High chemical resistant, high scratch resistant new UV-PUD

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In the field of wood & flooring industry, UV-PUDs are used as environmentally-friendly materials and the interests in these materials for furniture application are rapidly growing in emerging markets including China. General requirements for PUD's in furniture include high chemical resistance, hardness, scratch resistance, and compatibility with pigments and adhesion. In this paper we discuss UV-PUD's suitable for the furniture industry which show good chemical resistance and scratch resistance compared with conventional PUD's.

The advantages of water-based technology are that they are VOC-free and are applied by spray coating, thanks to their low viscosity, and these are considered unique properties compared to other coating types. It is well known that UV technology has advantages of fast curing speed, high productivity and good coating performance. UV-PUD is the combination of the best benefits from water-based and UV technologies. Unlike general UV polymers that incorporate diluting monomers, UV-PUD's have low viscosity in nature and are almost free of VOCs and they are non-irritating to the skin and eyes. Thus UV-PUD's are benefiting from a consistent growth in environmentally-friendly needs.

UV-PUD's are used in wood furniture as environmentally-friendly materials and their usage continued to rise in recent years. Low viscosity materials are needed in spray coating systems that are widely used in furniture, so UV-PUDs can be advantageous in this application. For topcoat use in furniture, the required properties include good chemical resistance, good scratch resistance, good adhesion, good leveling and high hardness. Especially high chemical resistance and scratch resistance are widely requested from American, European and Asian furniture markets including China and Korea.[1]
European market requires additionally tin-, BPA- and APEO-free compounds.

In preparing UV-PUD's, the prepolymer is synthesized first and dispersed into water. The polymeric structure of waterborne PUD's are usually formed by reacting an excess of aliphatic isocyanates with a polyol or mixture of polyols to form a prepolymer containing so called soft segment. The polyols are generally polyesters or polyethers. The hard segment comes from the urethane and urea domains which can have hydrogen bondings. Prepolymers can be prepared by optimal compostion of soft and hard segment, ionomer as well, and ionomer can provide dispersion stability. Then the prepolymer should be added into water, leading to UV-PUDs with nanometer-scale particle size. To improve hardness, high portion of hard segment and high cross-linking ratio are generally needed. However UV-PUDs in this case show low flexibility and poor adhesion property caused by relatively big shrinkage during the cure process. This means that the best selection of raw materials and composition is required. In this paper, we discuss the experimental results of UV-PUDs specifically designed for this purpose.

Experiment

It's not difficult to make 100 % radiation curable urethane acrylate resin having high chemical resistance and high scratch resistance. But in case of UV-PUDs, there are many limitations in process design because dispersion stability is very important. However we need to increase hard segment and use high functional group to achieve high cross-linking ratio, and high molecular weight prepolymer is also needed. The viscosity of prepolymer should increase and high viscosity can lead to a defect in dispersion process, which then may cause poor dispersion stability. Also storage stability becomes worse and wetting properties tend to deteriorate consequently. Optimizing composition of UV-PUDs can help reduce the defects. The purpose of experiment in this paper is to demonstrate good hardness, while maintaining minimized defects.

The basic components used to build up UV-PUDs include polyether, polyester, diisocyanate, aromatic or aliphatic, and acrylate compounds having double-bond for radiation curing, and neutralization base. A large number of compositions have been tested to obtain stable dispersion which shows various properties.

In this study, different isocyantes were used and various polyester polyols and acrylic compounds as unsaturated alcohols. Characteristics are described in Table 1.

- Table 1 –

	Resin soilds content [%]	Viscosity[cps,25℃]	pH	Particle Size[nm]
UV-WB-A	35	40	8,5-9.0	80
UV-WB-B	35	40	8,5-9.0	65
UV-WB-C	35	20	8,5-8.9	90
UV-WB-D	35	20	8,5-8.7	80
UV-WB-P	40	20	7,0 -7.5	75

UV-WB-A/B/C/D were designed for topcoat formulation, and UV-WB-P was prepared for primer use. These UV-PUDs were formulated for testing in wood application. All formulations included photoinitiator, which was adjusted to be equal in solids content.

