

Structure-property relationship study of UV-curable polyurethane dispersions

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Abstract

UV-curable waterborne resins are drawing more attention due to the combined advantages of UV-curable coatings and waterborne coatings, like easy to matte, monomer free, etc. Achieving good chemical resistance and physical drying from a waterborne UV coating, however, is always a challenge. In this paper, the physical performance of several UV-curable polyurethane dispersions will be discussed along with the structure-property relationship study.

1. Introduction

UV/EB curing has gained more attention in the coatings industry in recent decades.^[1-3] UV/EB curing can provide chemical resistance and hardness to coatings due to the high crosslink density of the film.^[4] There are also concerns with promoting this technology, such as skin sensitivity, shrinkage of the coating and poor matting capability.^[5,6] Thermally-cured waterborne coatings, another popular coating technology, are easy to matte, easy to handle, and provide warmth to wood. The thermoplastic nature, however, makes them less resistant to chemicals, scratching, and makes hardness development more challenging.^[7]

UV waterborne coatings are a new coating technology that combines the advantages of UV coatings and waterborne systems.^[8-9] The typical resins of UV waterborne coatings are polymers with acrylate groups on the backbone, which provide extra crosslinking when the UV coating is dried. The concern, though, is that the physical properties, such as chemical resistance and hardness, of waterborne UV coatings, are not comparable to a 100% solid UV coating. Slow physical drying is another issue that is often debated because the industry is looking for a waterborne UV coating that can build tack-free properties faster.

Two new approaches for waterborne UV resins that obtain good chemical resistance, hardness development, and physical drying for both clear and pigmented coatings are presented and discussed in this paper. The first resin, noted as **Resin A**, used the “Container Concept,” which requires adding a high functionality reactive diluent (RD) into a polymer dispersion. The reactive diluent is captured in the colloids and dispersed in the solution. Figure 1 shows a depiction of this concept. The reactive diluent could enhance the crosslinking density of a coating during the UV curing process, which will significantly improve the physical properties.



Figure 1. “Container Concept” with added RD to improve limited double bond density of the polymer backbone

The second resin, **Resin B**, used a strategy that did not focus on increasing the crosslinking density of the coating. It contains a non-aromatic hard segment in the polymer backbone, so that the coating can have good hardness even before UV cure. This technology could be a good fit for curved samples since shadow cure is always an issue for those samples. In addition, this resin contains an intrinsic dispersing agent which can significantly improve the pigment dispersion of the coating.

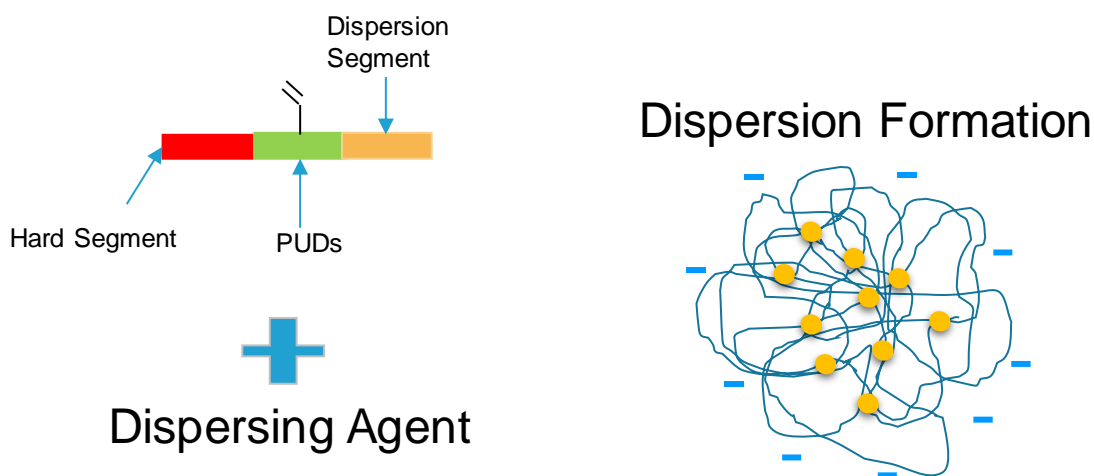


Figure 2. Concept of Resin B

Resin A and Resin B are UV-curable aliphatic polyurethane dispersions and will be compared with two other commercially available UV polyurethane dispersions (PUDs) in this paper.

