

# Hard coating films based on organosilane-modified boehmite nanoparticles under UV/thermal dual curing

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## Abstract

Hard coating sols and films were prepared for UV/thermal dual curing. The coating sols were composed of boehmite nanoparticles modified with organosilanes (e.g. methacryloxy-propyl trimethoxy silane, vinyl triethoxy silane, and 3-glycidoxy-propyltrimethoxy silane), a formulated initiator, and an inorganic or organic cross-linker as an additive. With this coating solution, hard coating films with a pencil hardness above 8H and transparency above 90% in the visible light range were prepared on poly(methyl methacrylate) substrates. In addition, the coating solution could be quickly cured in 35 min at a temperature of 100 °C by UV/thermal dual curing. The effects of the additive and initiator on the hardness and transparency of the resulting films are described.

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**Keywords:** Boehmite nanoparticle; Organosilane; Hard coating; UV/thermal curing; Scanning electron microscopy; Wear; Infrared spectroscopy

## 1. Introduction

Hard and transparent films on various substrates (e.g., glass, polymer, ceramic, and metal) have received considerable attention for optical applications such as windows, lenses, and wave guides [1–5]. Though some organic materials have been used to prepare the hard coating films by a sol–gel coating method such as spin coating [6], they have exhibited a relatively poor hardness. In order to solve this problem, organic/inorganic hybrid materials have been introduced to prepare the hard coating films [7–10]. There are several reports regarding the increased hardness and abrasion resistance of organic/inorganic hybrid films. Rubio et al. [7] reported that a pencil hardness higher than 8H can be obtained from poly(methyl methacrylate)–silica hybrid coatings. Other hybrid films such as acrylate–silica hybrid-coated films [8], poly(hydroxyl ethyl methacrylate) functionalized with alkoxysilane and hexamethylmelamine [9] and organosilane-modified TiO<sub>2</sub> [10] are known to have good scratch resistance and adhesion. However, they required relatively high temperature such as 140–150 °C

and a long curing time on the order of 24 h to achieve a high hardness.

In this study, we have synthesized organosilane-modified boehmite nanoparticles (OSBN) and a coating solution containing OSBN, a formulated initiator, and an additive such as silane coupling agents or organic cross-linkers for the UV/thermal dual curing. Hard coating films prepared by these organic/inorganic hybrid coating sols exhibited an excellent hardness and transparency within 35 min at a relatively low temperature of 100 °C. The effect of the initiator and additives on the hardness and transparency of the resulting film was also investigated.

## 2. Experimental details

### 2.1. Preparation of organosilane-modified boehmite nanoparticles (OSBN)

Boehmite nanoparticles were prepared by a peptization method [11]. Five hundred grams of aluminum isopropoxide (Al(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>, > 98%, Aldrich) was added to 5 L of deionized water with vigorous stirring to form a white precipitate. Then 20 mL of nitric acid (HNO<sub>3</sub>, 60%, Samchun Chemical, Korea) was added and the suspension was allowed to react at 80 °C for 6 h. The resulting peptized boehmite sol

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Table 1  
Composition of the formulated initiators

Initiators	Chemical name	Manufacturing company	Amounts (wt.% ratio)
HCPK, Irgacure 184	1-Hydroxy cyclohexyl phenyl ketone	Ciba Specialty Chemicals	5
PAG 199	Bis ( <i>p</i> -toluene sulfonyl) diacromethane	Wako Pure Chemical	1
V-65	2,2'-Azobis (2,4-dimethylvaleronitrile)	Wako Pure Chemical	0.06
VA-044	((2,2'-Azobis [2-(2-imidazolin-2-yl) propane] dihydrochloride	Wako Pure Chemical	0.02
SPS	Sodium persulfate	Aldrich	0.2
1-MeI	1-Methyl imidazole	Acros	10

solution was evaporated at 60% in a rotary evaporator to obtain boehmite nanoparticles.