Beech wood panels were mainly used for testing, because beech was widely used furniture market including China and Korea. All wood substrates were coated by UV-WB-P at a wet film thickness 90 ㎛(0.09mm), dried by air for 10minutes, dried in oven at 80℃(176℉) for 10 minutes. Then cured by UV and stored for 24hours. Beside wood beech panel, Leneta card and Glass panel were also used in some testing.

Test methods

Chemical Resistance

Chemical resistance was measured by the following procedures

1. Coat UV-WB-P on panel at a wet film thickness 90㎛(0.09mm), air dry 10 minutes. > 80℃(176℉) dry 10 minutes
2. UV curing
3. Sanding with #180 sand paper
4. Coat UV-PUD on panel at a wet thickness 90㎛(0.09mm), air dry 10 minutes > 80℃(176℉) dry 10 minutes

5. UV curing
6. Stored for 24hours after curing

As for 2K product, followed the below procedures

1. Coat UV-WB-P on panel at a wet thickness 90㎛(0.09mm) , air dry 10 minutes > 80℃(176℉) dry 10 minutes
2. UV curing
3. Sanding with #180 sand paper
4. Coat 2K on panel at a wet thickness 90㎛(0.09mm), air dry 10 minutes > 60℃(140℉) dry for approx. 2 hours
5. Stored for 24hours

Applied enough chemical to create a 0.5~1.0cm diameter spot on the test panel. Waited for 16~24 hours and removed chemicals using water/ethanol. Checked the surface condition of the panel such as softening, stain, destruction etc.
Rated each chemical on a scale of 1 to 5 (1 being no effect on the film and 5 being complete destruction)
Leneta card was also used for the test of chemical resistance without primer coating. Chemicals used were coffe, espresso, cola, ketchup, hand cream, ethanol (50%), and mustard.

Scratch Resistance

As for scratch resistance, a steel wool tester was used. A Leneta card without primer coating was used for the test of scratch resistance. Coated UV-PUD on panel at a wet film thickness 75㎛ (0.075mm) and dried in air for 10minutes, then dried in oven at 80℃(176℉) for 10minutes. Cured with a mercury lamp at 1,400mJ/cm^2 and waited for 24hours before testing. The coated surface was subjected to steel wool tester platform. Placed a 500g(1.1023lb) weight on surface of coating, and slid back and forth at constant velocity for 20cycles. We then removed the weight and checked the loss(%) of gloss(60℃(140℉)) at each 5cycles.

Coin Scratch

As for coin scratch test, beech wood panel coated primer was used. Coated UV-PUD's on panel at a wet film thickness 90㎛(0.09mm) and dried in air for 10minutes, then dried in oven at 80℃(176℉) for 10minutes. Cured with a mercury lamp at 1,400mJ/cm^2 and waited for 24hours before testing. Pushed coin heavily on surface of coating at a 45^o angle and checked the condition of surface of panel. Rated each samples on a scale of 1 to 5 (1 being no effect on the film and 5 being complete destruction)

Abrasion (Taber)

As for abrasion test, Taber was used. Beech wood panel coated primer was used. Coated UV-PUD on panel at a wet film thickness 90㎛(0.09mm) and dried in air for 10minutes, then dried in oven at 80℃(176℉) for 10minutes. Cured with a mercury lamp at 1,400mJ/cm^2 and waited for 24hours before testing. The coated surface was subjected to steel wool tester platform. Tested abrasion for 200cycles, measured weight loss by 5cycles

Pendulum Hardness (Koenig)

As for pendulum hardness (Koenig), glass panel was used. Coated UV-PUD on glass panel at a wet film thickness 60㎛(0.06mm) and dried in air for 10minutes, then dried in oven at 80℃(176℉) for 10minutes. Cured with a mercury lamp at 1,400mJ/cm^2 and waited for 24hours before testing. Measured Koenig hardness (sec.)