2. Experimental

Four waterborne UV-curable PUDs were selected for this study. The basic information of four resins is listed in Table 1.

	Resin A	Resin B	Control 1	Control 2
Viscosity @ 23C (cps)	5-350	132	50-500	50-300
Solid Content (%)	40	40	38	40

Chemistry	UV-curable Aliphatic PUDs with Reactive Diluents	UV-curable Aliphatic PUDs with Hard Segments and Intrinsic Dispersing Agent	Commercial Available UV-curable Aliphatic PUDs	Commercial Available UV-curable Aromatic PUDs
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Table 1. Resins Information

All the samples were placed in a 50 °C oven for 1 hour after draw down to remove water. An IST™ UV-curing apparatus with a medium pressure mercury lamp was used to fully cure the coatings. Details of the UV-curing information is listed in Table 2.

UV Light	Power (W/cm ²)	Dosage (J/cm ²)
UVA	0.36	0.548
UVB	0.36	0.506
UVC	0.054	0.08
UVV	0.45	0.678
Belt Speed (m/min)	10	

Table 2. UV Curing Data

Table 3 is a summary of tests that were used to evaluate the coating performance. Details of the test results are described in the next section.

Name	Test Method	Comments
Dry Time Test	ASTM D5895	Determine the physical dry capability of coating
Pendulum Hardness	ASTM D4366	Hardness of coating
Chemical Resistance	WDMA TM14-13; IKEA R2 IOS Mat 0066-P1; GMW14445	Details are included in the discussion part of paper
Scratch Resistance		Hoffman Scratch Tester
Taber Abrasion	ASTM D4060	
Matting Efficiency		Gloss of matted coating
Impact Resistance	ASTM D 4266	Toughness of coating
Conical Mandrel Bend	ASTM D 522	Stretch ability
Pigment Hiding		Pigment dispersion of coating

Table 3. Summary of Tests

3. Results

Prepared clear coating formulations are listed in Table 4. All the formulations have the same amount of solid content, leveling agent, wetting agent, matting agent and photoinitiator.

Clear Coating	Resin A	Resin B	Control 1	Control 2
Resin A	75.8			
Resin B		79.8		
Control 1			75.8	
Control 2				75.8

Leveling Agent	0.8	0.8	0.8	0.8
Rheology Modifier	0.6	0.6	0.6	0.6
Wetting Agent	0.5	0.5	0.5	0.5
Matting Agent	2	2	2	2
DI Water	18.8	14.8	18.8	18.8
Photoinitiator	1	1	1	1
Defoamer	0.5	0.5	0.5	0.5
Total	100	100	100	100
Solid Content (wt %)	34.98	34.98	34.98	34.98

Table 4. Formulations for Clear Coat

3.1 Dry time test

Dry times of the clear coatings listed in Table 4 were measured by a Gardco Drying Time Recorder. The coatings were first drawn down on cold rolled steel (CRS) by RDS 70 rod at 23 °C. The recorder was immediately placed on the wet film after drawing down and recording was initiated. The dry time was determined when the Teflon ball could not leave a mark on the coating.

Figure 3 shows the test results. Coatings with Resin A and B had dry times of 18.7 mins and 20.3 mins, respectively, which were slightly shorter than the coating with the aromatic PUD (Control 2, 22.7 mins) and much shorter than the coating with the aliphatic PUD (Control 1, 33.3 mins). This indicated that both resins take less time to reach the tack-free stage.

