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溶胶–凝胶法制备 SiO_2/有机硅复合涂料

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摘 要：以正硅酸乙酯(tetraethoxysilane，TEOS)、甲基三乙氧基硅烷、二甲基二乙氧基硅烷和甲基丙烯酰氧基丙基三甲氧基硅烷为原料，采用溶胶–凝胶法在聚碳酸酯(polycarbonate，PC)表面上制备透明硬质的 SiO_2/有机硅复合涂膜。用红外光谱、紫外光谱，热重、X 射线衍射、表面扫描电镜、原子力显微镜和接触角测量仪等方法对产物进行了表征。结果表明：复合膜中形成了 Si—O—Si 网络结构；采用浸涂工艺，经 120 ℃热固化制备的涂膜厚度为 0.84 μm，表面平整，致密均质，对 PC 基材具有一定的增透作用(透光率提高了将近 5%)；复合膜对水的接触角随固化时间的延长而增大，在 120 ℃固化 3 h 后接触角为 93°；随着 TEOS 含量增加，复合膜的耐热性得到提高；当 SiO_2/有机硅复合树脂的 n(R)/n(Si)(一个硅原子上平均连结的有机基团数目)值选择 0.78，划格法测定的复合膜的铅笔硬度为 2 H，附着力为 0 级。

关键词：溶胶–凝胶法；硅树脂；复合；聚碳酸酯；硬质涂料
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Synthesis of SiO_2/Organosilicone Hybrid Coating *via* Sol–Gel Method

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Abstract: The transparent and hard SiO_2/organosilicone hybrid coatings were prepared on polycarbonate (PC) with tetraethoxysilane (TEOS), methyltriethoxysilane, dimethyldiethoxysilane and 3-(methacryloxypropyl)-trimethoxysilane as the main raw materials by the sol–gel method. The structure and properties of the hybrid coating were characterized by Fourier transformed infrared, ultraviolet-visible spectroscopy, thermogravimetric analysis, X–ray diffraction, scanning electron microscopy, atomic mechanics microscope, contact angle measuring instrument, and hardness tester *etc*. It is found that the basic structure of the hybrid coating is Si—O—Si. After heat-cured at 120 ℃, the thickness of the hybrid coating is 0.84 μm by dipping-withdrawing manner. The hybrid coating is smooth, homogenous and densified, and can improve the transparency of PC (transmittance is increased by nearly 5%). The contact angle of the hybrid coating to the water increases with the increase of curing time. The contact angle is 93° after heat-cured at 120 ℃ for 3 h. The hybrid coating has excellent thermal stability, which increases gradually with the increase of TEOS content. When the mole ratio of R (organic groups) and Si in SiO_2/organosilicone hybrid resin is 0.78, the adhesion strength of hybrid coating on PC sheet is 0 class (cross-cut tape test), and it reaches a pencil scratch hardness of 2H.

Key words: sol–gel method; organosilicone; hybrid; polycarbonate; hard coating

Many transparent polymeric materials such as polycarbonate (PC), polymethyl methacrylate (PMMA) have excellent optical clarity, lower density, impact resistance, and easy processing than inorganic glasses, and can be widely utilized as windows in aircraft, buildings, and optical lens.[1] However, because of the poor wear resistance, polymeric windows or optical devices often quickly lose transparency during daily use and maintenance. To solve above problems, abrasion-resistant coatings have been developed over the past few years by plasma polymerization, photopolymerization and silicone modification. Silicone modification can be characterized by the formation of hard coatings on a polymer substrate through hydrolysis and condensation (sol–gel reactions) of alkoxy-

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silanes.[2–5]

In this wok, inorganic–organic hybrid silicone solutions were prepared by sol–gel method of a metal alkoxide along with organic siloxane. Hybrid coatings were made from these solutions on PC substrate. After curing, the structure and properties of the hybrid coating were characterized, and the relationships between coating compositions and coating properties were investigated.