The boehmite nanoparticles (100 g) were re-dispersed in 2 L of deionized water with a mechanical stirrer for 30 min. After adding the organosilane solution containing 225 mL of MPTMS (methacryloxy-propyl trimethoxy silane, C<sub>10</sub>H<sub>20</sub>O<sub>5</sub>Si, 98%, Aldrich), and 52 mL of VTES (vinyl triethoxy silane, C<sub>5</sub>H<sub>12</sub>O<sub>3</sub>Si, 97%, Aldrich), the resulting solution was heated to 70–80 °C for 1 h with vigorous stirring. The resulting precipitates of organosilane-coated boehmite nanoparticles (OSBN) were collected with a membrane filter.

## 2.2. Preparation of additives

PVPS (PTMS and VTES based polysiloxane, where PTMS is phenyltrimethoxy silane and VTES vinyl triethoxy silane) solution was prepared as an additive to the OSBN coating solution to provide better film hardness and transparency. Both the PTMS (8.5635 g, C<sub>9</sub>H<sub>14</sub>O<sub>3</sub>Si, > 94%, Aldrich) and VTES were hydrolyzed in excess water containing 1.9 mL of HNO<sub>3</sub> with vigorous stirring. The PVPS gel was formed during the heating of the hydrolyzed solution at 60 °C for 6 h. The solvent was removed with a membrane filter and the obtained gel was re-dispersed in warm IPA (isopropyl alcohol, 99.9%, J. T. Baker). A clear solution of PVPS was prepared after heating at 60 °C for 6 h with constant stirring.

As another additive, a multifunctional acrylate monomer (MFAM) was prepared to enhance film hardness through the

organic cross-linking. MFAM was composed of trimethylolpropane triacrylate (TMPTA, (H<sub>2</sub>C=CHCO<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>CC<sub>2</sub>H<sub>5</sub>, Aldrich) and pentaerythritol triacrylate (PETA, (H<sub>2</sub>C=CHCO<sub>2</sub>-CH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>OH, Aldrich) with TMPTA/PETA ratio of 3/1 (by weight), where they can act as a trifunctional and tetrafunctional cross-linker, respectively.

## 2.3. Preparation of dually curable hard coating sols

The OSBN (2 g) was completely dispersed in 20 mL of IPA with a magnetic stirrer. Then 2.8 mL of hydrolyzed GPTMS (3-glycidioxy-propyltrimethoxy silane, C<sub>9</sub>H<sub>20</sub>O<sub>5</sub>Si, 98%, Aldrich) solution, which was prepared by mixing 17.6 mL of GPTMS and 4.5 mL of H<sub>2</sub>O with 0.1 mL of HNO<sub>3</sub>, was added to the OSBN dispersion because the epoxy groups in GPTMS could be easily cured by thermal energy induced by ring opening. After stirring for 1 h, a dually curable hard coating sol was prepared by adding 0.067 g of benzophenone (C<sub>13</sub>H<sub>10</sub>O, 99%, Acros) or a formulated initiator to the solution. The formulated initiator was prepared by mixing HCPK/PAG/V-65/VA-044/SPS/1-MeI and the compositions of the formulated initiator are summarized in Table 1.

The coating sol was prepared by mixing IPA solution of OSBN, an initiator (benzophenone or formulated initiator), a hydrolyzed GPTMS solution and an additive such as PVPS or MFAM (Table 2). The hard coating film was prepared by spin coating on the PMMA substrate and subsequent UV/thermal dual curing.