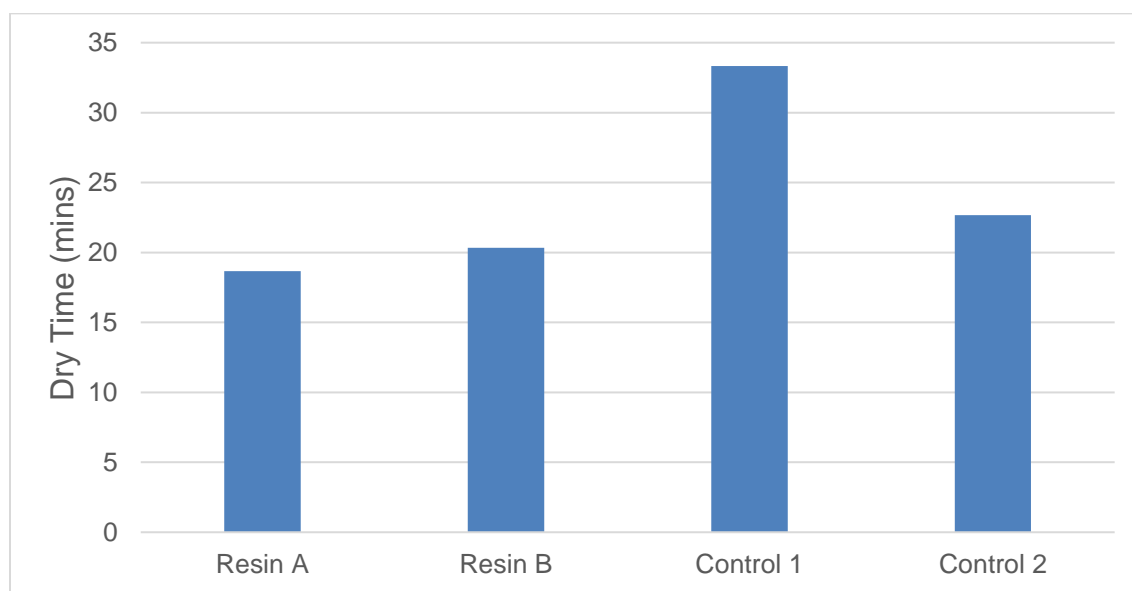


Figure 3. Dry time of clear coating formulations on CRS

3.2 Hardness and Flexibility

The hardness of the coatings before and after UV cure was measured by the König Pendulum Hardness Tester at 23 °C. Coating samples were prepared on cold rolled steel panels with a cured dry film thickness of 1.2 mil.

Test results are shown in Figure 4. The coating with Resin B had hardness of 45 swings before UV cure, which was the highest among all four coatings. This is mainly contributed by the hard segment that is grafted into the mainchain of the PUDs. This property could be beneficial to samples with a UV shadow cure issue, since the area doesn't get exposure by UV yet can still have good hardness development. After curing the coating by UV light, the hardness of the coatings was increased due to the crosslinking of the acrylate group. Coating with Resin A had the most significant enhancement of hardness from 23 swings before UV cure to 81 swings after UV cure. The existence of UV-curable monomers in Resin A provided extra crosslinking compared with the other resins.

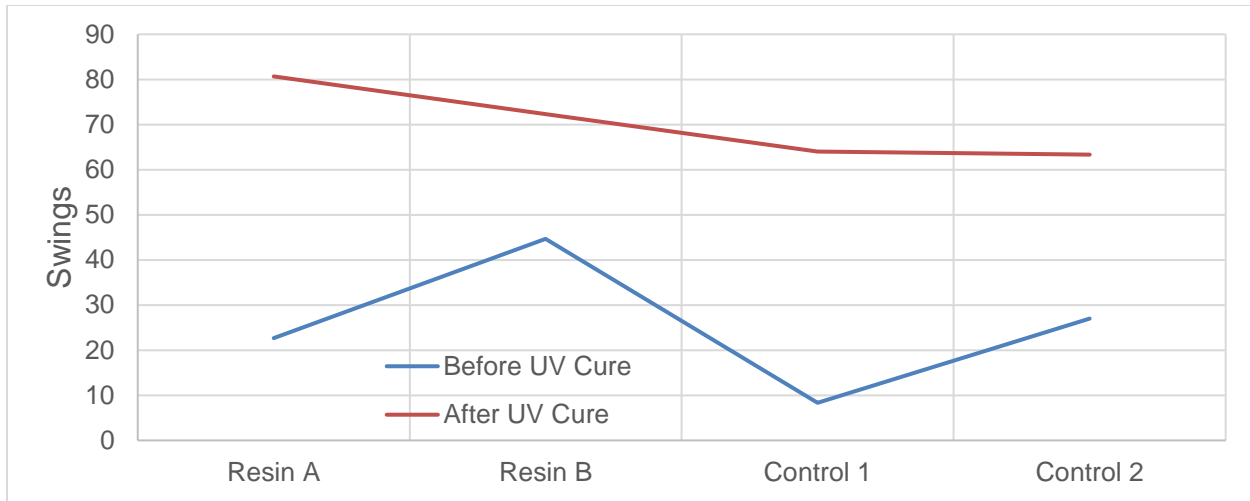


Figure 4. Pendulum hardness of the coatings before and after UV cure

Flexibility of the coating was evaluated based on the impact resistance test and conical mandrel bend test. Samples for both tests were prepared by coating on cold rolled steel with a dry film thickness of 1.2 mil. The impact resistance test followed the ASTM D 4226 test method, and it recorded the maximum force before a coating cracked. It also indicated the brittleness of the coating. The mandrel bend test followed the ASTM D 522 test method, and it recorded the elongation of the coating when it broke.

