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Synthesis of Hybrid Sol Based on ZrO_2-SiO_2 System and their Coating Properties

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ABSTRACT

Organic-inorganic hybrid sol based on ZrO_2-SiO_2 system was prepared by sol-gel process. Firstly, ZrO_2 non-aqueous precursor sol was synthesized and then organosilane compounds which include epoxy silane (GPTS; 3-glycidoxypropyl tri-methoxysilane) and acryl silane (ACS; (3-(tri-methoxysilyl)propylmethacrylate)) were added to ZrO_2 precursor sol for hybridization. Finally, commercial silica sol was added to improve the mechanical properties. Synthesized organic-inorganic Zr-hybrid sol was coated on polycarbonate substrate for enhancing it's mechanical properties, especially hardness. Vicker's hardness of polycarbonate substrate was increased from 13.6 to 17.8 MPa and its pencil hardness was increased from 2 to 7 H, respectively, after coating and drying at 100°C for 30 min.

Key words : Hybrid sol, Non-Aqueous ZrO_2 precursor sol, Non-Scratching, Polycarbonate

1. Introduction

Since Schmidt,[1-4] sol-gel technology has been widely used for synthesis of hybrid materials. Most of these papers and patents[5-8] have been focused on SiO_2-, Al_2O_3-, and TiO_2-organosilane hybrid fabrication. Anyway, these new materials offer many opportunities for applications in different fields such as optical devices, catalysis, electronics etc on.

Recently, thermoplastic substrates such as polycarbonate sheet and film are used to the construction field for shielding window and electronic component because of their lightness and economical needs. While polycarbonate resin is a tough transparent material, it is generally desirable to improve the abrasion resistance and weathering resistance. Also, their mechanical properties, especially, hardness is not so good comparing to inorganic materials. Accordingly, many efforts to improve these properties have been done by coating using the above mentioned sol-gel hybrid compositions.

Stabilized-ZrO_2 ceramics, however, is well-known material which has been widely used in ceramic field due to its superior mechanical properties. So, in this present work, we have focused on ZrO_2 oxide to fabricate hybrid sol and enhance the mechanical properties of the polycarbonate substrate and investigated coating properties of its hybrid film.

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2. Experimental Procedures

2.1. Non-Aqueous ZrO_2 Precursor

At first, non-aqueous ZrO_2 precursor has been prepared before hybridizing with organic silane compounds. Non-aqueous ZrO_2 sol fabrication is based on Yoldas process,[9] which have been widely used and very easy method to prepare aqueous oxide sol and bulk ceramic, for example, Al_2O_3. In Yoldas process, water as solvent and acids for peptizing precipitated sol were used without controlling water contents. Comparing to Yoldas process, here, non-aqueous ZrO_2 sol uses methanol as solvent replacing of water and excess acid for peptizing the precipitates in solvent. By using this process, transparent ZrO_2 sol without precipitates was obtained by refluxing at 50°C for 24 h, in which $Zr(O^iPr)_4$ concentration range from 0.71 mole/L(Zr-10) to 2.12 mole/L(Zr-30) in methanol solvent adding nitric acid (63 wt%). Subsequently, organic silane compound are added to this sol for hybridization as mentioned in the next section.

2.2. Hybridization of ZrO_2-Based Sol with Organic Silane

Organic silane used in this works for hybridization with the above mentioned ZrO_2 non-aqueous sol are epoxy silane (GPTS; 3-glycidoxypropyl tri-methoxysilane) and acryl silane (ACS; (3-(tri-methoxysilyl)propylmethacrylate)). And the $Zr(O^iPr)_4$/silane mole ratio is 1.99, 2.98, 3.38, 3.98, 5.98, which sols are named as Zr-10, Zr-15, Zr-17, Zr-20, and Zr-30, respectively. Here, GPTS/ACS mole ratio is fixed as 2.2. GPTS and ACS is added to ZrO_2 precursor sol in turns and refluxed at 50°C for 24 h, respectively. Finally,

