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Three Hardness Test Methods and Their Relationship on UV-Curable Epoxy Acrylate Coatings for Wooden Flooring Systems

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Abstract: UV-curable epoxy coatings consist of oligomers, monomers, and a photoinitiator with no additives. The oligomer and photoinitiator used in this study were diacrylate ester of bisphenol A epoxy resin and dimethylhydroxyacetophenone. The monomers used were 2-hydroxypropyl acrylate (HPA), 1,6-hexanediol diacrylate (HDDA), and trimethylol propane triacrylate (TMPTA). To investigate the performance of UV-curable epoxy acrylate coatings at various trifunctional acrylate monomer ratios for application to wooden flooring systems, we investigated the hardness using three methods: pencil hardness, pendulum hardnesss, and microhardness; in addition we investigated their relationship and the effect of the substrate.

Keywords: *UV-curable coating, pencil hardness, pendulum hardness, microhardness, substrate*

Introduction

One of the most important environmental issues in the coating industry is the use of volatile organic compounds (VOCs) because they are all sourced from organic solvents. To reduce VOC usage in the coating industry, ultraviolet light (UV) curing technology is widely used. UV-curable coatings are one of the most popular coatings used in the wood industry. Recently, wooden flooring systems coated with UV-curable coatings on the surface have become widely used indoors in Korea. Compared to conventional coatings, the advantages of UV-curable coatings are short curing times, low VOC contents, and low space requirements [1-4].

The market share by sales of UV-curable coatings in 1995 consisted of coatings for wood (31.9 %), PVC (32.7 %), plastic (10.9 %), paper (11.8 %), and others (2.1 %), but UV-curable coatings for wood accounted for ca. 40 % of products. Applications of UV-curable coatings for wood were mostly for furniture and flooring systems. Flooring system products undergo surface coating to protect the surfaces, improve their physical and chemical properties (resistance to acid and alkali), and to enhance their appearance for decoration.

We have focused on determining the hardness of the UV-curable epoxy acrylate coating as a measure of the physical properties by using three different test methods: pencil hardness, pendulum hardness, and microhardness.

The pencil hardness test (ASTM D 3363-74) measures the hardness of coatings using pencils of hardness from 6B to 6H. The procedure consists of making scratches or penetrations of the coating with a pencil positioned at a 45° angle against the coated substrate; the hardness corresponds to the softest pencil that forms scratches. This method is used in industry because it is inexpensive and fast.

The pendulum hardness (ASTM D 4366) is measured with respect to pendulum oscillation times on the coatings and is performed in a laboratory. The microhardness (ISO 14577-1) test is used to measure the hardness of thin films. It measures the force of an indenter penetration and the penetration depth, and calculates the hardness of the coatings [5-8]. The pendulum hardness and microhardness tests are relatively new measurement methods.

In this study, we investigated the hardness of UV-curable coatings using the three methods: pencil hardness, pendulum hardness, and microhardness; their we also investigated relationship and the effect of the substrate.

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Experimental

Materials

Diacrylate ester of bisphenol A epoxy resin was obtained from SK UCB Co. (Korea). 2-Hydroxypropyl acrylate (HPA), 1,6-hexanediol diacrylate (HDDA), and trimethylol propane triacrylate (TMPTA) were obtained from MIWON Commercial Co. (Korea) and used as reactive diluents. The photoinitiator, dimethylhydroxyacetophenone, was also obtained from MIWON Commercial Co. (Korea).

Preparation of UV-Curable Epoxy Coatings

UV-curable epoxy coatings consist of oligomers, monomers, and a photoinitiator, with no additives. Because the objective of this paper was to confirm the functionality effects of the monomers, the oligomer and photoinitiator contents were the fixed and the monomers ratio was varied.

Hardness

Pencil Hardness

The film hardness determined using the pencil test, a rapid and inexpensive method to determine the film hardness of an organic coating on a substrate, has been used in the coating industry for many years. A coated sample is placed on a firm horizontal surface and the pencil is held firmly against the film at a 45° angle and pushed away from the operator in a 6.5 mm stroke. The measurement of pencil hardness begins with the hardest pencil and continues down the scale to determine the minimum hardness able to scratch the surface of the cured film (ASTM D 3363-74, 2000).