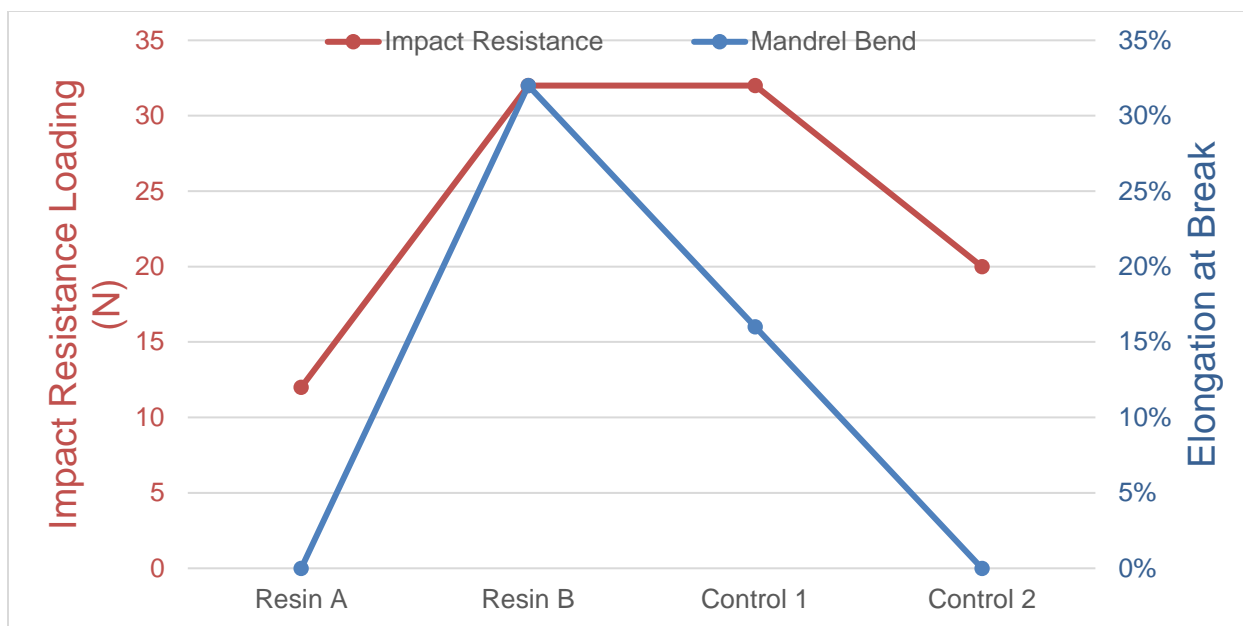


Figure 5. Impact resistance and stretch ability of the coating

Figure 5 shows the impact test and mandrel bend test results. The coating with Resin B, which contains the hard segment in the main chain, showed the best impact resistance (32 N) and elongation (>32%) among all four resins. The results indicate that it had both good flexibility and toughness. The coating with Resin A had the worst impact resistance (12 N) and elongation (0%) results, which means the coating was brittle. This is mainly because of the high crosslink density of the coating. By combining the pendulum hardness test result shown in Figure 4, we can conclude that the coating made by Resin A possessed good hardness but sacrificed flexibility due to the existence of extra UV-curable monomers.

3.3 Chemical resistance

Coatings used in the floor and furniture industry need resistance to many household chemicals. Chemical resistance of the four coatings was evaluated by chemical spot tests. The coating was first applied and cured on maple wood with a dry film thickness of 2.5 mil. The chemicals were then placed onto the coatings and covered with watch glass. Test results were evaluated after a certain period of time and rated on a zero to 5 scale, where five indicates no damage and appearance change, and zero means complete failure. Details of tested chemicals are listed in Table 5.

