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PREPARATION, CHARACTERIZATION AND APPLICATION OF ABRASION-RESISTANT HYBRID COATINGS ON POLYCARBONATE TRANSPARENCIES

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Abstract

Abrasion-resistant hybrid coatings for polycarbonate transparencies were synthesized using methyltrimethoxysilane (MTMS) as organic phase, tetraethoxysilane (TEOS) as the inorganic network percursor, and methacyloxypropyltrimethoxysilane（MEMO）as a silane coupling reagent between the organic and inorganic phase via sol-gel method. In comparison, the neat organic silicone coating material derived only from MTMS and the hybrid coatings from MTMS and TEOS without MEMO were also prepared. These coatings were coated onto the surface of PC substrates and thermally cured. The optical properties, hardness, adhesion and abrasion resistance of coated PC substrates were investigated compared with those of pure PC substrate. Fourier transform infrared spectra of the coatings before and after being cured demonstrated that the cross-linked structure of Si–O–Si was formed due to the hydrolysis-condensation reactions of alkoxy silane. The optical test results showed that coated PC substrates possessed higher transmittance and lower haze than pure PC substrate. The hardness data demonstrated that PC substrates coated with the hybrid coatings (MTMS/TEOS/MEMO coatings) owned the greatest hardness and optimal adhesion. The adhesion tests revealed that the hybrid coatings MTMS/TEOS/MEMO possess better adhesion than the MTMS/TEOS or pure resin from MTMS and demonstrated that the incorporation of MEMO with MTMS and TEOS can significantly improve the adhesion between the coatings and PC because the MEMO acts as a coupling agent between the organic and inorganic moieties in the final coating network. In an abrasion test, PC substrate with MTMS/TEOS/MEMO coatings showed some grooves and wear tracks without any spallation or delamination, and there were a decrease of only 0.8-1.2% in transmittance and an increase of only 3.26-4.98% in haze after 500 wear cycles. Whereas pure PC substrate and substrates with MTMS and MTMS/TEOS (mole ratio is 1.5:1) coatings exhibited a decrease of 3.8%, 3.6% and 2.7% in transmittance and an increase of 42.27%, 16.32% and 10.69% in haze, respectively. Finally MTMS/TEOS/MEMO coatings were applied to aircraft polycarbonate canopy. This kind of hybrid coating can meet the demand of aircraft transparencies and has shown a good prospect.

1 Introduction

Polycarbonate (PC) has been used as an aircraft canopy material for years due to its high impact resistance, low density, high thermal stability and excellent optical properties. [1-2] However, polycarbonate exhibits low hardness and poor abrasion resistance. Various functional protective coatings, such as inorganic coatings, organic coatings and inorganic-organic hybrid coatings, have been explored to apply directly to the manufactured transparencies. But few coatings can meet the demand of aircraft transparencies.

Traditionally, abrasion-resistant coatings for polycarbonate substrates include inorganic coatings and organic coating. Inorganic protective coatings prepared by chemical vapor deposition (CVD), plasma enhanced chemical vapor deposition (PECVD) and sputtering possess excellent abrasion resistance.[3-6] But these methods require complicated equipment and the adhesion of coatings on substrates are poor due to the different thermal expansion coefficients. Pure organic coatings such as polyurethane, silicone and acrylic coatings show better adhesion to PC substrates. Several kinds of polyurethane coatings have applied to aircraft transparencies. But abrasion resistance of organic coatings needs to be improved.

In the last few years, the inorganic-organic hybrid coatings prepared by sol-gel method have been extensively studied, [7-15] since they can combine the toughness and flexibility of organic component with the hardness and thermal stability of inorganic component. Silicon, aluminum, titanium, and zirconium metal alkoxides have been used as inorganic precursors. And a variety of oligomers, as well as low molecular weight organics, have been used as organic components. Now, many studies have focused on the preparation of abrasion-resistant coatings deriving from one or two kinds of siloxanes. In this paper, the coatings based on MTMS, MTMS/TEOS, and MTMS/TEOS/MEMO were synthesized by a sol-gel process and their optical properties, hardness and adhesion and abrasion resistance were investigated. Finally the coating having the optimal properties was applied to aircraft polycarbonate canopy

2 Experimental

2.1 Materials

MTMS and MEMO were purchased from Alfa Aesar Company. TEOS was supplied by Xilong Chemical Co. Ltd., China. Dibutyltin dilaurate was purchased from Beijing Finechem. Isopropyl alcohol (IPA) was supplied by Sinopharm Chemical Reagent Co. Ltd., China. Hydrochloric acid (HCl) and deionized water were provided by Beijing Institute of Aeronautical Materials. Bisphenol A polycarbonate substrates were commercial, untreated, uncoated, transparent sheets (3 mm thick, LEXAN®9030, from Sabic Corp.). The polycarbonate substrates were cut into a size of 100mm×100mm×3mm, annealed at 120 ℃ for 3h，and cleaned with deionized water. Then the traces of grease on the substrates were removed by vapor of a hexane/isopropyl alcohol azeotrope. Finally, the polycarbonate substrates were treated with a primer solution of 0.5wt% MEMO in isopropyl alcohol and dried at room temperature for a few minutes before applying the coating. The purpose of such treatment is to activate the surface for better wetting and achieve good adhesion between the coating and the substrate.