1 Experimental procedures

1.1 Preparation of hybrid coating solution

Raw materials used in the test include tetraethoxysilane (TEOS) purchased from Guangzhou Chemical Reagent Factory; and methyltriethoxysilane (MTES), dimethyldiethoxysilane (DMDES) and 3-(methacryloxypropyl)-trimethoxysilane (TMSPM) supplied by Blue Star New Chemical Material CO.; ethanol (EtOH) and isopropanol (IPA) obtained from Sinopharm Chemical Reagent Co.; ethylene glycol monomethyl ether (EM) purchased from Tianjin kemiou Chemical Reagent Development Center; acetic acid supplied by Tianjin Damao Chemical Reagent Factory. All the above raw materials were used as received without further purification. Polycarbonate (PC) sheets (Lexan®, GE) with a thickness of 1.5 mm were purchased from Bomaner Guangzhou Trading Co., and were cleaned with isopropanol before use.

The chemical composition for preparing the hybrid coating solution is schematically shown in Table1. Proper amounts in mass of TEOS, MTES, DMDES and compound solvent (m_{EtOH}:m_{IPA}:m_{EM} = 3:4:1) were poured into flask and stirred slowly at room temperature. To control the acidity of the solution and increase hydrolysis reaction rate, a mixture of acid catalyst and water were dropped slowly into the alkoxide solution within thirty minutes. After the mixture has been stirred for several hours, TMSPM was added to the it to continue the reaction. Then the coating solution was kept aging for several days at room temperature. Finally, appropriate amount of coating agents was added, partially condensed and hydrolyzed coating solution with 20% in mass of solid content was obtained.

Table 1 Chemical composition of hybrid coating solution

Sample No.	n(R)/n(Si)	Mass fraction/%			
		TEOS	MTES	DMTES	TMSPM
S1	0.95	24	43	14	19
S2	0.78	38	34	10	18
S3	0.60	52	24	7	17

n(R)/n(Si) is the mole ratio of R (organic groups) and Si in SiO_2/organosilicone hybrid resin.

1.2 Coating preparation and heat curing

The coating was carried out on the PC substrates in dipping-withdrawing manner at the atmospheric temperature. The relative humidity was 40%–50%, the lifting velocity of dipping PC sheet was 25 cm/min. The obtained coating was pre-heated at 60 and 80 ℃ respectively for 10 min for the removal of any residual solvent and condensation by-products, and then heat-treated extensively at 120 ℃ for 2 h. The hard and transparent hybrid coating was obtained after natural cooling.

1.3 Characterization

Fourier transformed infrared (FTIR) spectroscopic measurements in KBr pellets were performed on a spectrometer (Model NICOLET 380, Thermo Electron Co., USA). Thermogravimetric analyses (TGA) were conducted on a thermogravimeter (Model STA449C, Netzsch Co., Germany) in nitrogen atmosphere, at a heating rate of 10 ℃/min from 30 to 800 ℃.

The transmittance of the hybrid coatings was measured using a ultraviolet–visible (UV–VIS) spectroscopy scanner (Model U–3010, Hitachi Co., Japan).

Refractive index was also evaluated using a spectroscopic ellipsometry (Model SC600HG, Shanghai Xianke Instrument Co., China).

The contact angle of the coating surface was conducted on a JC2000C1 contact angle measuring instrument (Model JC2000C1, Shanghai Zhongchen Technical Apparatus Co., China) at 25 ℃.

Morphology and thickness of the hybrid coatings were observed using a field-emission type scanning electron microscope (FESEM, Model 1530 VP, LEO, Germany). Surface roughness was measured with an atomic force microscope (AFM, Model CSPM–2003, Guangzhou Being Nano-Instrumetns, Co., China) by tapping mode.

The crystal phases of curing hybrid materials were analyzed by Automatic X-ray diffractometry (XRD, Model D/max–IIIA, Rigaku Co., Japan).

The pencil hardness of coatings was measured with a pencil hardness tester (Model QHQ, Tianjin Yonglida Materials Testing Machine Co., China) according to the GB/T 6739–1996, national standards of China. To obtain a qualitative impression of the adhesion between the coating and the substrate, the cross-cut tape test was applied in accordance with GB/T 9286–1998, national standards of China. Adhesion can be classified from 0, which represents a good adhesion, to 5, which represents a poor adhesion.

