moreover, it did not cover the symphony surface patterns and affect the metallic luster on the surface of gold commemorative coins.

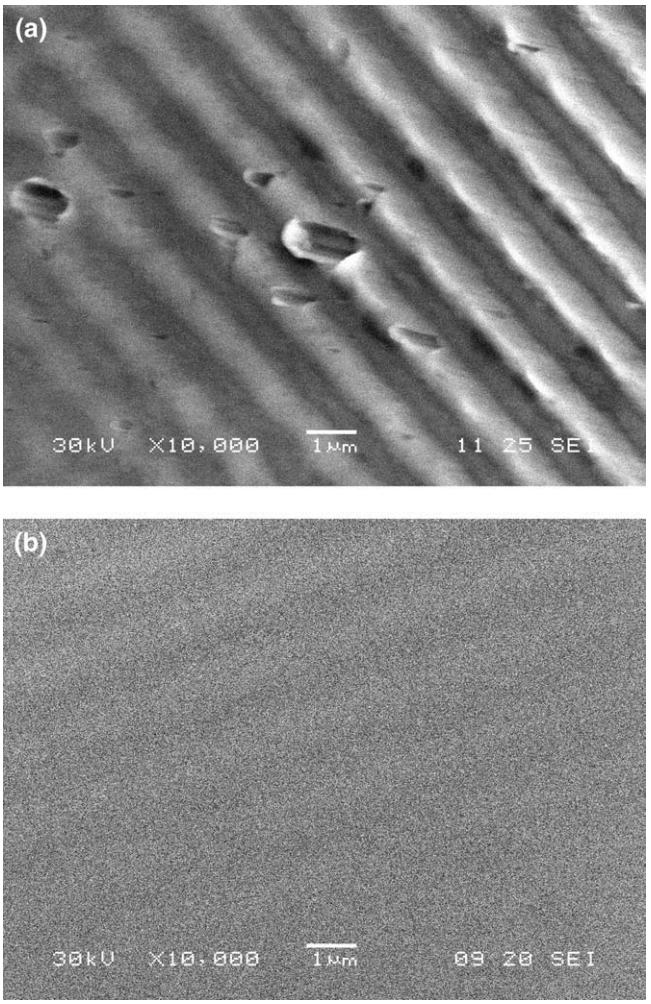

Figure 6 SEM photographs of gold coins without (a) and with coating films (b).

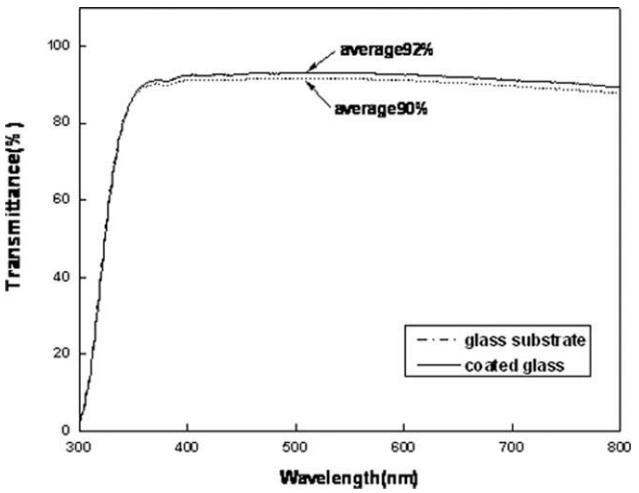

Figure 7 Light transmittance of glass sheets without and with coating films.

Light transmittance

The glass sheets were used as the substrates instead of the coins since the gold commemorative coin could not be taken to do the test of light transmittance directly due to its non-transparent. The transmittance spectra of glass sheets without and with coating films were shown in Figure 7. In general, the change of refractive index (RI) influences on the light transmittance. The classical optics theory suggests that the coating film causes spectroscopic effect

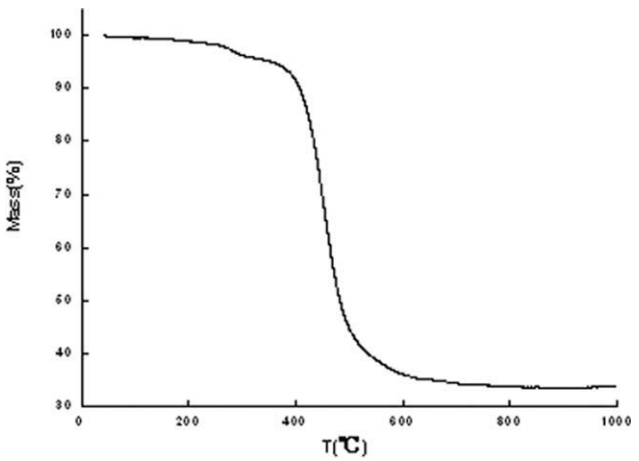

Figure 8 TG of polysilicone coating films.

TABLE II
Properties of Polysilicone Coating Films

Test item	Test method	Test result
Appearance of coating solution	Visual observation	Light yellow transparent liquid
Appearance of the film	Visual observation	Bright and smooth
Thickness of the film/μm	Chinese national standards (GB) 1764-79	25
Pencil hardness	Chinese national recommended standards (GB/T) 6739-1996	HB-4H
Adhesion/scale	GB 1720-79	1
Impact resistance/cm	Falling ball test GB/T 1732-93	50
Water resistance	GB/T 1733-93, 20 days	Unchanged
Salt resistance	3%NaCl, 10 days	Unchanged
Acid resistance	5%H_2SO_4, 24 h	Unchanged
Alkali resistance	5%NaOH, 24 h	Unchanged

on the substrate when the RI of coating film is higher than that of the substrate. On the contrary, it causes antireflective effect on the substrate. Compared with that of uncoated glass sheets (about 90%), the light transmittance (about 92%) of glass sheets with coating films increased over (2%) in all visible light range (400–780 nm) probably due to lower RI. It is also considered that the high transparent coating films reduced light scattering.

Analysis of TG

In the TG analysis of polysilicone coating films (Fig. 8), there was a slight weight loss in the beginning of heating. This was maybe caused by the volatilizing of small organic solvent molecules and excess small siloxane molecules from coating films. The little bigger weight loss at about 260°C presumptively resulted from the further elimination reaction of Si—OH groups. During the period of temperature increase between 350°C and 600°C, there was a great weight loss which probably caused by the decomposition of polysilicone. The results demonstrated that the polysilicone coating films had a good heat-resistance.

Other properties of the coating films

Some other properties of polysilicone coating films were also tested and these result data were shown in Table II. The coating films possessed some good properties, such as adhesion and weatherability.

CONCLUSIONS

Novel polysilicone coatings were prepared successfully to protect the surfaces of gold commemorative coins. These coating films obtained possessed some good properties including high hydrophobicity, high water contact angles, high light transmittance, good heat-resistance, adhesion, hardness, and weatherability. Moreover, the protective films formed on the surface of coins were uniform, clear, transparent, and dense and did not cover the symphony surface patterns or affect the metallic luster.

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