2.2 Preparation of coating solutions

First, one or more kinds of siloxanes were weighed accurately and dissolved in H_2O, followed by adding IPA, HCl solution and dibutyltin dilaurate and stirring at 50 ℃. The pH value of the mixed solutions was controlled at 2 ~ 4 to ensure hydrolysis reactions. The MTMS sol, MTMS/TEOS sols and MTMS/TEOS/MEMO sols were prepared by the pre-hydrolysis and condensation of MTMS, MTMS and TEOS, MTMS, TEOS and MEMO, respectively.

2.3 Preparation of coatings on PC substrates

The pre-treated PC substrates (100mm×100mm×3mm) were placed at a 45° angle and then the coating sols were curtain coated on the PC substrates. The coated PC substrates were then placed in a 50 ℃ oven where the coatings were then allowed to dry for about 40 minutes. The coatings were then allowed to cure at 120 ℃ for approximately 3 hours. The PC substrate coated with MTMS coating was expressed as M. The molar ratios of MTMS to TEOS in MTMS/TEOS coatings are 1.0, 1.5, 2.0, 3.0 and 4.0, so the PC substrates coated with MTMS/TEOS coatings were expressed as MT-1.0, MT-1.5, MT-2.0, MT-3.0 and MT-4.0, respectively. Similarly, the molar ratios of MTMS to TEOS to MEMO in MTMS/TEOS/MEMO coatings are 1.5:1.0:0.5, 1.5:1.0:1.0 and 1.5:1.0:1.5, therefore the substrates coated with MTMS/TEOS/MEMO coatings were expressed as MTM-0.5, MTM-1.0 and MTM-1.5, respectively.

2.4 Characterization

The chemical structures of coatings before and after being cured were characterized by a Magna-IRTM 750 FTIR instrument. The optical properties including transmittance and haze were tested according to ASTM D1003 on a WGT-S Transmittance/Haze tester. The pencil hardness of these coatings was characterized by a commercial pencil hardness tester conforming to ASTM D3360-00, where a vertical force of 7.5±0.1 N was applied at 45° angle to the horizontal film surface as the pencil was moved over the coated surface. The cross-cut test was applied according to ISO 2409 to obtain a qualitative impression of the adhesion of coatings on PC substrates. The abrasion resistance of coatings on PC substrates was determined by an abrasion tester (see Fig. 1) according to ASTM F 735-11. The size of specimen is 100 mm × 100 mm. The quartz sands were used as the abradant. Before testing, sufficient abradant of different sizes was used to fill the sand cradle 13 mm above the sample surface. Then, the specimen was rubbed by these quartz sands in a circular manner and then tested by a Transmission/Haze Tester. The increase in haze or the decrease in transmittance as a result of the abrading can be used to represent the abrasion resistance of coatings. The morphologies of coating surfaces after being worn were observed using a CS3400 scanning electron microscopy (SEM) measurement.

Table 1: The quartz sands used in the abrasion test

Sieve Designation		Mean % on Sieve	Cululative %
No.	mm		Retained, Mean
4	4.75	0	0
6	3.35	7.6	7.6
7	2.8	22.3	29.9
8	2.36	45.1	75.0
10	1.00	21.9	96.9
12	1.70	2.6	99.5
Pan	…	0.5	100.0

3 Results and discussion

3.1 The properties of MTMS and MTMS/TEOS coatings

3.1.1 The chemical structure

The FTIR spectrum of MTMS coating before being cured is presented in Fig. 1 (a). The broad absorption band appearing at 3200 ~ 3600 cm^{-1} indicates the presence of –OH group. The bending vibration of –OH can be observed at 1636 cm^{-1}. The peak at around 901 cm^{-1} is due to the stretching vibration of Si–O in silanols (Si–OH).[16-18]This result suggests that the hydrolysis reaction of Si–O–CH_3 in MTMS has occurred. The characteristic absorption peak at about 1102 cm^{-1} is assigned to the stretching vibration of Si–O–Si, which indicates the condensation reaction between silanols has occurred. The peak at 2973 cm^{-1} corresponds to the C–H stretching vibration of Si–O–CH_3 group and the in-plane bending of C–H vibration can be observed at 1275 cm^{-1}. The peak at 766 cm^{-1} is assigned to the Si–C stretching vibration.[19-20] Fig. 1 (b) shows the FTIR spectra of MTMS/TEOS coatings before being cured with various molar ratios. Though the feed molar ratios of MTMS to TEOS were in the range of 1.0 to 4.0, the characteristic absorption peaks for MTMS/TEOS coatings before being cured are similar.