Table 2  
Curing conditions and pencil hardness results for the hard coating sols with various compositions

Sample code	Curing system		Initiator		Additives		Pencil hardness	
	UV Time (min)	Thermal Temp. (°C)	Thermal Time (min)	Temp. (°C)	PVPS solution [PVPS]/[OSBN] <sup>a</sup>	MFAMs [MFAMs]/[OSBN] <sup>b</sup>		
A1	5	25	360	100	Benzophenone	–	5H	
A2	5	25	30	100	Formulated initiator <sup>c</sup>	–	6H	
B1						0.25	8H	
B2	5	25	30	100	Formulated initiator <sup>c</sup>	1	7H	
B3						4	6H	
C1						–	0.02	7H
C2						–	0.05	8H
C3	5	25	30	100	Formulated initiator <sup>c</sup>	–	0.10	7H
C4						–	0.15	6H
C5						–	0.25	5H

<sup>a</sup> Mole ratio of OSBN and PVPS.

<sup>b</sup> Mole ratio of OSBN and MFAMs.

<sup>c</sup> See the composition of initiators in Table 1.

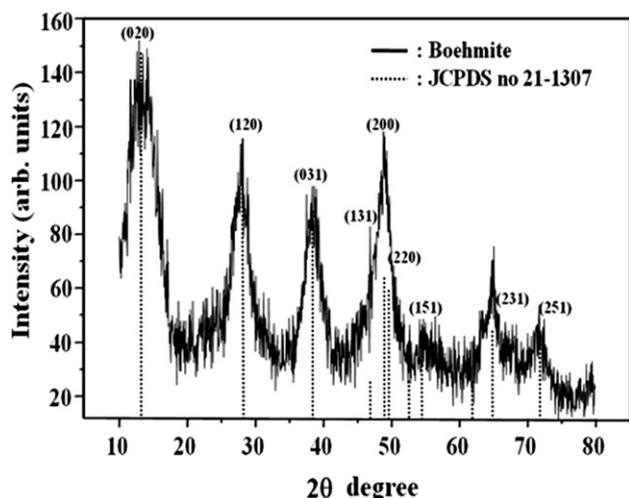


Fig. 1. XRD pattern of the boehmite nanoparticles.

#### 2.4. Hard coating film preparation

Poly(methyl methacrylate), PMMA, was used as a substrate for all hard coating films. The PMMA substrates were pretreated by cleaning with IPA, drying, and ion-showering prior to coating. Ion-showering was carried out by Ar-plasma treatment according to Huang's method [12]. It was reported that the plasma treatment for polymer substrates could make active sites at the surfaces and form strong covalent bonds between films and substrates after coating [13,14].

Hard coating films were formed with the pretreated substrates on a spin coater, which the revolutions were controlled by three continuous steps: 3000 rpm for 10 s, 5000 rpm—30 s, and 3000 rpm—10 s. The coated films on the PMMA substrates were cured at 100 °C for 30 min after irradiating with UV light for 5 min at room temperature with two mercury lamps of 250 and 354 nm.

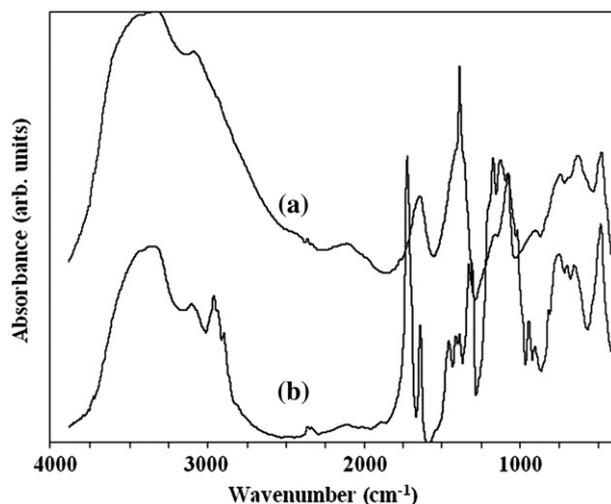


Fig. 2. FT-IR spectra of (a) pure boehmite and (b) organosilane-modified boehmite nanoparticles.