The pencil hardness was measured using a No. 553 pencil hardness tester (Yasuda Seiki Seisakusho LTD.) with a 500 gf. loading. Pencils were supplied by Staedtler Mars Lumograph 100 (Germany).

Table 1. Chemical Structures of Materials

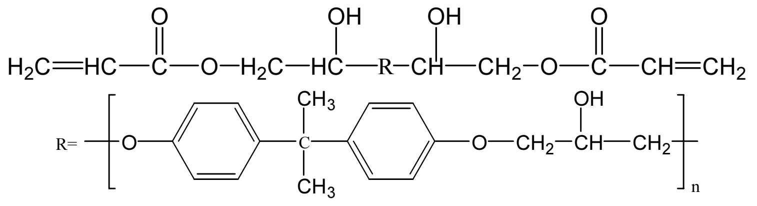
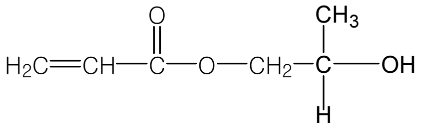
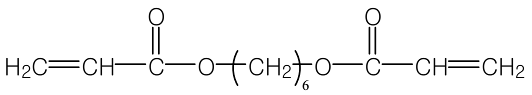
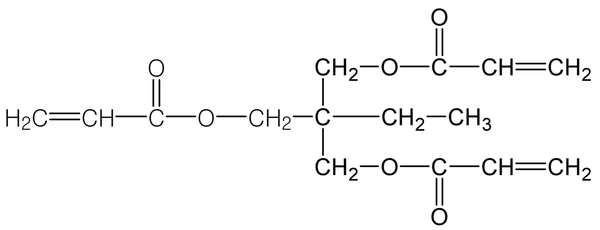
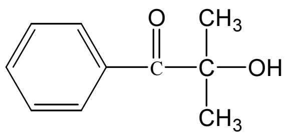
Types	Chemical structures
Oligomer	 Epoxy Resin
Monomers	 $H_2C{=}CH{-}C({=}O){-}O{-}CH_2{-}CH(CH_3){-}OH$ HPA
	 $H_2C{=}CH{-}C({=}O){-}O{-}(CH_2)_6{-}O{-}C({=}O){-}CH{=}CH_2$ HDDA
	 TMPTA
Photoinitiator	 Dimethylhydroxyacetophenone

Table 2. Formulations of UV-Curable Epoxy Coatings

	Formulations (wt%)				
	Oligomer	Monomers			Photoinitiator
	Epoxy Resin	HPA	HDDA	TMPTA	Dimethylhydroxy-acetophenone
EMD	45	20	30	0	5
EMix1	45	20	24	6	5
EMix2	45	20	18	12	5
EMix3	45	20	12	18	5
EMix4	45	20	6	24	5
EMT	45	20	0	30	5

Pendulum Hardness

A König pendulum hardness tester (Sheen Instruments Ltd, UK) was used to monitor the surface hardness of the cured film during UV curing. After UV exposure, the pendulum hardness of the UV cured film surface was measured with respect to the pendulum oscillation time from 6° to 3° at 23±1 °C and 50±2 % R.H., as illustrated in Figure 1. The pendulum hardness test is based on the principle that the harder a measured surface, the greater the amplitude time of pendulum oscillation (ASTM D 4366).

The König pendulum consists of a triangular open framework with an adjustable counterpoise weight; it weighs 200±0.2 g. The pendulum pivots on two bearings of 5 mm diameter that rest on the test surface [9,10].

