The Cost Reduction Research of GPTMS-Boehmite Transparent and Hard Coating Film

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Abstract. In order to reduce cost and contain properties, GPTMS-boehmite transparent and hard coating film was prepared by replacing boehmite with aluminium isopropoxide (AIP), and modified by hydrolyzed TEOS. By the research of the process, a cheap transparent coating film with a pencil hardness of 4H and adhesion of 2 on the surface of inorganic glass is obtained.

Introduction

Transparent and hard films on various substrates have received considerable attention for optical applications. Inorganic coating films have excellent hardness, abrasion resistance and thermal resistance, but in addition to high cost, they are brittle and need high processing temperature [1]. Though some organic materials have been used to prepare the hard coating films, they have exhibited a relatively poor hardness [2]. In order to solve this problem, organic-inorganic hybrid materials have been introduced to prepare this transparent and hard coating film [3].

Indeed the Al-OH on the surface of boehmite can occur condensation reaction with Si-OH obtained by the hydrolysis of organosiloxane under a certain contain, and form Al-O-Si. Chemical bonds between boehmite and organosiloxane is achieved by this reaction, by which not only hybrid film combining the hardness of boehmite with the flexibility of organosiloxane can be obtained, but also the transparency of film is realized [2~4]. Therefore, over the past few years, there has been a growing interest in organosiloxane-boehmite hybrid coating film. However, the introduction of this material on an industrial scale is still in the stage of development for the high prices of boehmite.

To reduce cost and make the price more competitive, this paper attempts to replace boehmite with cheap aluminium isopropoxide (AIP), i.e., prepare hybrid film by AIP and organosiloxane directly, then modify this film with hydrolysis production of tetraethyl orthosilicate.

Experiments

Materials

γ-(2, 3-epoxypropoxyl) propyltrimethoxyl silane (GPTMS, chemically pure) was supplied by Guangzhou Baoxin Chemical Materials Co., Ltd; AIP (chemically pure) was supplied by Shanghai Fortune Bio-Technology Co., Ltd; Tetraethyl orthosilicate (TEOS, analytical reagent) was supplied by Tianjin Yongda Reagent Development Center.

Preparation of Hydrolysis Productions

Hydrolyzed GPTMS and TEOS solutions were prepared in the previous work respectively [5, 6].

Preparation of GPTMS-boehmite Prepolymer

A certain mass ratio of AIP, hydrolysis production of GPTMS and deionized water were put in a reactor equipped with a mechanical stirrer and reflux condenser. The mixture was heated to a certain temperature for a few hours with vigorous stirring to obtain GPTMS-boehmite prepolymer.

Preparation of GPTMS-boehmite Hybrid Film

The above prepolymer was coated on the surface of a 0.3 cm ×9.0 cm×12.0 cm inorganic glass.

After air drying 30 min, the coated glass was placed in the oven with air circulation. Transparent film was prepared after curing 2.5 h at 125 ℃.

Modification of Hybrid Film with TEOS

A certain mass ratio of GPTMS-boehmite prepolymer and hydrolyzed TEOS were put in a reactor, and then stirred stably under room temperature for 30 min. Just like the preparation of GPTMS-boehmite hybrid film, the mixture was coated on the surface of an inorganic glass. After air drying 30 min, the coated glass was placed in the oven with air circulation. Transparent film was prepared after curing 2 h at 110 ℃.

Measurements

The chemical bonds of coating film were evaluated by a Nexus470 Fourier transform infrared spectroscopy (FTIR) produced by America Thermo Nicolet Company. Pencil hardness and adhesion of coating film were carried out by GB/T5739-1996 and GB/T9286-1998 respectively.

Results and Discussions

Influence of AIP Content

When hydrolyzed GPTMS solution and deionized water were 100 and 75 g respectively, and the prepolymer was prepared at 80 ℃ for 13 h, the influence of AIP content to properties of GPTMS-boehmite coating films is shown in Table 1. As can be seen, pencil hardness of coating film increases with the increase of AIP content while adhesion is almost the same. But it is found by the experiment that,when the content of AIP is higher than 12.5 g, delamination is occurred in prepolymer, and transparent coating film can't be achieved accordingly. Therefore, 12.5 g was determined as the content of AIP in following work.