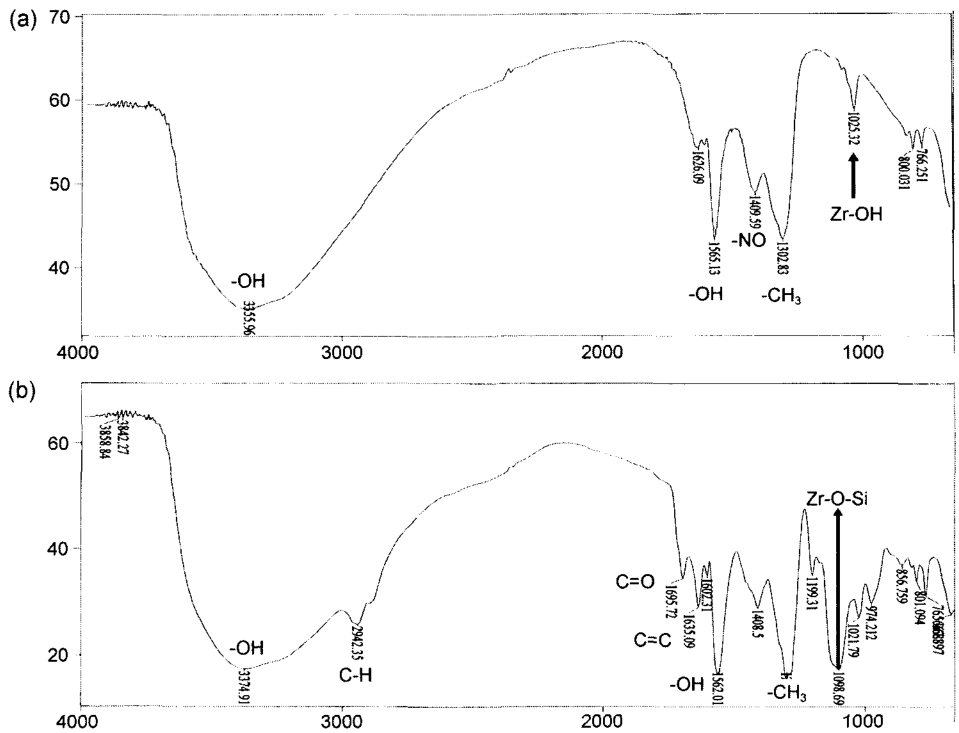

Fig. 1. FT-IR spectra of (a) Zr-15; non-aqueous ZrO_2 precursor sol and (b) Zr-15+ silane; hybrid coating sol.

commercial silica sol (Ludox, HS-40, Dupont Co.) was added to the above hybrid sol by 10% volume to improve the mechanical properties. Obtained sol is transparent and viscous liquid and coated on polycarbonate substrate by rolling method and dried at 100°C for 30 min in drying oven.

FT-IR (Bomen MB-104,CANADA) is used to confirm the hybridization of ZrO_2 sol with silane and hardness measurement of coating film on polycarbonate was done about Vickers hardness (Fv-7e, Future-Tech Corp., load : 0.3/Kg, *Dwell time : 15 sec) and Pencils hardness (100 g load).
*Dwell time : Current load pressurization time.

3. Results and Discussion

Fig. 1 shows the FR-IR spectra of non-aqueous ZrO_2 sol and Zr-15 hybrid sol. In Fig. 1(a), absorption bands around 3355 cm^{-1} and 1565 cm^{-1} are assigned to OH vibration of methanol and water and their first overtone absorption peak, respectively. Absorption band at 1302 cm^{-1} is attributed to CH_3 stretching and 1409 cm^{-1} and 1025 cm^{-1} are due to NO and ZrOH, respectively. In fig. (b), absorption band of 2942 cm^{-1} is C-H stretching of CH_3 and CH_2- group and 1695 cm^{-1} and 1635 cm^{-1} is assigned to C=O and C=C of stretching of an ester carbonyl in silane compound, respectively.[10] Especially, it is shown that 1098 cm^{-1} new absorption peak seems to be attributed to Zr-O-Si metalloxane bond. Generally, it is well-known that, Si-O, that is, metalloxane bonds absorption peak appears around in the range 1000 – 1100 cm^{-1} in case of SiO_2 sol derived by sol-gel process. Accordingly, it