Pencil Hardness (ASTM D3363-05)

As for pencil hardness, glass panel was used. Coated UV-PUD on glass panel at a wet film thickness 60㎛(0.06mm) and dried in air for 10minutes, then dried in oven at 80℃(176℉) for 10minutes. Cured with a mercury lamp at 1,400mJ/cm^2 and waited for 24hours before testing. Started with a dry, clean, well-sanded piece of wood. Determined pencil hardness after removing graphite dust by prepared rubber. Determined the first pencil that did not scratch the surface of coating.

$$\underset{\text{Softer} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{Harder}}{\underline{6B-5B-4B-3B-2B-B-HB-F-H-2H-3H-4H-5H-6H}}$$

Weathering Test (QUV)

As for weathering test (QUV), Q-panel was used. Coated UV-PUD on glass panel at a wet film thickness 60㎛(0.06mm) and dried in air for 10min, then dried in oven at 80℃(176℉) for 10minutes. Cured with a mercury lamp at 1,400mJ/cm^2 and waited for 24hours before testing. Tested yellowing at 60℃(140℉) with QUV.

Heat stability

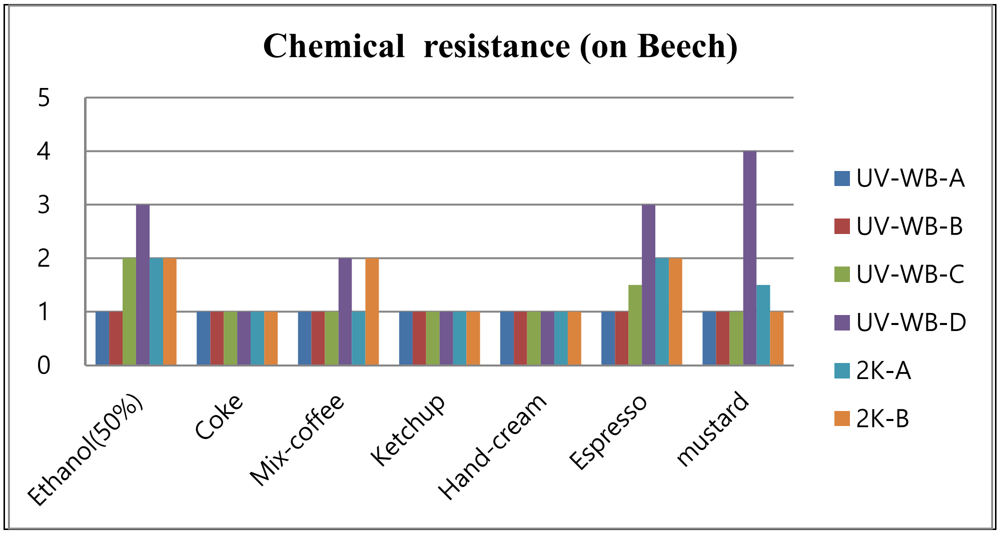
100ml of UV-PUDs were charged into 200ml glass bottle. Placed in oven at 60℃(140℉) for 7days. Checked the sample conditions, such as sedimentation, big visible particles, separated layers. Rated each samples on a scale of 1 to 5 (1 being no sedimentation and visible particle and 5 being complete sedimentation)

2K-urethane for comparison

In this evalutation, two commercial two-component (2K) solvent-borne urethane varnishes were included for comparison. The first (2K-A) is widely used in the market of furniture topcoat in Asia, and this varnish needs isocyanate for crosslinking. The other (2K-B) is widely used in the market of plastic coating, especially coating for cellular phones in Asia. Same panels with UV-PUDs were used for testing. In case of wood beech, the primer-coated panels were used. Coated vanish on panel at a wet film thickness 90㎛(0.09mm) and dried in air for 10minutes, then dried in oven at 60℃(140℉) for 2hours and waited for 24hours before testing.