Tab. 1 Influence of AIP content to properties of coating films

AIP /g	0	6.5	9.5	12.5
Pencil hardness	3B	B	HB	F
Adhesion	1	3	3	3

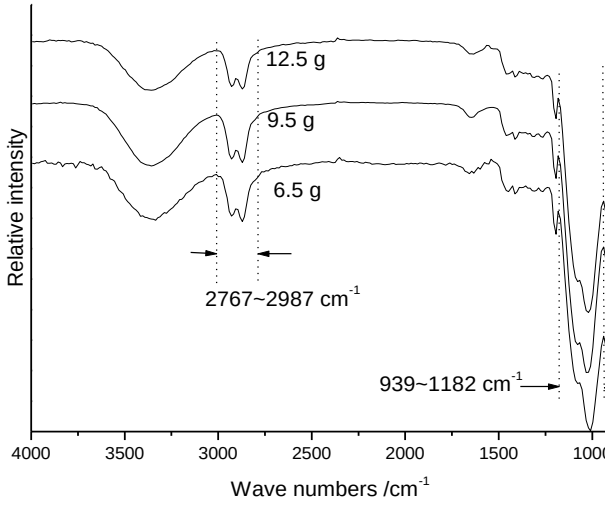

Fig.1 FTIR spectra of hybrid films with different AIP content

Figure 1 is FTIR spectra of GPTMS-boehmite coating films with different AIP content. Regarding stretching vibration peak of C-H bond as internal standard, the influence of AIP content to the contents of Si-O-Si and Si-O-Al was researched (see Table 2). Here S_{m1} is the integral area of

Si-O-Si and Si-O-Al peaks of the film that *m* g AIP is added. The integral range is 939～1182 cm^{-1}. And S_{m2} is the integral area of stretching vibration peak of C-H bond of the film that *m* g AIP is added. The integral range is 2767～2987 cm^{-1}. S_m is the ratio of S_{m1} to S_{m2}, which represents the ratio of peaks area of Si-O-Si and Si-O-Al to that of C-H bond. It can be seen from Table 2 that, the variation of S_m with AIP content is coincident with that of the hardness (see Table 1), which shows that the variation of hardness is controlled by the contents of Si-O-Si and Si-O-Al.

Tab. 2 Transformation of Si-O-Si and Si-O-Al by FTIR spectral analysis with AIP content

AIP /g	S_{m1}	S_{m2}	S_m
6.5	3423.75	827.41	4.14
9.5	3997.26	820.79	4.87
12.5	3767.60	672.29	5.60

Influence of Deionized Water Content

When hydrolyzed GPTMS solution is100 g, and the prepolymer was prepared at 80 ℃ for 13 h, the influence of deionized water content to properties of GPTMS-boehmite coating films is shown in Table 3. As can be seen, both pencil hardness and adhesion of coating film reduce with the increase of water content. But experiment shows that when water content is lower than 75 g, hydrolysis effect of AIP becomes worse, and prepolymer appears delamination. Finally 75 g is determined as the content of water in following work.