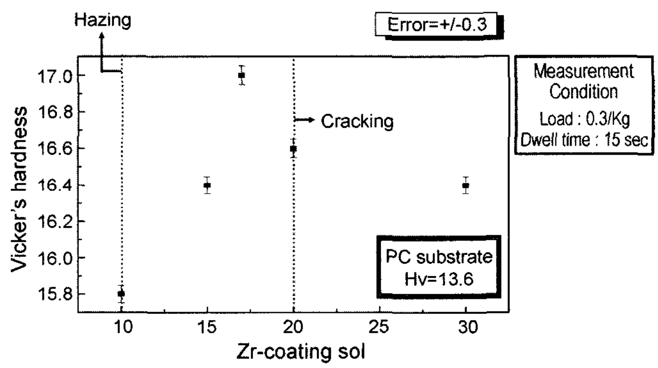

Fig. 2. Vicker's hardness of each Zr-hybrid coating film on PC substrate.

was confirmed that hybrid sol successively was prepared by this process.

Fig. 2 shows the results of measured Vicker's hardness of coating film on substrate comparing to bare polycarbonate which value is 13.6 MPa and Fig. 3 shows their resulting optical photographs. As shown in Fig. 2, Vicker's hardness value of each coating film is 15.8 (Zr-10), 16.4(Zr-15), 17.2 (Zr-17), 16.6(Zr-20), 16.4 MPa(Zr-30), respectively, and the value was averaged by 10 time measurements. However, in Fig. 3, cracks were observed in Zr-20 and Zr-30 coating film before and after the measurement. In case of lower ZrO_2 concentration in hybrid sol (Zr-10; $Zr(O^iPr)_4$/Silane mole ratio is 1.99), hazing of coating film on the polycarbonate substrate occurred after drying at 100°C for 30 min. The other compositions besides Zr-10 in this

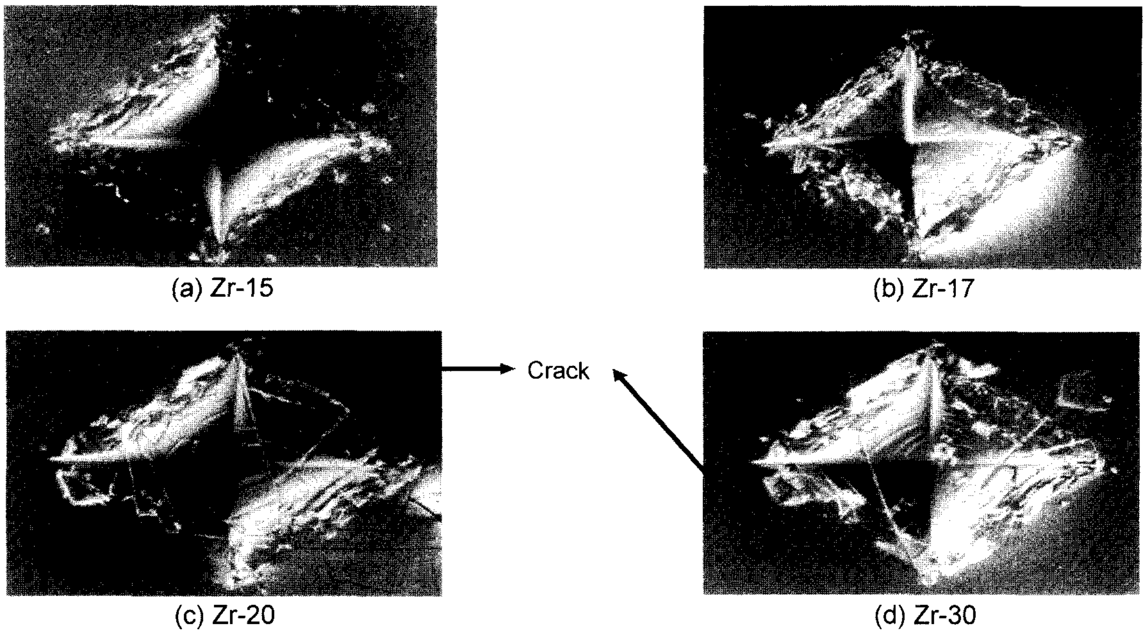

Fig. 3. Optical photographs after Vicker's hardness measurement. (a) Zr-15, (b) Zr-17, (c) Zr-20, and (d) Zr-30 hybrid coating films.