Microhardness

The microhardness was measured using a computer-controlled Fischerscope H100 XYp microhardness tester to monitor the surface hardness of the cured film during UV curing. The universal hardness HU and plastic hardness HU_{pl} measured by this apparatus are defined by Equations (1) and (2).

$$HU = F_{max} \;/\; 26.43 \times (h_{max})^2 \qquad (1)$$

$$HU_{pl} = F_{max} / 26.43 \times (h_{corr})^2 \qquad (2)$$

where F_{max} is the indentation maximum force, h_{max} is the indentation maximum depth, and h_{corr} is the bounced back indentation depth in Figure 2. The mechanical work W_{total} expended during the indentation of the indenter is only partially consumed as plastic deformation work W_{plast}. The remainder is released upon unloading as elastic recovery work W_{elast}. The elastic portion (η_{IT}) of the indentation work of a sample is given by Equation 3.

$$\begin{aligned}\eta_{IT} &= W_{elast} / (W_{elast} + W_{plast}) \times 100 \\ &= W_{elast} / W_{total} \times 100 \qquad (3)\end{aligned}$$

The indenter used to measure the microhardness was a Vickers diamond indenter. The microhardness tests were performed at a maximum load of 10 mN. The loading time was 20 s. This experiment was performed according to ISO 14577-1.

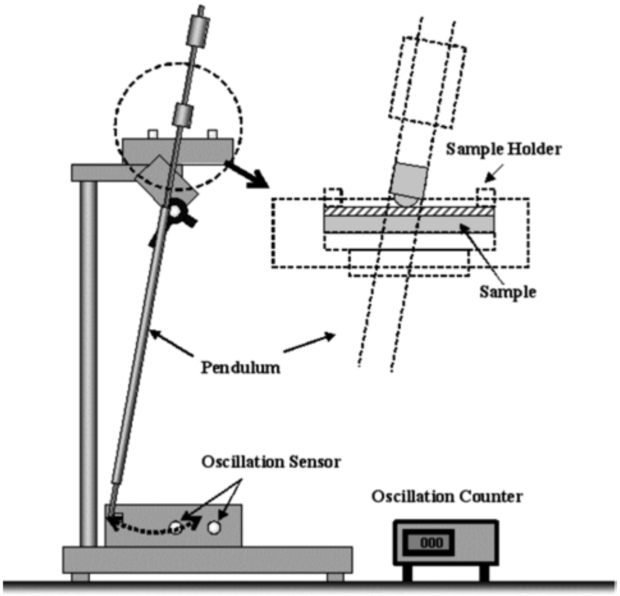


Figure 1. Schematic illustration of the pendulum hardness tester.

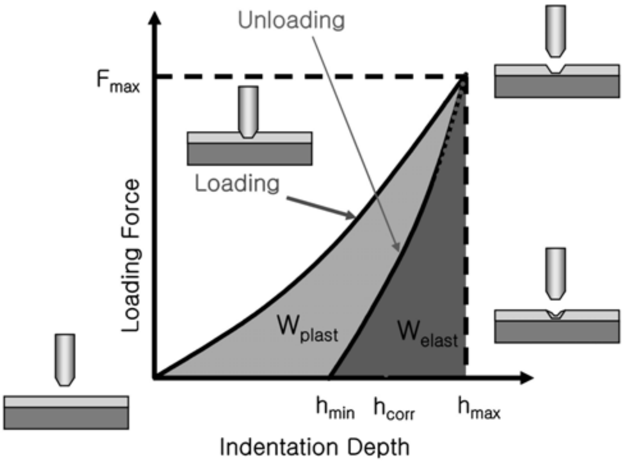


Figure 2. Schematics illustration of the process for measuring microhardness.