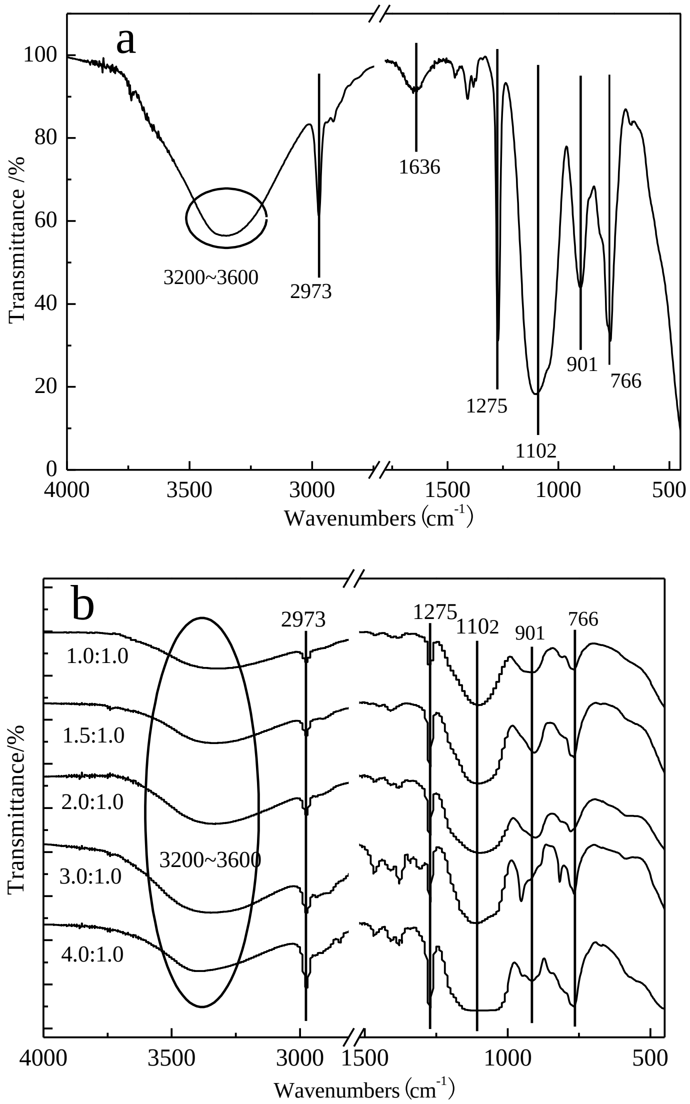


Fig. 10. The FTIR spectra of the coatings before being cured: (a) MTMS coating; (b) MTMS/TEOS coatings

The FTIR spectra of MTMS/TEOS coatings (molar ratio is 1.5:1) before and after being cured are presented in Fig. 2. As shown in Fig. 2, the broad absorption bands appearing at 3200 ~ 3600 cm^{-1} which indicating the presence of –OH group can be observed in both cured and uncured MTMS/TEOS coatings. The difference is that the peaks shift from 3344 cm^{-1} for uncured coating toward 3433 cm^{-1} for cured coating, moreover, the peak area at 3200 ~ 3600 cm^{-1} is larger for uncured coating than that for cured coating. The peak area at around 901 cm^{-1} assigning to the stretching vibration of Si–O in silanols also decreased after being cured. This suggests that the amounts of silanols decrease during the curing process, and the degree of condensation reactions between silanols or silanos and Si–OC_nH_{2n+1} (n=1 or 2) increase as a result of being cured. The characteristic absorption peaks at about 1102 cm-1 assigning to the stretching vibration of Si–O–Si can also be observed in both cured and uncured coatings, which indicates the condensation reaction between silanols or silanos and Si–OC_nH_{2n+1} (n=1 or 2) has occurred before being cured.