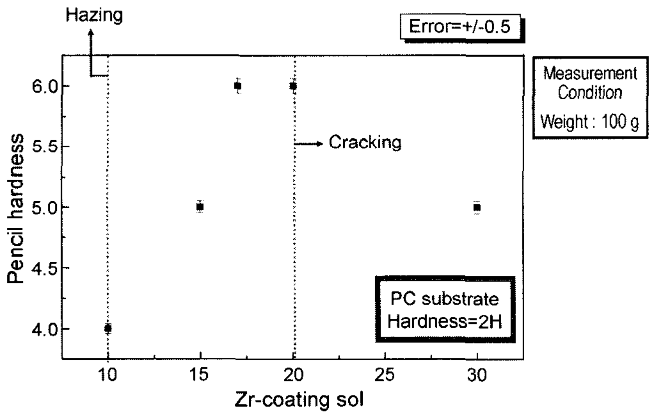

Fig. 4. Pencil hardness of each Zr-hybrid coating film on PC substrate.

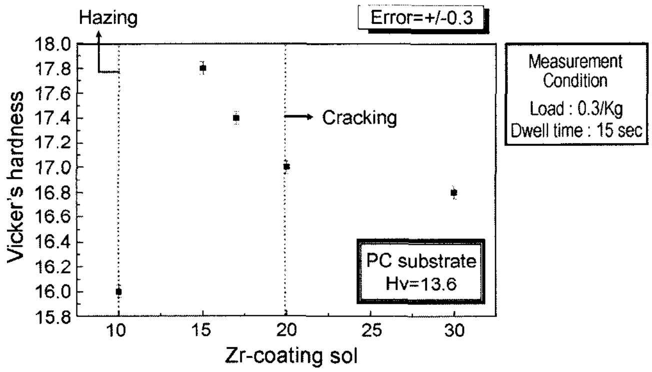

Fig. 5. Vicker's hardness of each Zr-hybrid coating film on PC substrate with adding 10 vol% colloidal silica (HS-40).

work, became a transparent coating film on the substrate after drying. But as shown in Figs. 2 and 3, cracks appeared at the $Zr(O^iPr)_4$/silane mole ratio compositions over 3.98 (Zr-20 and Zr-30).

As soon as sol was coated on the substrate, hazing did not occur. But it appeared just after dried neither at room temperature nor at 100°C. At present, its not clear whether it is attributed to adhesion problem between coated film and substrate or bonding problem between ZrO_2 precursor and silane. Anyway, its vickers hardness (15.8 MPa) shows the lower value comparing to Zr-30 (16.4 MPa) which has many cracks in coating film , even if the value was higher than bare polycarbonate substrate (13.6 MPa). Therefore, it is thought that hazing is probably attributed to the adhesion problem between coated film and substrate.

Cracking in Zr-20 and Zr-30 coating film seems to be caused by ZrO_2 content increase, that is, oxide content portion added up because ZrO_2 has no flexibility.

Fig. 5 shows the result of measurement of Vicker's hardness of coating film, which included the additional silica sol (HS-40, Dupont Co). In this case, vickers hardness values of each coating film increased higher than non-adding hybrid sols, which value were 16.0 (Zr-10), 17.8(Zr-15), 17.4(Zr-17), 17.0 (Zr-20), 16.8 MPa(Zr-30), respectively.

Fig. 6 shows their optical photographs after Vickers measurement. As shown in the Fig. 5, by addition of silica sol to the Zr-hybrid sol, hazing was not avoid, but in the Fig. 6, cracking in the coating film was prohibited by silica sol addition, especially, in Zr-20 coating film and also pencil hardness became higher than non-adding Zr-hybrid sols value, as shown in Fig. 7. Its attributed to colloidal silica particles pin effect to block crack propagation.