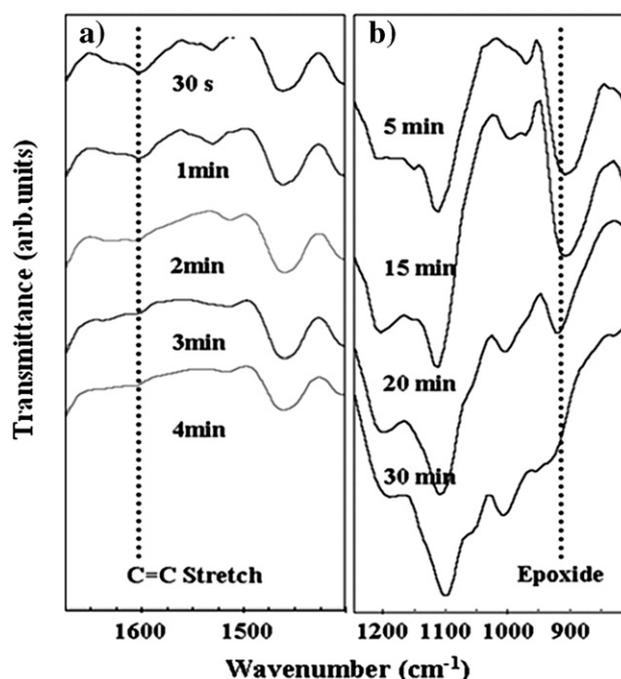


Fig. 3. FT-IR spectra of the hard coating films obtained from sample A2 with curing time: (a) UV curing and (b) thermal curing.

#### 2.5. Characterization

The crystal structure was characterized by an X-ray diffractometer (XRD, Rint-2000, Rigaku) using Cu-K $\alpha_1$  radiation under 40 kV and 100 mA. The coating of organosilanes on the boehmite nanoparticles was confirmed by Fourier transform infrared spectroscopy (FT-IR, Magna 760, Nicolet). The morphology and thickness of the resulting films were observed by field-emission scanning electron microscopy (FE-SEM, JEM-6340F, JEOL). A differential scanning calorimeter (DSC, DSC 2010, TA instruments) analysis was conducted under nitrogen flow at a heating rate of 5 °C/min to estimate the curing temperature. The transparency of the

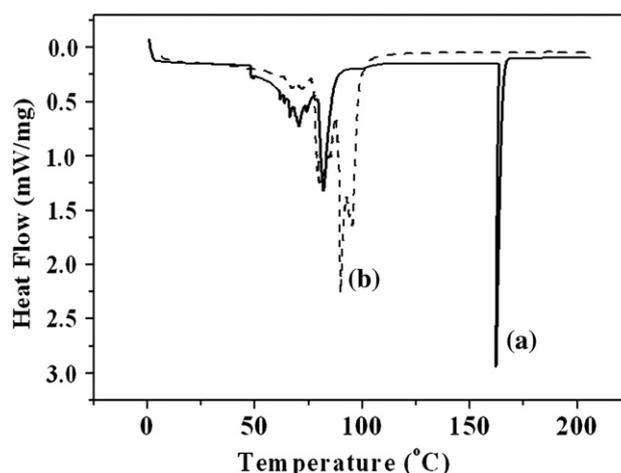


Fig. 4. DSC curves for the OSBN hard coating sols (a) without initiator (solid line) and (b) with the formulated initiator (dashed line).