Results and Discussion

Figure 1



Chemical resistance testing was performed on both wood beech panel (Figure1) and Leneta card (Figure 2). UV-WB-A/B/C show good chemical resistance, especially in ethanol and mustard, UV-WB-A/B are better than 2K varnish. In case of coke, ketchup and hand-cream, all samples including 2K show good chemical resistance, but as for mix-coffee and espresso, UV-WB-D and 2K samples are weaker compared to other samples. UV-WB-A/B/C incorporated polyester polyol with low molecular weight, whereas U-WB-D a polyether polyol is used. Polyester polyol used in UV-WB-A/B/C, even though it is soft segment, was selected among many polyester polyols by evaluation of chemical resistance, so that it reacted with diisocyanate to form hard urethane domain, which then leads to good chemical resistance. Weight(%) ratio of hard segment of UV-WB-A/B/C would be higher than that of UV-WB-D since the molecular weight of the polyether polyol used in UV-WB-D is much higher than the polyester polyol used in UV-WB-A/B/C. The cross-linking density of UV-PUD is obviously higher than 2K varnishes because acrylate compounds are incorporated into UV-PUD, so the high cross-linking density is the major reason UV-A/B/C show better chemical resistance.

Figure 2

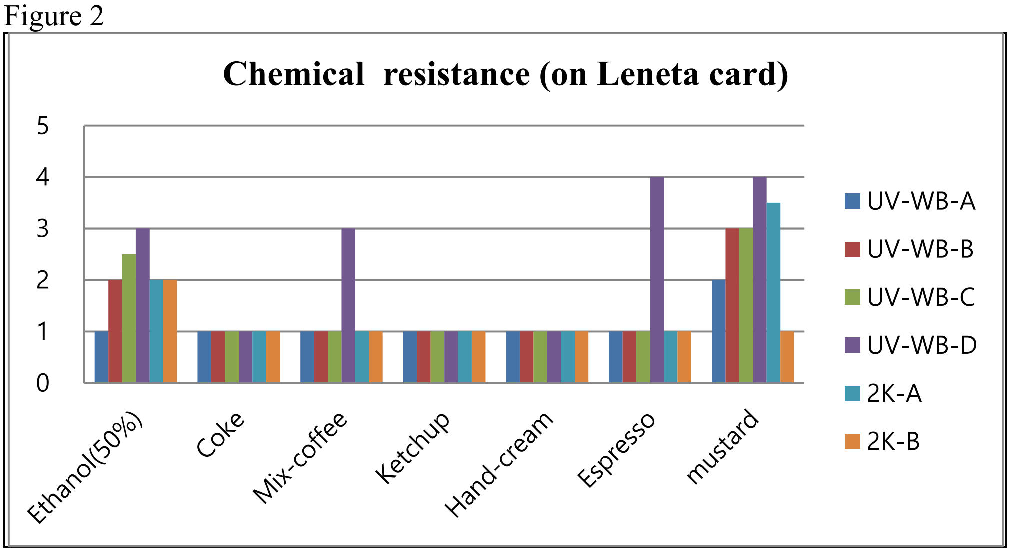


Figure 3

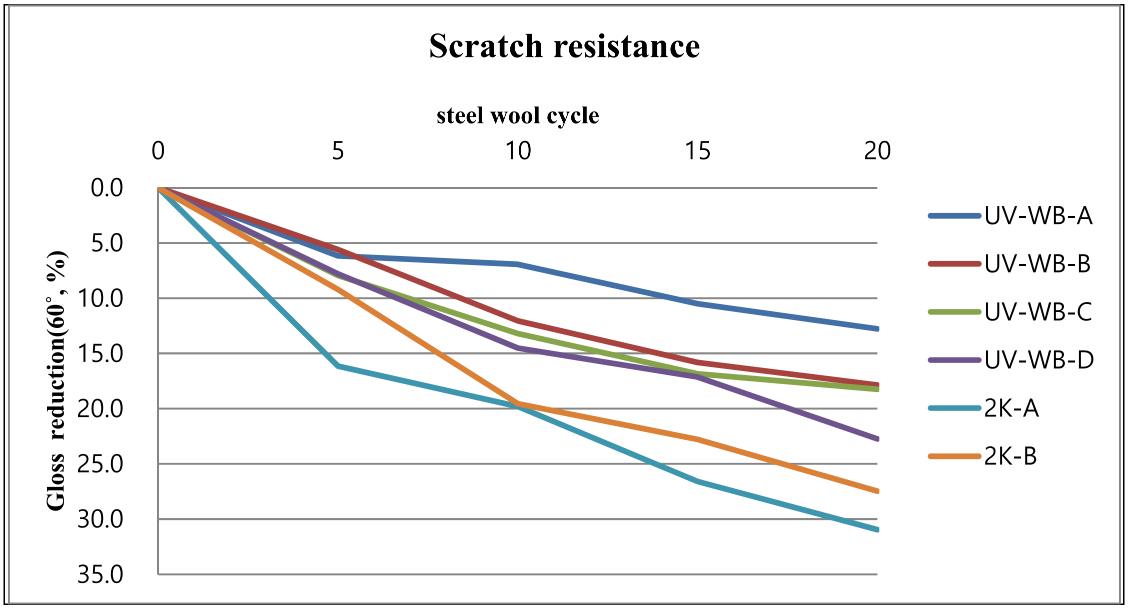


Figure 3 shows the evaluation results for scratch resistance. UV-WB-A/B/C show much better scratch resistance than 2K varnishes, and UV-WB-D also shows good scratch resistance as well. This result is different