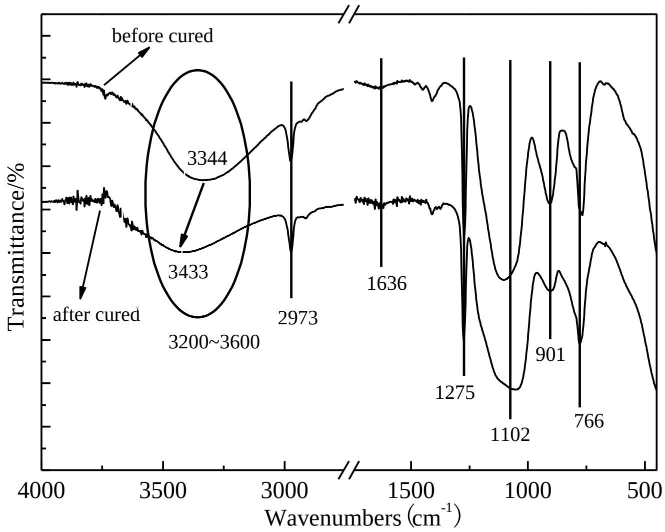


Fig. 2. The FTIR spectra of cured and uncured MTMS/TEOS coatings (molar ratio is 1.5:1)

3.1.2 The optical properties

The optical properties including transmittance and haze of coated and uncoated PC substrates are expressed in Table 2. As indicated in Table 2, the transmittance and haze of uncoated PC substrate are 87.9% and 0.27%, respectively. After being coated with the coatings (MTMS or MTMS/TEOS coatings), the PC substrates show a slight increase in transmittance, and their haze are all less than 1%, except for MT-1.0. This can be explained in the following way. The transmittance of coated substrates will increase if the refractive index of the coating is less than that of the substrate.[21] In this paper, the refractive index of these coatings are in the range of 1.41 ~ 1.43 while the index of PC substrate is 1.58. Therefore the coated PC substrates have a slight increase in transmittance. As shown in Table 2, when the molar ratio of MTMS to TEOS is less than 1.5, PC substrate with MTMS/TEOS coating (MT-1.0) becomes opaque with transmittance of 85.4% and haze of 56.68%. The poor optical properties of MT-1.0 may be affected by the high content of TEOS.

In the series of MTMS/TEOS coatings, TEOS was used as the inorganic network precursor. With the increase of TEOS content, nano silicon dioxide particles will be generated via self-condensation between TEOS. And agglomerates may also occur during the drying and curing processes. The miscibility between the organic and inorganic components becomes poor, resulting in low transmittance and high haze.

Table 2: The optical performance of coated and uncoated PC substrates

Properties	Uncoated PC	M	MT-1.0	MT-1.5	MT-2.0	MT-3.0	MT-4.0
T /%	87.9	90.9	85.4	90.4	89	90.4	90.8
H /%	0.27	0.15	56.68	0.34	0.60	0.87	0.26

Note: T represents transmittance; H represents haze

3.1.3 The hardness and adhesion

The hardness and adhesion of MTMS and MTMS/TEOS coatings on PC substrates were evaluated and presented in Table 3. As shown in Table 3, the hardness of PC substrates increases obviously after being coated. For MTMS/TEOS coatings, with the increase of TEOS content, the hardness increases, the adhesion first are almost unchanged, then decreases. According to the previous statements, with the increase of TEOS content, the percentage of inorganic network structure increases, which causes an increase in hardness. When the molar ratio of TEOS is greater than 50%, high concentration nano silicon dioxide will cause the coatings to delaminate, thus causes a decrease in adhesion.

Table 3: The hardness and adhesion of MTMS and MTMS/TEOS coatings on PC substrates

Properties	Uncoated PC	M	MT-1.0	MT-1.5	MT-2.0	MT-3.0	MT-4.0
Hardness	6B	B	HB	H	HB	B	B
Adhesion grade	-	2	4	2	2	2	2

3.1.4 The abrasion resistance

The optical properties of PC substrates with coatings after being worn were used to characterize their abrasion resistance. The transmittance and haze as function of wear cycles of coated and uncoated PC substrates are expressed in Fig. 3 (a) and (b), respectively.