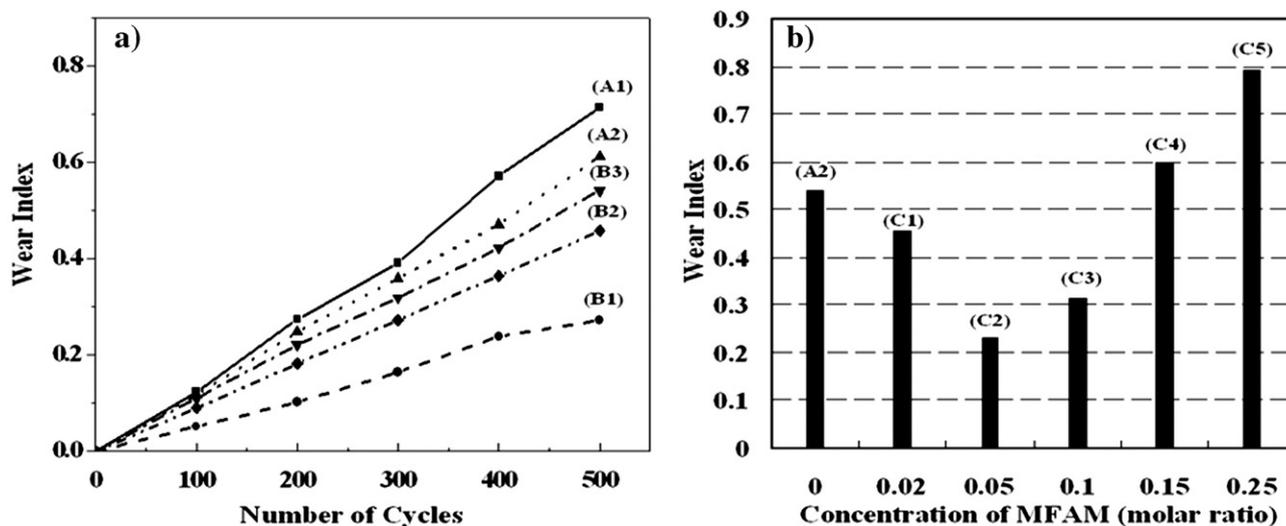


Fig. 5. The wear index of the various hard coating films (a) on the number of cycles in the Taber abrasion test and (b) in dependence of the MFAM contents after a Taber abrasion test of 500 cycles.

films was analyzed by a UV/Vis spectrophotometer (S-2150, Scinco) with the hard coating films on the PMMA substrates. The film hardness was measured using a pencil hardness tester (C221-D, Yoshimitsu Tokyo Co. Ltd.) with a loading weight of 1000 g and an angle of  $45^\circ$ , according to ASTM D 3363-92 [15] over a range from of 6B to 8H. According to ASTM D 4060-95 [16], the hardness of the films was also analyzed by a Taber abraser (5130 Abraser, TABER Industries) at loading of 500 g per wheel with S-39 leather.

### 3. Results and discussion

Boehmite nanoparticles were prepared by a peptization method in an aqueous nitric acid solution. Peptization is a process in which coagulated precipitates dissolve and recrystallize to form nanoparticles with an acid or base [17]. Various metal oxide nanoparticles including boehmite are reported to be prepared by the peptization method [18,19]. Fig. 1 shows an

XRD pattern of the prepared boehmite nanoparticles which is in accordance with that of the  $\gamma$ -AlOOH in the JCPDS file 21-1307 for (020), (120), (031) and (200) peaks [20]. The highly broadened peaks of the XRD result indicated that the synthesized boehmite particle has a nanometer-ordered crystallite size.

The surface of the obtained boehmite nanoparticles was modified with MPTMS and VTES to prepare organosilane-modified boehmite nanoparticles (OSBN). OSBN was well-dispersed in various kinds of alcohols and organic solvents such as tetrahydrofuran and acetonitrile because the surface of the particles had changed from hydrophilic hydroxide groups to hydrophobic methyl methacrylate and vinyl groups as a result of the modification. Due to the methacrylate and vinyl functional groups in the organosilanes, OSBN could be cured by UV-irradiation. FT-IR spectra are shown to confirm the organosilane modification of boehmite nanoparticles (in Fig. 2). Pure boehmite (Fig. 2(a)) shows several peaks at  $3348\text{ cm}^{-1}$ ,