from the case of chemical resistance. Superior scratch resistance of UV-PUD compared to 2K varnishes is a result of high cross-linking density of UV-PUD since UV-PUD used acrylate which can develop dense cross-linked network.

As for coin scratch resistance, all samples except 2K-A show good performance. The scratch resistance of UV-PUDs is better than 2K varnishes overall.

As for abrasion test, UV-WB-A/B and 2K-B show relatively good performance, while UV-WB-C/D and 2K-A show inferior performance. (Figure 4) However the difference between samples are not so big compared with the case of chemical resistance and scratch resistance. 2K-B shows better abrasion performance than 2K-A,

Figure 4

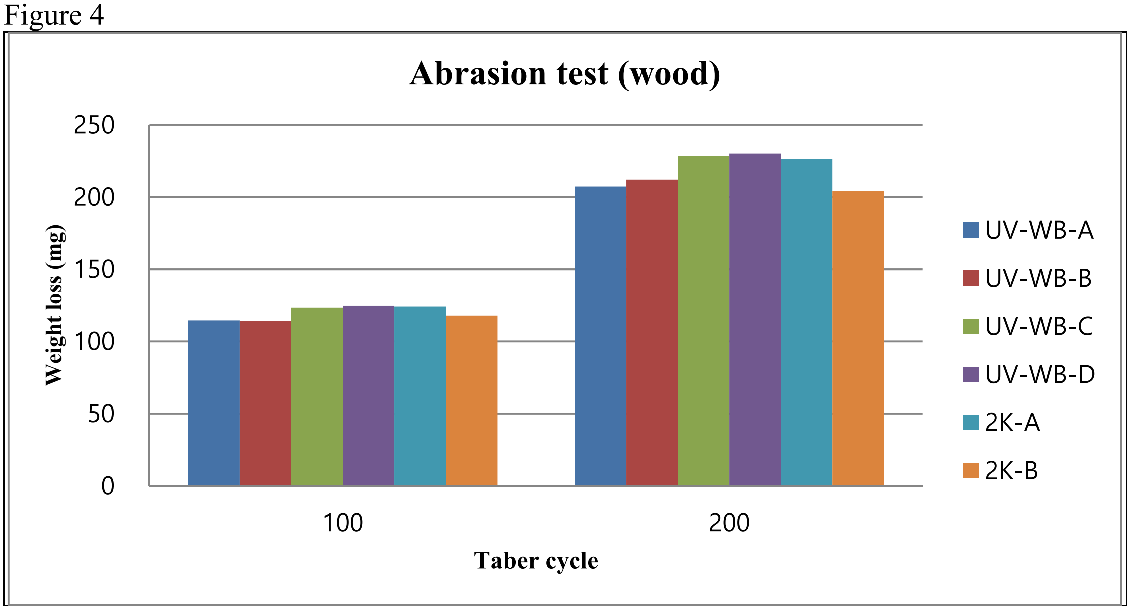
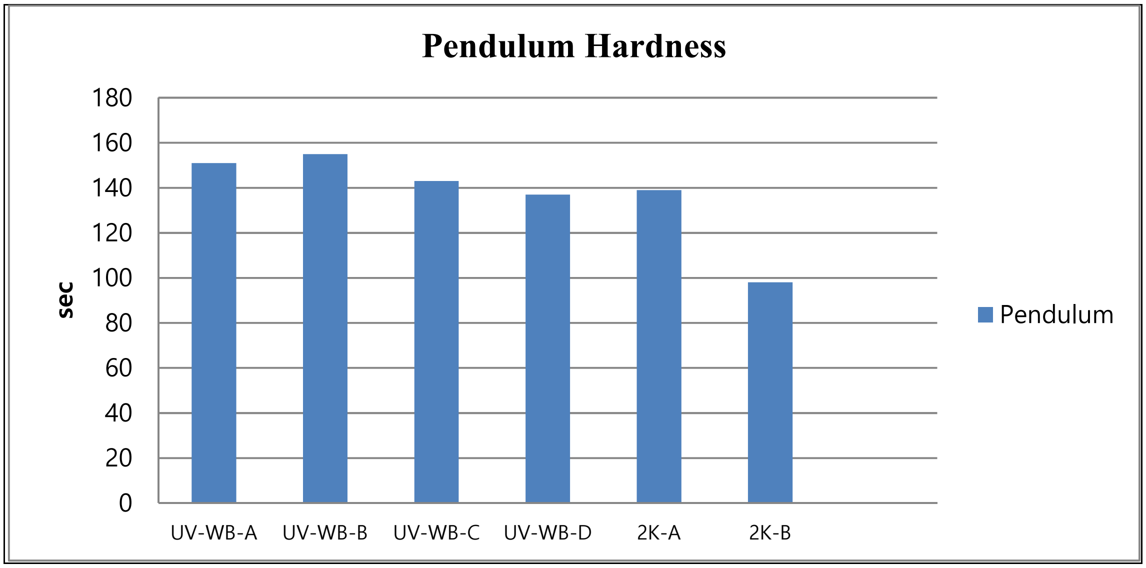