Results and Discussion

Hardness is one of the most important properties of a coating surface. There are three methods used to measure the surface hardness of a coating. The pencil hardness test is commonly used in industry, as is sometimes the pendulum hardness test. These methods give more approximate hardness values than does the microhardness test. Therefore, in this study we used these three methods to measure the hardness of coating surfaces in

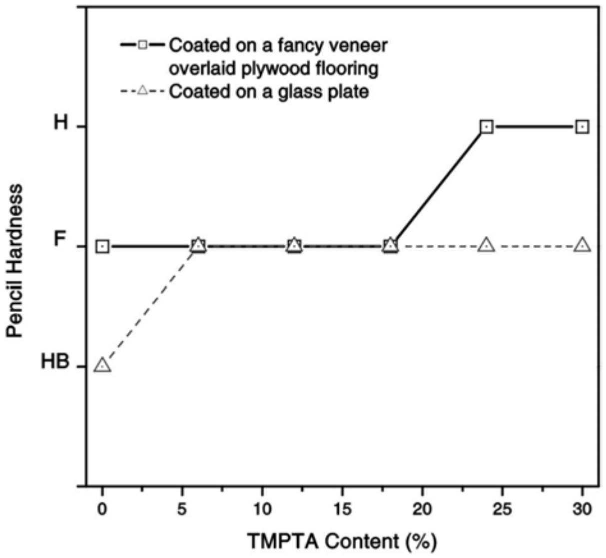


Figure 3. Pencil hardness of cured films coated on a fancy veneer-overlaid plywood flooring and on a glass plate at various TMPTA contents.

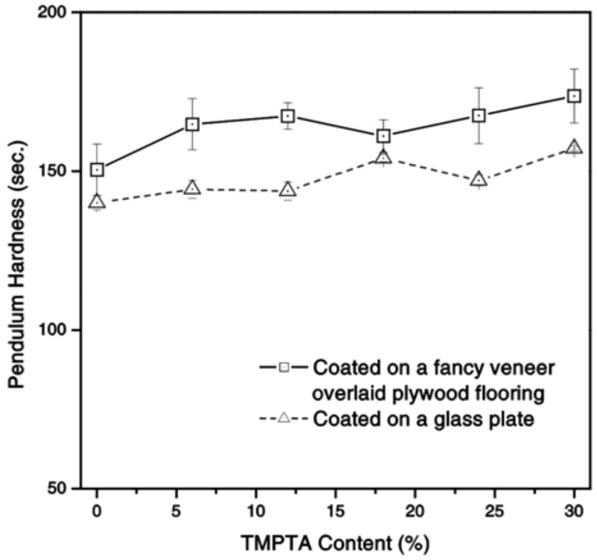
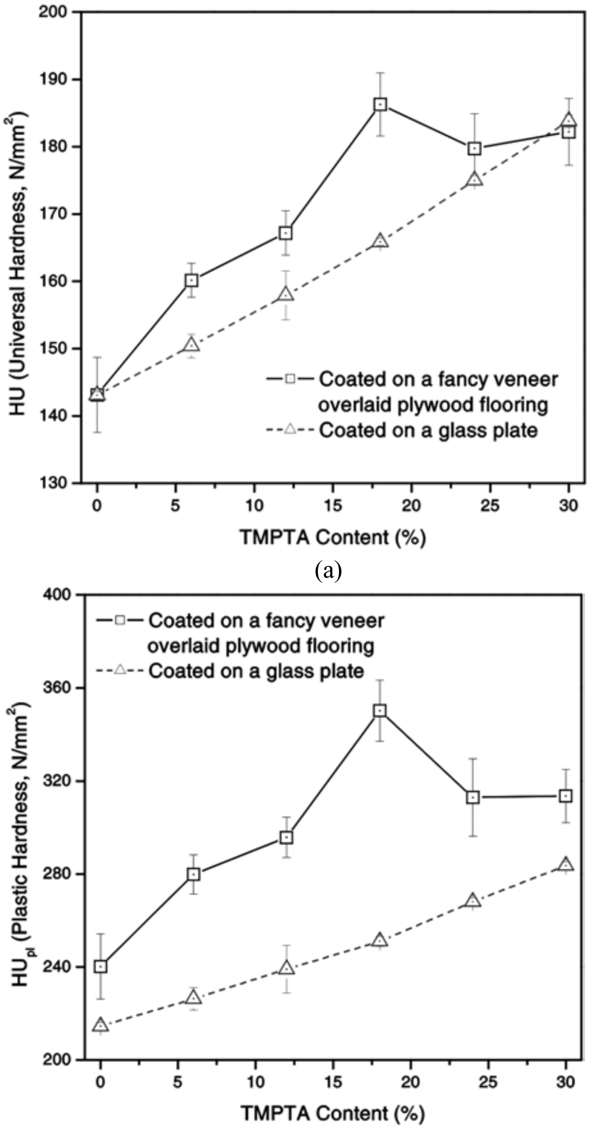