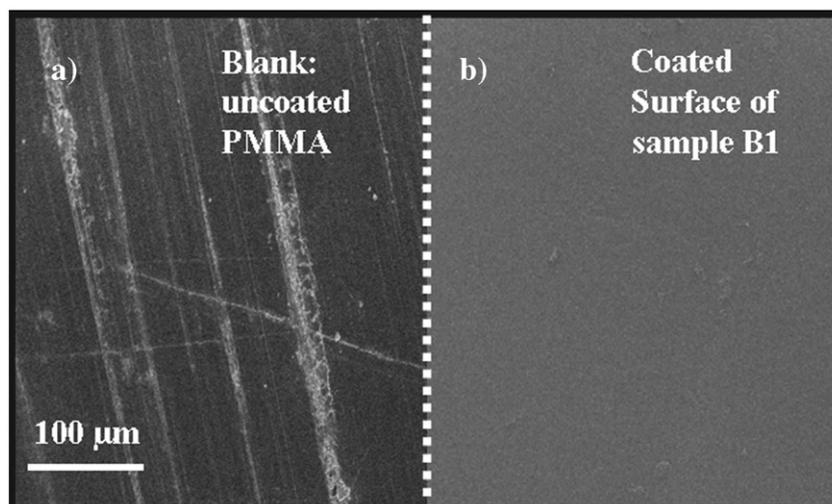


Fig. 6. SEM images for the surfaces of (a) uncoated and (b) B1-coated PMMA substrates after Taber abrasion test of 500 cycles.

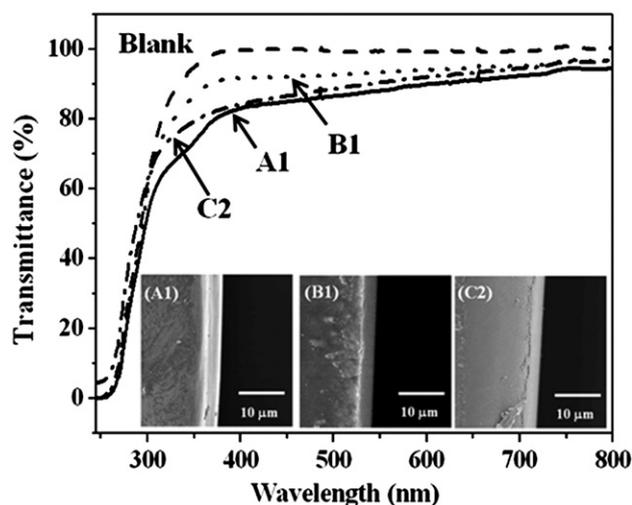


Fig. 7. Variation of the transmittance of the dually cured hard coating films. (Insets are SEM images of the hard coating films for samples A1, B1, and C2. The thickness of each film is approximately 3  $\mu\text{m}$ ).

1637  $\text{cm}^{-1}$ , 1355  $\text{cm}^{-1}$ , and 1078  $\text{cm}^{-1}$  which can be assigned to O–H, Al=O, Al–O–H, and Al–O–Al bonds, respectively. Meanwhile, OSBN (Fig. 2(b)) shows the characteristic peaks for MPTMS and VTES at 1720 (C=O), 1637 (C=C), 2942 and 2875  $\text{cm}^{-1}$  (C–H). The peaks for inorganic networks at 1175  $\text{cm}^{-1}$  (Si–O–Si), 1160  $\text{cm}^{-1}$  (Si–O–Al), and 1113  $\text{cm}^{-1}$  (Al–O–al) are also observed.

The effect of a formulated initiator on the film property was investigated. Sample A2 containing a formulated initiator exhibited pencil hardness of 6H, which was slightly higher than that of sample A1 (5H) with a benzophenone as an initiator. However, the curing time required to reach each hardness value was 6 h and 30 min for samples A1 and A2, respectively. FT-IR was used to evaluate the curing rate by observing the disappearance of organic functional groups in hard coating sol on curing. As can be seen in Fig. 3, the C=C stretching vibrational peaks at 1600  $\text{cm}^{-1}$ , from vinyl groups in VTES and MPTM, were vanished within 4 min under UV curing, while the peak at 908  $\text{cm}^{-1}$ , corresponding to the epoxide group in the GPTMS, was disappeared in 30 min under thermal curing.