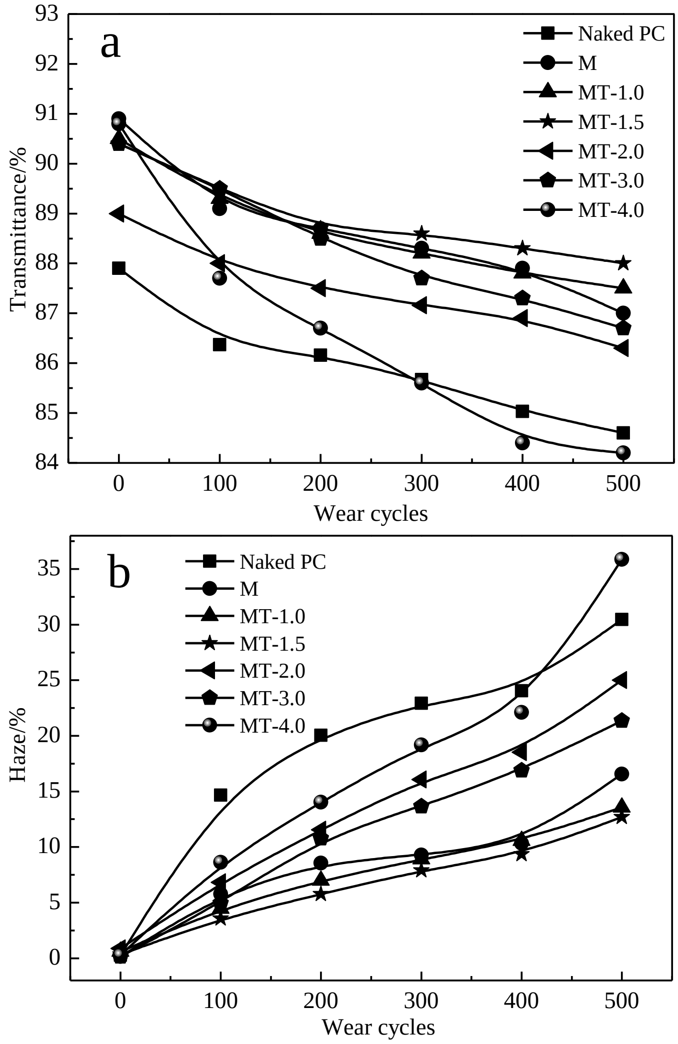


Fig. 3. The optical performance of coated and uncoated PC substrates after being worn: (a) transmittance; (b) haze

As indicated in Fig. 3 (a), with the increase of wear cycles, the transmittance of coated and uncoated PC substrates decreases slightly except for MT-1.0. MT-1.5 possesses the highest transmittance after 200 wear cycles. PC substrates with coatings exhibit higher transmittance than uncoated PC substrates. As shown in Fig. 3 (b), with the increase of wear cycles, the haze of coated and uncoated PC substrates increases obviously. Uncoated PC substrate possesses higher haze than coated substrates and MT-1.5 exhibits the lowest haze. After 500 wear cycles, the increase in haze for uncoated PC substrate is the biggest, from

0.27% to 30.46%. And the increase in haze for MT-1.5 is the smallest, from 0.34% to 12.69%. Based on these experimental results, the abrasion resistance of PC substrates can be obviously improved by the coatings. And the abrasion resistance of PC substrates with MTMS/TEOS coatings is higher than that of substrates with MTMS coatings. Meanwhile, the optimum molar ratio of MTMS/TEOS is 1.5.

According to the previous context, MT-1.5 possessed the best abrasion resistance and excellent hardness and adhesion. Hence in this section, the molar ratio of MTMS to TEOS is kept at 1.5 to 1.0. MEMO as a silane coupling reagent was added to the MTMS/TEOS system to synthesize the abrasion-resistant coatings. And their chemical structures, optical properties, hardness, adhesion and abrasion resistance were investigated.

3.2 The properties of MTMS/TEOS/MEMO coatings

3.2.1 The chemical structure

The FTIR spectra of MTMS/TEOS/MEMO coatings before and after being cured are expressed in Fig. 4 (a, b, c). The broad absorption bands assigning to the stretching vibration of –OH appear at 3200 ~ 3600 cm^{-1} and the bending vibration of –OH can also be observed at 1636 cm^{-1}. Before being cured, the peaks of MTM-0.5, MTM-1.0 and MTM-1.5 in the broad band are 3368 cm^{-1}, 3398 cm^{-1} and 3400 cm^{-1}, respectively. After being cured, the peaks of MTM series shift toward 3435 cm^{-1}, 3449 cm^{-1} and 3458 cm^{-1}, respectively. The peaks at 901 cm^{-1} are due to the stretching vibration of Si–O in silanols and the peak area at 901 cm^{-1} after being cured become smaller than that before being cured. This suggests that the amounts of –OH group decrease during the curing process. The reason for this phenomenon is that during the curing process, the network structure of Si–O–Si is formed through self-condensation of Si–OH, resulting in the decrease of –OH group. And another reason can be attributed to the release of residual H_2O in the coatings. The characteristic absorption peak at 1728 cm^{-1} corresponds to the C=O stretching vibration in MEMO. The characteristic absorption peak at 1102 cm^{-1} is assigned to the stretching vibration of Si–O–Si.