Figure 4. Pendulum hardness of cured films coated on a fancy veneer-overlaid plywood flooring and on a glass plate at various TMPTA contents.

an attempt to compare the results. Two different substrates were employed to determine the effect of the substrate: a glass plate and a fancy veneer-overlaid plywood flooring.

Figure 3 shows the pencil hardness of the cured film which was coated on a fancy veneer-overlaid plywood flooring and a glass plate at various TMPTA contents. The pencil hardness of the cured films coated on both substrates, measured between HB and H, were almost flat. However, the pencil hardness of the cured film coated on a fancy veneer-overlaid plywood flooring increased upon increasing the TMPTA content at higher TMPTA content and was higher than that on a glass plate.



(a)

(b)

Figure 5. (a) Universal hardness and (b) plastic hardness of cured films coated on a fancy veneer-overlaid plywood flooring and on a glass plate at various TMPTA contents.

The pendulum hardness of the cured films coated on a fancy veneer-overlaid plywood flooring and a glass plate at various TMPTA contents is shown in Figure 4. The pendulum hardness of the cured films coated on the two substrates showed similar tends, but the pendulum hardness of a cured film coated on a fancy veneer-overlaid plywood flooring was higher than that on a glass plate. The pendulum hardness displayed a distinct difference between the hardness of cured films coated on a fancy veneer-overlaid plywood flooring and a glass plate.

Figure 5 shows the universal hardness (a) and plastic hardness (b) of cured films on the two substrates at various TMPTA contents. The values of universal hard-

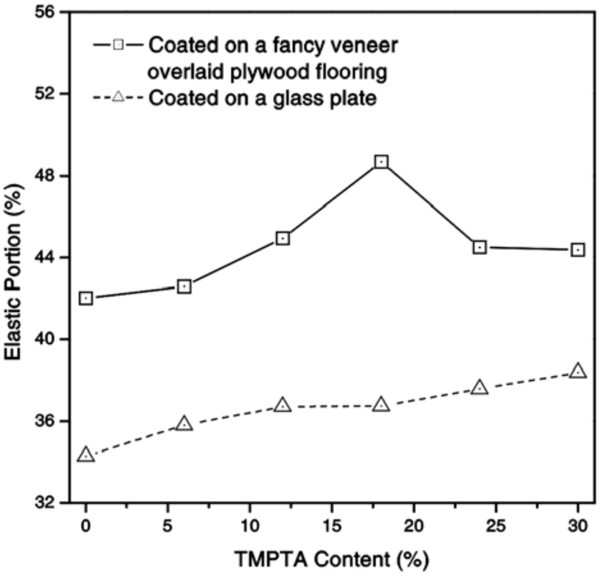


Figure 6. Elastic portion of cured films coated on a fancy veneer-overlaid plywood flooring and on a glass plate at various TMPTA contents.