With the aid of a formulated initiator, the curing temperature as well as the curing time could be reduced. Prolongo et al. [21] reported that the temperature required to etherificate epoxide groups can be measured by observing the exothermic peak in DSC analysis. In this study, we also used DSC analysis to observe the curing temperature of the coating sol with a formulated initiator and without an initiator. As shown in Fig. 4, the exothermic peak for the opening of the epoxide group shifted to lower temperature under 100  $^{\circ}\text{C}$  when the formulated initiator was used. Heise and Martin [22] also observed that the temperature for curing epoxide groups was lowered significantly with an imidazole compound. The formulated initiator in this study also contained an imidazole compound and the hard coating sol with a formulated initiator was quickly cured within 35 min at relatively low temperature of 100  $^{\circ}\text{C}$ . The composition of a formulated initiator was listed in Table 1.

On the other hand, the films prepared with a formulated initiator exhibited a pencil hardness of 6H (sample A2, see Table 2). In order to improve the hardness and transmittance of the films, the effect of additives such as PVPS and MFAM, as an inorganic and organic cross-linker, was investigated. Generally, cross-linkers have a great effect on the physical properties of cured films depending on their structure and content [23]. The addition of PVPS or MFAM caused the cross-linking density in the cured films to increase, which eventually enhanced the surface hardness. When PVPS was added to the hard coating sol with [PVPS]/[OSBN] of 0.25 (B1), the film with a maximum pencil hardness of 8H was obtained (Table 2). In the case of MFAM added hard coating sol, [MFAM]/[OSBN] of 0.05 (C2) yielded the highest pencil hardness of 8H. For the higher concentration of PVPS or MFAM than above values, the brittle film was formed due to excess cross-linking, which had an adverse effect on the hardness.

Wear index values for the films were measured to estimate their ability to prevent scratches by the Taber abrasion test. The wear index,  $I$ , of a test specimen was calculated as follows [17]:

$$I = (A - B) 1000 / C$$

where  $A$  is the weight of the test specimen before abrasion (in mg),  $B$  is the weight of test specimen after abrasion (in mg), and  $C$  is the number of cycles of abrasion recorded. As shown in Fig. 5, the lowest wear index was obtained in samples B1 and C2 which coincided with the pencil hardness result. SEM images of the films' surface after 500 cycles of the abrasion test also showed the difference in the hardness of the samples. Severe scratches on the uncoated PMMA substrate could be seen, while there was no scratch on the surface of sample B1 after the abrasion test, as shown in Fig. 6.

The transparency of the hard coating films was investigated by a UV/Vis spectrophotometer. Sample C2 with MFAM exhibited almost the same transmittance of 80–90% as sample A1 with no additive. Meanwhile, sample B1 with PVPS had a transmittance above 90% over the visible light range (Fig. 7).

#### 4. Conclusion

Boehmite nanoparticles were synthesized by a peptization method in an aqueous acidic solution and modified with organosilane coupling agents such as VTES and MPTMS for the dispersion in alcohol solvents. Hard coating sols for UV/thermal dual curing were prepared by mixing organosilane-modified boehmite nanosols with a hydrolyzed GPTMS solution, a formulated initiator, and an additive such as PVPS or MFAM. By virtue of the formulated initiator, the films were rapidly cured on the PMMA substrates in 35 min (5 min for UV and 30 min for thermal curing) at a relatively low temperature of 100  $^{\circ}\text{C}$ . The addition of PVPS or MFAM, as an inorganic and organic cross-linker, significantly enhanced the film hardness. With an optimal amount of the additive, a pencil hardness of 8H could be obtained, which was also confirmed by the Taber abrasion test. Moreover, when PVPS was used as an additive to the hard coating sol, the transparency of the film increased above 90% over the entire visible light range.

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