Tab. 3 Influence of deionized water content to properties of coating films

H_2O /g	50	75	100	125
Pencil hardness	H	F	HB	B
Adhesion	3	3	4	4

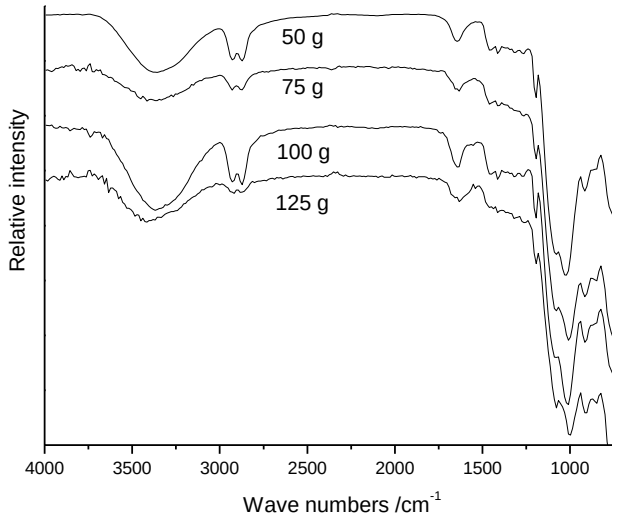

Fig. 2 FTIR spectra of films with different water content

FTIR spectra of GPTMS-boehmite coating films with different deionized water content are shown in Figure 2. Just like Figure 1, it was worked out also from Figure 2 that the variation of hardness of film is controlled by the contents of Si-O-Si and Si-O-Al. Here will not elaborate.

Influence of Reaction Temperature

When the prepolymer was prepared for 13 h, The influence of preparation temperature to

properties of GPTMS- boehmite coating films is shown in Table 4. As can be seen, hardness of film increases with the increase of preparation temperature while adhesion increases first, then declines. It was found by the experiment that when the temperature is lower (75 ℃), the reaction effect of hydrolyzed GPTMS and AIP becomes worse, and prepolymer appears delamination. When the temperature is higher (85 ℃), viscosity of prepolymer becomes high, and prepolymer is e asy to form gel, which leads to a more difficult of process control. Hence, reaction temperature in following work was determined to be 80 ℃ finally.

Tab. 4 Influence of preparation temperature to properties of coating films

Preparation temperature /℃	75	80	85
Pencil hardness	B	F	H
Adhesion	4	3	5

Influence of Reaction Time

Table 5 is the influence of reaction time to properties of GPTMS- boehmite coating films. As can be seen, pencil hardness of film increases with the extending of reaction time while adhesion increases first, then declines. Experiment also shows that, just like the influence of reaction temperature, when reaction time is too short, interaction of hydrolyzed GPTMS and AIP is poor, and prepolymer is easy to occur delamination. When reaction time is too long, it is easy to appear gel. Thus reaction time was determined to be13 h according to the properties of film.

Tab. 5 Influence of reaction time to properties of coating films

Reaction time /h	7	9	11	13	15
Pencil hardness	2B	B	HB	F	H
Adhesion	5	4	3	3	4

According to the above study, the process that preparing GPTMS-boehmite prepolymer is obtained: AIP, hydrolyzed GPTMS solution and deionized water (the mass ratio were 12.5 :100 : 75) are put together and churned up 13 h under 80 ℃.

Influence of Hydrolyzed TEOS Content

Table 6 is the influence of hydrolysis TEOS content to properties of GPTMS-boehmite coating films. As can be seen, both pencil hardness and adhesion of film increase obviously with the increase of hydrolyzed TEOS, which is consistent with what we expected. But experiment shows that, hydrolysis product of TEOS itself is very brittle after drying, film can't form when the content of hydrolyzed TEOS is higher than 20% by weight. Therefore, the content of hydrolyzed TEOS was determined to be 20 %, correspondingly pencil hardness and adhesion of film reach 4H and 2 respectively, which means that coating film prepared here has the same properties as that prepared by GPTMS and boehmite while cost is reduced [7].

Tab. 6 Influence of TEOS content to properties of coating films

Hydrolyzed TEOS/prepolymer	0	0.09	0.13	0.18	0.20
Pencil hardness	3B	H	2H	3H	4H
Adhesion	5	4	3	2	2

Conclusion

Based on the research of the process, cheap GPTMS-boehmite transparent and hard coating film modified by hydrolyzed TEOS was prepared. AIP, hydrolyzed GPTMS and deionized water (the mass ratio were 12.5 : 100 : 75) are put together and vigorous stirred 13 h under 80 ℃. Then add

20% hydrolyzed TEOS and stir stably under room temperature for 30 min. Curing the above mixture 2 h at 110 ℃ on the surface of inorganic glass, transparent coating film with a pencil hardness of 4H and adhesion of 2 can be obtained.

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