2 Results and discussion

2.1 FTIR Spectroscopy

FTIR spectra of different n(R)/n(Si) of hybrid coating in the full mid-infrared spectral region are given in Fig.1. The H-bonded Si–OH group is recognized by a broad band at around 3 400 cm^{-1} with the absorption band at 910 cm^{-1}. The band at 2 971 cm^{-1} is the ν-CH_2, and the strong peak at 1 727 cm^{-1} is the $\nu_{C=O}$. The Si–CH_3 group is easily recognized by a sharp band at 1 275 cm^{-1} together with the absorption peak at 800 cm^{-1}. A very strong

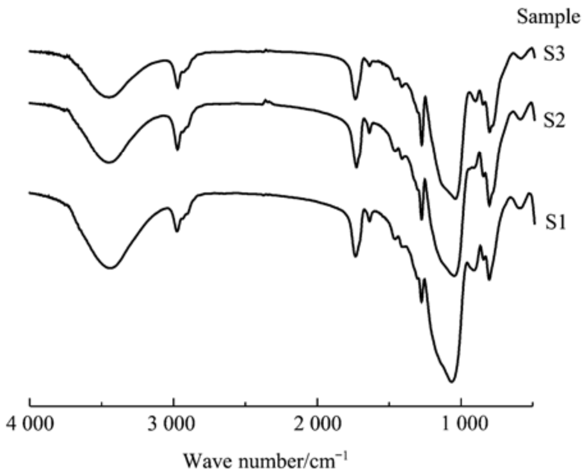

Fig.1　FTIR spectra of S1, S2 and S3 hybrid coatings

infrared band assigned to Si–O–Si band stretching vibration is observed in the region 1 134–1 030 cm^{-1}. There is also an characteristic absorption peak at 582 cm^{-1} assigned to cyclic siloxane. These peaks indicate that inorganic/organic hybrid coating formed by the hydrolysis-condensation reaction between TEOS and organic siloxane, whose base backbone is Si–O–Si network structure.[6] Moreover, the peak intensities of Si–O–Si stretching mode at about 1 134–1 030 cm^{-1} increase with the decrease of n(R)/n(Si) (that is the increase of TEOS), and characteristic peak intensity at 582 cm^{-1} decreases slightly, indicating that the hybrid coating has higher wear resistance.

2.2　Properties of heat-curing coating

As seen from Table 2, the pencil scratch hardness of PC improves from 2B to H–2H after coated with hybrid coatings, apart with a good adhesion of coating films to substrate. Incorporation of TEOS with the silane functionalized organics greatly improves the abrasive resistance, which increases with the increasing amount of inorganic network. This high abrasion resistance is attributed to the Si–O–Si backbone of the inorganic network, formed by condensation of the TEOS. When the n(R)/n(Si) is 0.78, the hardness of coated PC reaches 2 H, the adhesion of the coating film on substrate is classified to be 0 grade according to the cross-cut tape test.

Table 2　Hardness and adhesion of hybrid coating

Sample No.	Pencil hardness grade	Adhesion grade
S1	H	0
S2	2H	0
S3	2H	1

2.3　Thermal behavior

The TGA curves obtained in nitrogen atmosphere for hybrid coating materials with various n(R)/n(Si) are shown in Fig.2. The characteristic mass loss temperatures and residue at 800 ℃ are presented in Table 3. The TG material

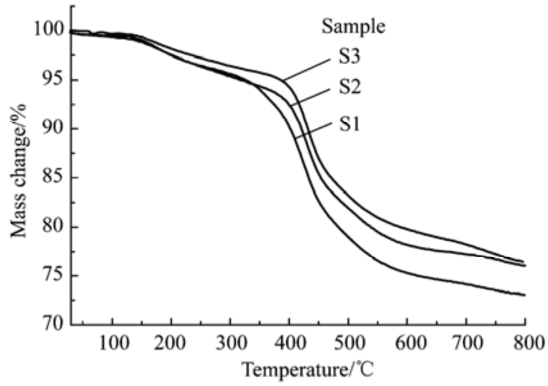

Fig.2　TGA curves of S1, S2 and S3 materials in N_2

was prepared by drying the coating solution at room temperature for one day and then heating at 40 ℃ for 2 h. As shown in Fig.2, the TGA curves of different n(R)/n(Si) values of hybrid materials are approximately similar. The mass loss below 150 ℃ are caused mainly by the evaporation of adsorbed water and organic solvents. The mass loss range from 150 to 375 ℃ relates to the dehydration reaction between Si–OH and Si–OH, and dealcohol reaction between Si–OH and Si–OR. The large mass loss range from 375 to 520 ℃ indicates the decomposition of the organic groups. After 600 ℃, TGA curve becomes flat.