Test Time	Chemicals	Test Methods
5 hrs	Red Wine	
5 hrs	Mustard	
5 hrs	Black Shoe Polish	
5 hrs	Betadine	
16 hrs	Powder Coffee 40 g/l	
16 hrs	Grape Juice	
16 hrs	Lipstick	

16 hrs	Black Ball Pen Paste	WDMA TM14-13
24 hrs	Windex®	
24 hrs	Vinegar	
24 hrs	70% IPA	
24 hrs	Formula 409® Cleaner	
24 hrs	1% Dish Detergent	
24 hrs	Water	IKEA R2 IOS Mat 0066-P1.
6 hrs	Alcohol 48%	
24 hrs	Liquid Paraffin	
6 hrs	Powder Coffee 40g/l	

Table 5. Chemical resistance tests on maple

The chemical resistance test results are listed in Table 6. The total score listed in the bottom of the table is a sum of all the chemical resistance ratings, which indicates the overall chemical resistance performance of the coatings. The coating with Resin A had the best resistance performance and was able to resist most chemicals except the lipstick. This should be credited to the high crosslinking density provided by the monomers in the resin. The coating with Resin B and Control 1 had similar overall resistance rating, but Resin B had better lipstick resistance.

Chemicals	Resin A	Resin B	Control 1	Control 2
Red Wine	5	5	5	4
Mustard	5	4	5	4
Shoe Polish	5	4	4	3
Betadine	5	4	4	3
Alcohol 50%	5	5	5	5
Coffee	5	5	5	4
Grape Juice	5	5	5	5
Lip Stick	4	4	2	2
Pen Paste	1	1	1	1
Water	5	5	5	5
Windex	5	5	5	5
Vinegar	5	5	5	4
70% IPA	5	5	5	5
409 Cleaner	5	5	5	5
1% Dish Detergent	5	5	5	5
Total Score	70	67	66	60

Table 6. Chemical resistance test results

General Motor’s sunscreen and insect repellent resistance test, GMW14445, is a crucial chemical resistance test for the automotive industry. Testing was initiated by preparing the cured coating on PC/ABS (Polycarbonate/Acrylonitrile Butadiene Styrene composite) with a 1.2 mil dry film thickness. Then, the test solution was dropped onto the clean surface of the test sample in three different places and

then placed in the oven for 1 h at 80 °C. The sample was taken out of the oven to cool to 23 °C before the final reading. The evaluation was based on the appearance of the coating. Figure 6 shows the GMW14445 test results. The coating with Resin A had the best result and no appearance change was observed. Coatings with Resin B and Control 2 had slight appearance changes after the test.