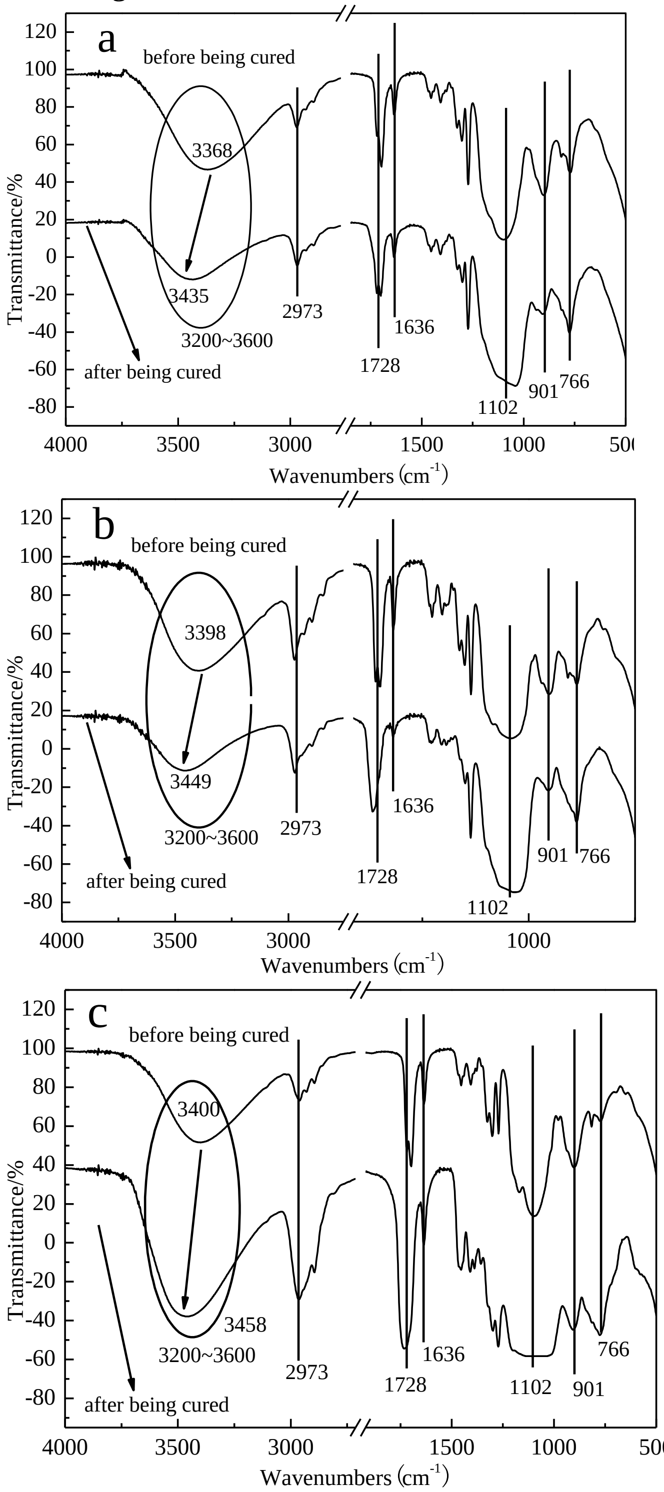


Fig. 4. The FTIR spectra of MTMS/TEOS/MEMO coatings: (a) MTM-0.5; (b) MTM-1.0; (c) MTM-1.5

3.2.2 The optical properties

The transmittance and haze of PC substrates coated with MTMS/TEOS/MEMO coatings are displayed in Table 4. The optical performance of uncoated PC substrate, M and MT-1.5 were added for comparison. As indicated in Table 4, comparing with M and MT-1.5, the transmittance of MTM series shows a slight decrease. However, the transmittance of MTM series is higher than uncoated PC substrate. And the haze of MTM series also decreases a little, indicating that the incorporation of MEMO can improve the optical properties.

Table 4: The optical performance of coated and uncoated PC substrates

properties	Uncoated PC	M	MT-1.5	MTM-0.5	MTM-1.0	MTM-1.5
T/%	87.9	90.9	90.4	90.0	90.0	89.8
H/%	0.27	0.15	0.34	0.21	0.14	0.10

Note: T represents transmittance; H represents haze

3.2.3 The hardness and adhesion

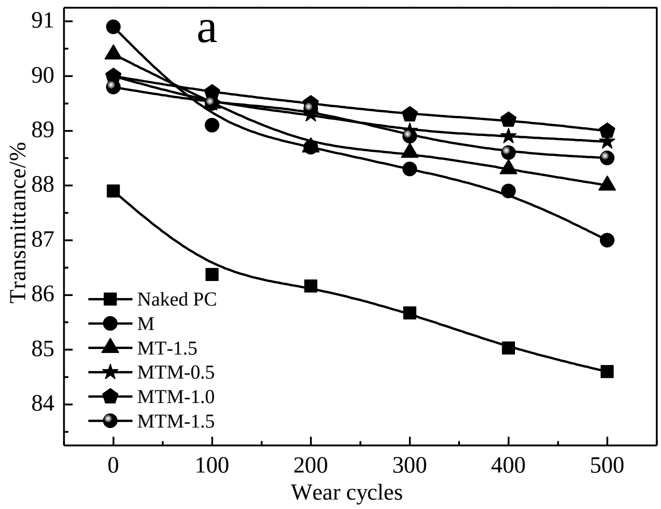
The hardness and adhesion of coated and uncoated PC substrates are presented in Table 5. As indicated in Table 5, comparing with uncoated PC substrate, M and MT-1.5, the hardness and adhesion of MTM series are obviously improved. The improvement of hardness and adhesion may be due to the addition of MEMO. MEMO acts as a silane coupling reagent between the organic and inorganic silicone. On the other hand, the silane coupling reagents (here means MEMO) can interact with silsesquioxane/silica materials through siloxane bonding formed by condensation of silanol groups. As a result, MEMO strengthens the bonding of the hybrid MTMS/TEOS/MEMO coatings and promotes the adhesion of the coatings on PC substrates.