As shown in Table 3, except the degradation onset temperature, the characteristic temperatures of hybrid coating are shifted to higher temperatures with the decrease of n(R)/n(Si). Furthermore, the degradation residue of the tested hybrid coating at 800 ℃ are rather high, 73.1% (S1), 76.0% (S2) and 76.4% (S3) of the initial mass respectively. The thermal stability of the hybrid coating is determined by the TEOS concentration, which is beneficial to form a crosslink in the solid residue. The crosslink reduces the flexibility of remaining polymers and retards further pyrolysis.[7–8]

Table 3　The TGA data of hybrid coating obtained in a nitrogen atmosphere

Sample No.	Onset of degradation*/℃	Temperature for 10% mass loss/℃	Temperature for 20% mass loss/℃	Residue in mass at 800 ℃/%
S1	151	402	484	73.1
S2	139	421	539	76.0
S3	163	431	588	76.4

* Temperature for 1% mass loss.

2.4　Light Transmittance

Figure 3 shows the total light transmittance in the range of visible light. In the case of coated PC sheet with hybrid coating (S2), light transmittance (about 93.6%) increases more than 4% in all visible light range (400–800 nm) compared with uncoated PC sheet (about 89%). In general, the change of refractive index (RI)

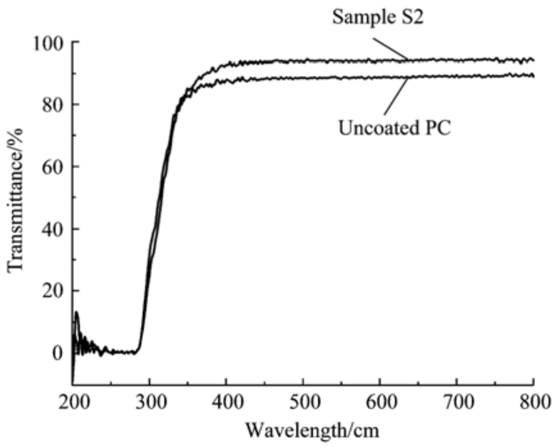

Fig.3　Light transmittance of PC sheets uncoated and coated with hybrid coating (S2) by dipping

influences on the light transmittance. The RI of PC sheet with 1.5 mm thickness is 1.584, and that of hybrid coating (S2) with 2.1 μm is 1.517 ($\lambda = 632.8$ nm). Higher light transmittance of hybrid coating is probably due to lower RI of hybrid coatings than that of the PC sheet. It is also considered that the hybrid coating reduces light reflection on the surface of the substrate.

2.5　Coating surface contact angle with water

Contact angle (θ) is one of the important parameters in judging the level of wetting ability of liquid to solid. The θ changes with curing time when the hybrid coating (S2) heat-curing at 120 ℃ are shown in Fig.4. As seen from Fig.4, the θ increases more quickly in the early stages of curing, and changes very little afterwards. The θ reaches to 93° after condensation at 120 ℃ for 180 min, more than the θ of PC surface (76°). This can be ascribed to coating surface containing more hydrophilic Si–OH groups, which makes the coating have a higher surface free energy, and results in the θ less than 90° in initial curing time. The Si–OH content decreases and the Si–O–Si content increases because of the condensation

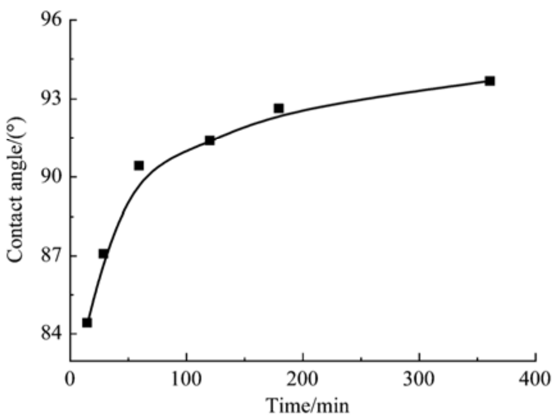

Fig.4　Relationship between the hybrid coating (S2) contact angle and curing time

reaction between the Si–OH during the condensation progress. Thus, the coating contains a large number of hydrophobic methyl, which tends to concentrate in the coating surface to reduce the surface free energy. Thereby the θ of coating surface is more than 90°, which leads to good anti-fog effect.[9]

2.6　Surface morphology and roughness

It is obvious that surface roughness affects abrasion resistance, light scattering and adhesion of coating.[10] Figure 5 shows AFM images of the hybrid coating (S2) comparable with uncoated PC sheet. The smooth surface with an unevenness of 0.82 nm is obtained in coated PC sheet with hybrid coating, while the unevenness of uncoated PC sheet is a rough surface larger than 6.58 nm.