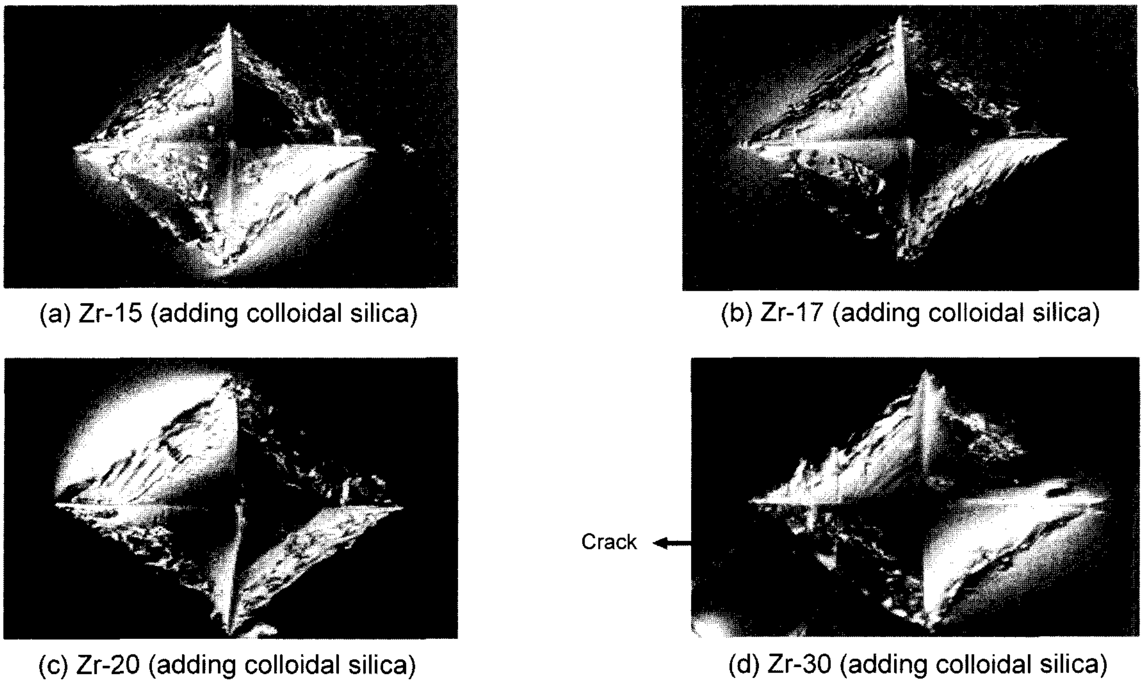

Fig. 6. Optical photographs after Vicker's hardness measurement. (a) Zr-15, (b) Zr-17, (c) Zr-20, and (d) Zr-30 hybrid coating films with adding 10 vol% colloidal silica (HS-40).

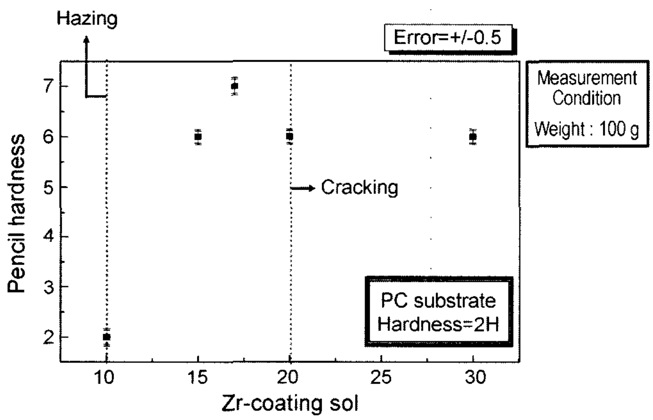

Fig. 7. Pencil hardness of each Zr-hybrid coating film on PC substrate with adding 10 vol% colloidal silica (HS-40).

4. Conclusions

ZrO_2-SiO_2 hybrid coating sol successively was prepared by sol-gel process and coated on the polycarbonate substrate by rolling method. Then, Vicker's hardness of polycarbonate on substrate was increased from 13.6 to 17.7 MPa and its pencil hardness was increased from 2 to 7 H, respectively, after coating and drying at 100°C for 30 min.

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