Table 5: The hardness and adhesion of coated and uncoated PC substrates

Property	Uncoated PC	M	MT-1.5	MTM-0.5	MTM-1.0	MTM-1.5
Hardness	6B	HB	H	2H	2H	H
Adhesion grade	-	2	2	1	1	1

3.2.4The abrasion resistance

The transmittance and haze as function of wear cycles of MTM-0.5, MTM-1.0 and MTM-1.5 are indicated in Fig. 5 (a) and (b), respectively. Comparing with uncoated PC substrate, M and MT-1.5, the transmittance of MTM series is higher and the haze is lower after the same wear cycles (＞100). There is a decrease of 3.8% in transmittance for uncoated PC substrate, 3.6% for M and 2.7% for MT-1.5. And the decrease in transmittance for MTM-0.5, MTM-1.0 and MTM-1.5 are 1.0%, 0.8% and 1.2%, respectively. The increase in haze for uncoated PC substrate, M and MT-1.5 are 42.27%, 16.32% and 10.69%, respectively. And the increase in haze for MTM-0.5, MTM-1.0 and MTM-1.5 are 3.26%, 3.87% and 4.98%, respectively. The experiment results indicate that the addition of MEMO can effectively improve the abrasion resistance of coatings.



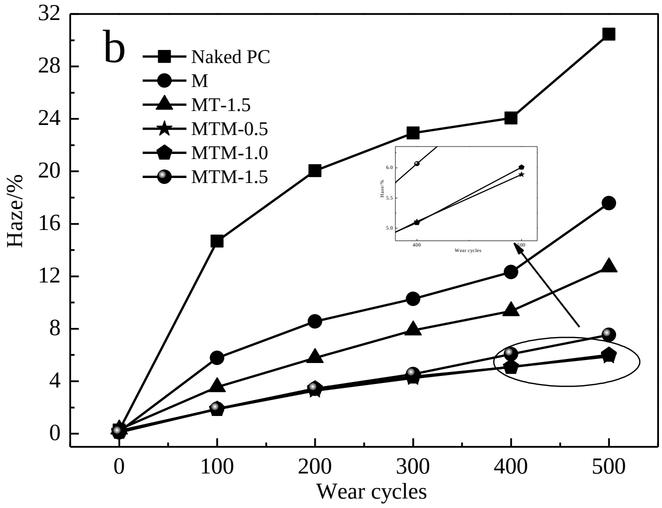


Fig. 5. The optical performance of coated and uncoated PC substrates after being worn: (a) transmittance; (b) haze

3.2.5 Morphological observations of M and MTM-1.0 before and after being worn

The obtained SEM images of M and MTM-1.0 before and after being worn are shown in Fig. 6 (a, b, c, d). Observed from the SEM images, the surface of MTM-1.0 before being worn is smooth and uniform without any agglomerates with enlargement of 500 times. And the surface of M before being worn is smooth with some agglomerates. As indicated in Fig. 6 (c), the surface of M becomes coarse and has obvious delamination, which is a typical surface fatigue. As shown in Fig. 6 (d), the grooves and wear tracks are visible on the surface of MTM-1.0, and there is no spallation or delamination. This result is in accord with the transmittance and haze after being worn. That is to say that the SEM images can also prove that MTM series have better abrasion resistance than other coatings.