Figure 5



As for pendulum hardness, UV-PUDs show higher hardness than 2K varnishes. (Figure 5). As for pencil hardness, UV-WB-A ranks top in hardness.

Figure 6

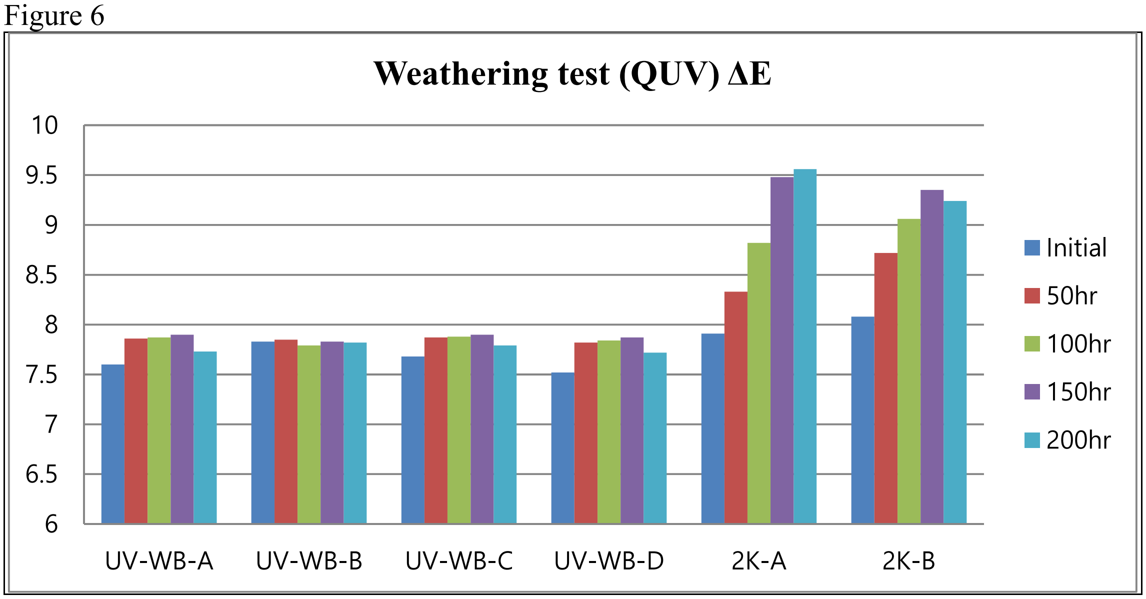


Figure7

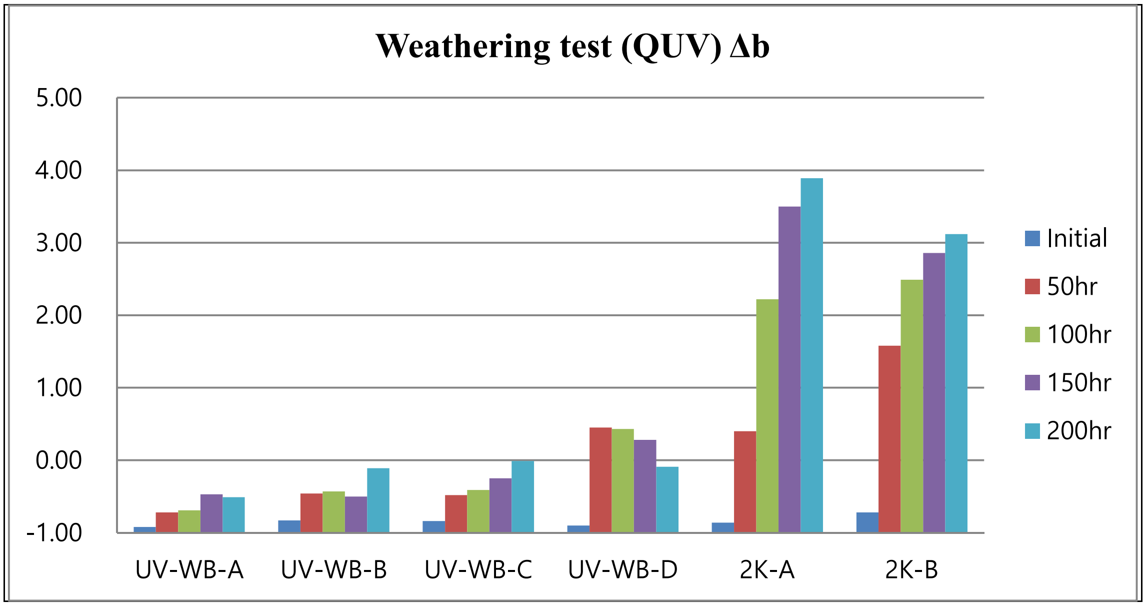


Figure 6&7 show the evaluation result of accelerated weathering test. There are big difference in performance between UV-PUDs and 2K varnishes. This gap come from aromatic component of 2K-B and phthalic component of 2K-A.

Conclusion

Excellent chemical and mechanical performance of UV-PUDs can be obtained by incorporating proper polyols and cross-linking of acrylates. UV-PUDs can show high hardness, good chemical resistance, good scratch resistance, abrasion and adhesion which are required in the field of furniture topcoat, and optimal design and composition of UV-PUDs can meet various market needs. UV-PUDs in this study performed very well in all test areas compared with 2K varnishes that are widely used as standard materials in wood. UV-PUDs provide the advantages of spray coating by low viscosity and the advantages of safe application by VOC-free composition, so these advantages draw more interests in wood market, where regulations for environment becomes more strict as time goes on. UV-PUDs will be highly valued as the solution that helps to meet both performance and important needs from an environmental perspective, and the penetration into wood coating market will be accelerated.

It is expected that UV-PUDs will soon be considered for broader areas, such as plastic, OPV and concrete tiles. Further developments are actively progressing to achieve tin-free, harmful materials-free, favorable chemical and mechanical resistance so as to meet needs of other applications.

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