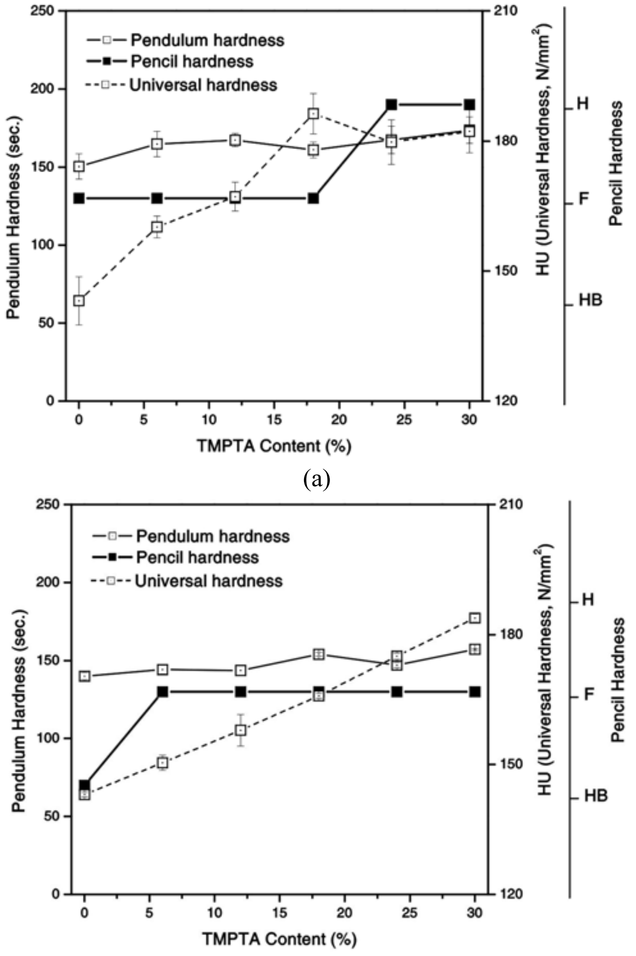
ness and plastic hardness follow similar trends, but do not conform exactly. Because the plastic hardness incorporates the elastic recovery of the cured film, its values were higher than those of the universal hardness. The microhardness showed a greater gradient than the pendulum hardness in terms of increasing TMPTA content.

All three methods provided similar results in that the hardness of the films coated on the fancy veneer-overlaid plywood flooring was higher than that on the glass plate. This result is due to the effect of the substrate. For a soft film on a hard substrate, the hardness is decreased; for a hard film on a soft substrate, the hardness increased [11-14]. The hardness of UV-curable epoxy coatings was higher than that of the fancy veneer-overlaid plywood flooring, but lower than that of the glass plate. Therefore, the hardness of the cured film on the fancy veneer-overlaid plywood flooring was higher than that on the glass plate.

Figure 6 shows the elastic portion of cured films coated on the two substrates at various TMPTA contents. The elastic portion of the cured films was not a viscous area, but the elastic area of the film. The film recovery did not appear if the elastic portion was 100 %, only if it was less than 100 %. The elastic portion of the cured films followed similar trends with respect to the microhardness results, but did not conform exactly. The elastic portion increased upon increasing the TMPTA content.

As shown in Figures 3～ , the properties of the cured films coated on the two substrates were similar, but did not conform exactly. The hardness values tended to be higher on the fancy-veneer overlaid plywood flooring than on the glass plate.

Figure 7 shows the pencil, pendulum, and universal hardnesses of the cured films coated on (a) a fancy veneer-overlaid plywood flooring and (b) a glass plate, to visualize their intercorrelations. All three methods for measuring hardness follow similar trends, and the film surfaces exhibited increased hardness upon increasing the TMPTA contents and with the higher functionality of the acrylate end group. Nevertheless, the microhardness test provided the most definitive results, confirming that this method is the most appropriate among the three, followed by the pendulum hardness test and, lastly, by the pencil hardness test.



(a)

(b)

Figure 7. Correlation between pendulum hardness, microhardness, and pencil hardness at various TMPTA contents: (a) coated on a fancy veneer-overlaid plywood flooring; (b) coated on a glass plate.

Conclusions

This study investigated the relationship between three hardness tests of UV-curable epoxy acrylate coatings at various acrylate monomer mixing ratios. The hardness values (pencil hardness, pendulum hardness, and microhardness) of the cured film increased upon increasing the TMPTA content. The hardness was affected by the hardness of substrate: the harder the substrate, the lower the hardness of the cured film. The sensibility test surface hardness of cured films followed the order micro-hardness > pendulum hardness >> pencil hardness.

Acknowledgment

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