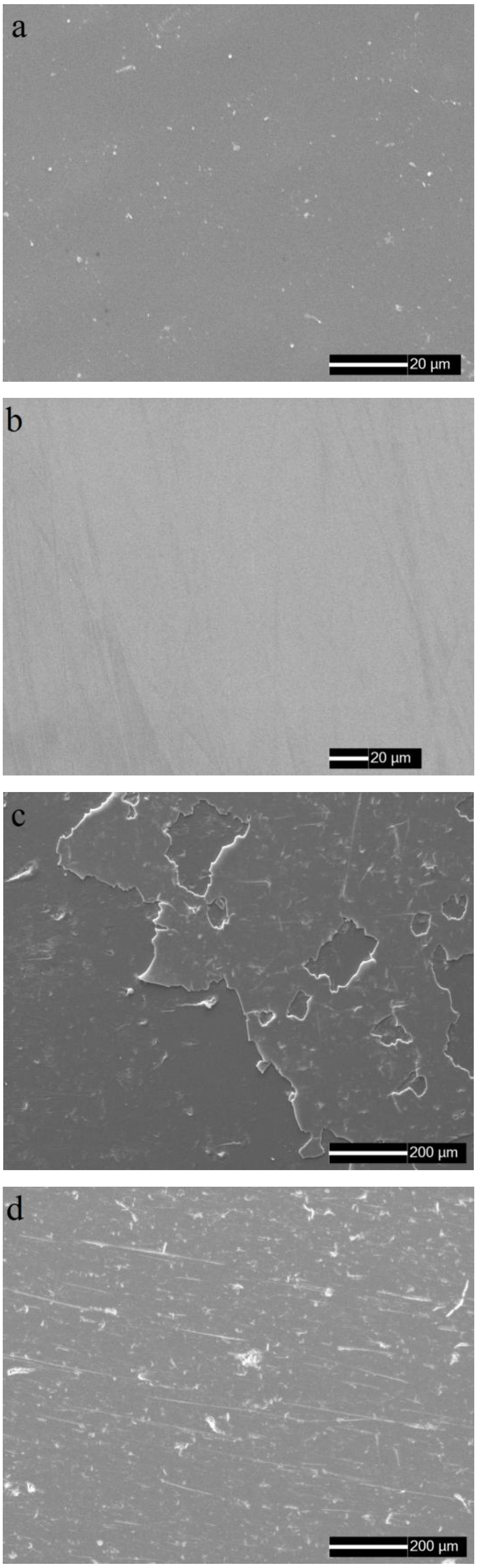


Fig. 6. SEM images of coated PC substrates: (a) M before being worn; (b) MTM-1.0 before being worn; (c) M after 500 wear cycles; (d) MTM-1.0 after 500 wear cycles

3.3 Application of MTMS/TEOS/MEMO coatings

The study above reveals that PC coated with MTMS/TEOS/MEMO coatings exhibit better hardness, adhesion, and abrasion resistance than pure PC or PC coated with MTMS or MTMS/TEOS coatings. Then MTMS/TEOS/MEMO coating was applied to aircraft polycarbonate canopy as shown in Fig. 7. This kind of hybrid coating can meet the demand of aircraft transparencies and has shown a good prospect. Another application is polycarbonate automotive glazing. This plastic glazing coated with MTMS/TEOS/MEMO coating has been adopted by some car windows as shown in Fig. 8.

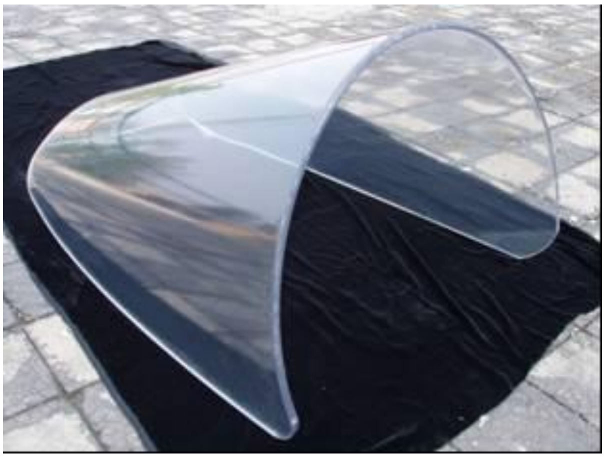


Fig. 7. Polycarbonate aircraft windshield coated with MTMS/TEOS/MEMO coating

Fig. 8. Polycarbonate automotive windows coated with MTMS/TEOS/MEMO coating

4 Conclusions

The abrasion-resistant coatings based on MTMS, MTMS/TEOS and MTMS/TEOS/MEMO were successfully prepared via sol-gel method. The properties of MTMS/TEOS/MEMO coatings were investigated compared with MTMS, MTMS/TEOS coatings. Some conclusions are summarized in the following.

(1) The cross-linked structure of Si–O–Si can be formed through the hydrolysis–condensation reactions of alkoxy groups before and during the curing process.

(2) The optical tests indicated that coated PC substrates exhibited higher transmittance and lower haze than uncoated PC substrate (except for MT-1.0).

(3) The hardness of coated PC substrates was improved and the adhesion of hybrid coatings on PC substrates was excellent.

(4) Comparing with uncoated PC substrates, the abrasion resistance of coated PC substrates was obviously improved. For the coatings, MTMS/TEOS/MEMO series possessed the optimum abrasion resistance than MTMS/TEOS series and MTMS coating. After 500 wear cycles, there was an increase of only 3.26-4.98% in haze and a decrease of only 0.8 ~ 1.2% in transmittance for MTMS/TEOS/MEMO coatings.

(5) MTMS/TEOS/MEMO coatings have exhibit the best properties and have shown a good prospect in aircraft transparencies.

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