Figure 6 shows a cross-sectional SEM micrograph of the coating. As demonstrated in Fig.5, the coating is homogeneous without cracks, excludes the presence of large SiO_2 particles in the hybrid materials.[11] After heat-treated, the thickness of hybrid coating on PC is 0.84 μm by dipping manner.

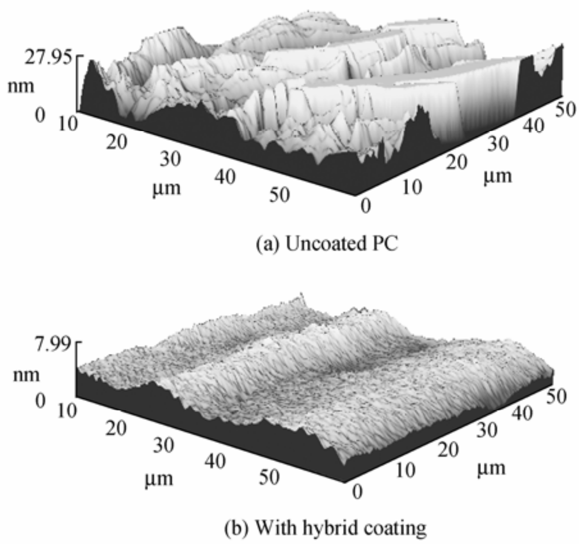

Fig.5　AFM photos of uncoated PC and coated PC with hybrid coating (S2)

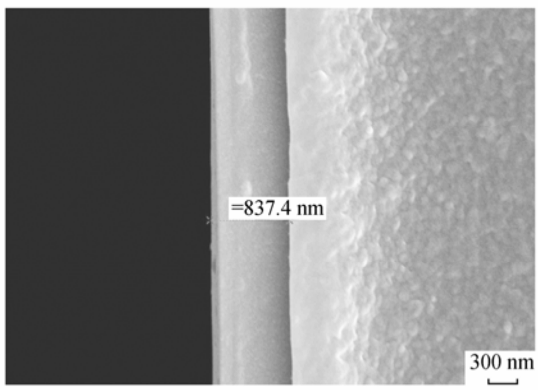

Fig.6　Cross-sectional SEM image of the hybrid film (S2)

2.7 X-ray diffraction pattern

Figure 7 illustrates the XRD pattern of S2 hybrid material. The pattern shows a broad and low peak around $2\theta=9.4^\circ$ and $2\theta=22.5^\circ$, respectively. It indicates that the S2 hybrid material is typical of amorphous nature, silica network and organosilicone chain are incorporated through the covalent bond and hydrogen bond.

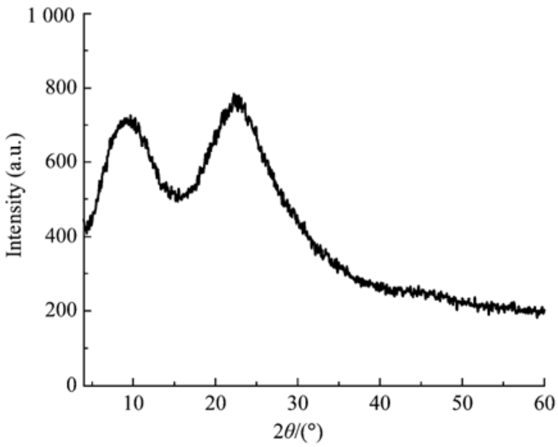

Fig.7 XRD pattern of S2 hybrid material

3 Conclusions

Transparent abrasion-resistant coatings have been developed on polycarbonate by sol–gel reactions of organic siloxane and TEOS. After heat-cured, the coating is uniform and densified. It has efficient adhesion to the substrate, and obviously increases the transparency and hardness of PC. The contact angle of hybrid coating with water is more than 90°, which exhibits good hydrophobicity. The thermal stability of the hybrid coating increases gradually with the increase of TEOS content. Considering that the overall process does not require expensive equipment and high temperature operation, this finding will greatly expand the variety and the volume of utilization of hybrid coatings.

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