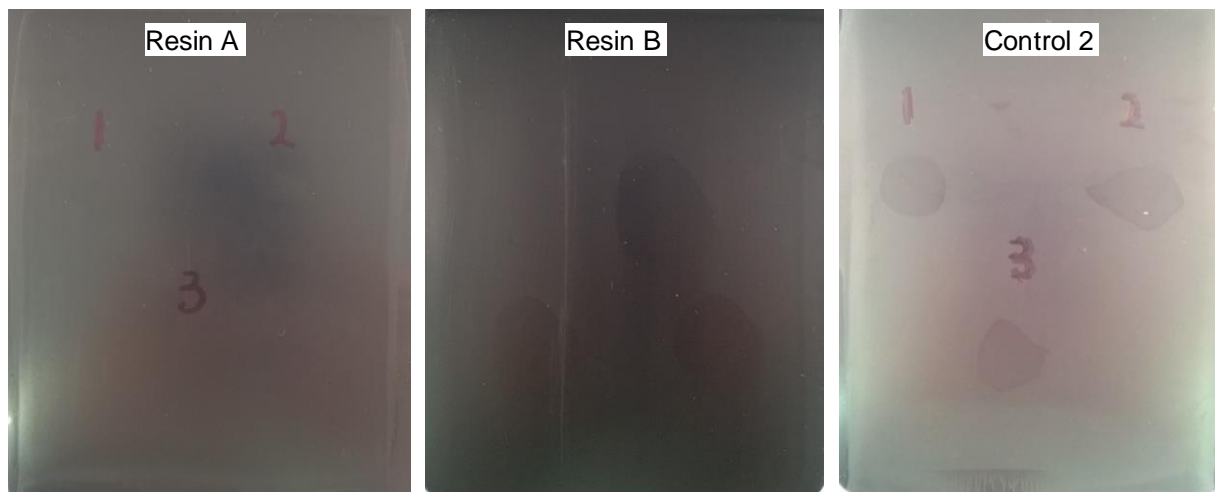


Figure 6. GM sunscreen and insect repellent resistance test on PC/ABS

3.4 Resistance to scratch and taber abrasion

Scratch resistance testing was started by applying a scratch on the coatings from the Hoffman Scratch Tester with 500g loading. The coating was prepared on cold rolled steel with 1.2 mil dry film thickness. Pictures of the scratch were then taken by KEYENCE VK-X250 confocal microscope. As shown in Figure 7, the coating with Resin A had the least amount of materials being removed. In contrast, coatings with Control 1 and Control 2 resins had significant material loss during the scratch. This indicates both Resin A and B have better scratch resistance than commercially available aliphatic and aromatic PUDs.

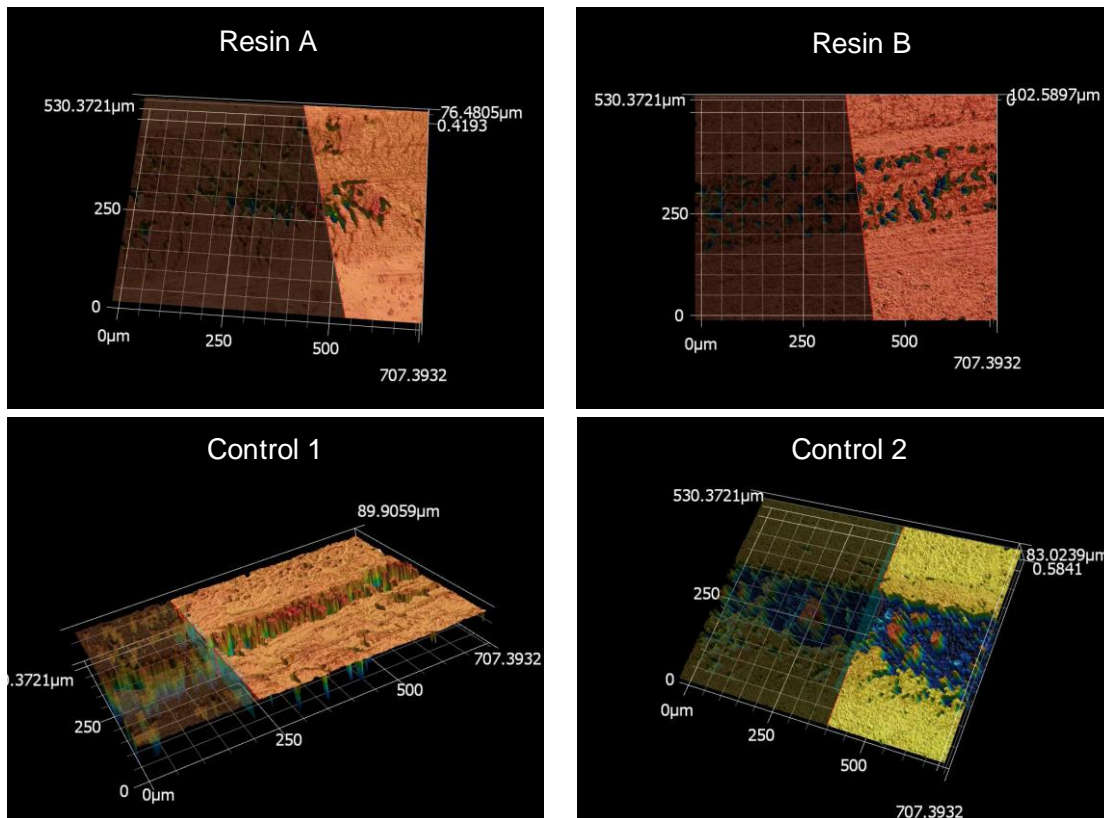


Figure 7. Confocal microscope pictures of scratched coatings

Abrasion resistance of the coatings was evaluated based on ASTM D4060 test method. Coatings were first prepared by drawing down on a glass plate. Then the water was removed by putting the glass plates in a 50 °C oven for 1 hour. The samples were then fully cured by UV light. The dry film thickness of the coating was around 2.5 mil. Five hundred cycles of abrasion were run using a CS 17 abrasion pad and 1000 g loading. Weight loss of the coatings was recorded after the test.

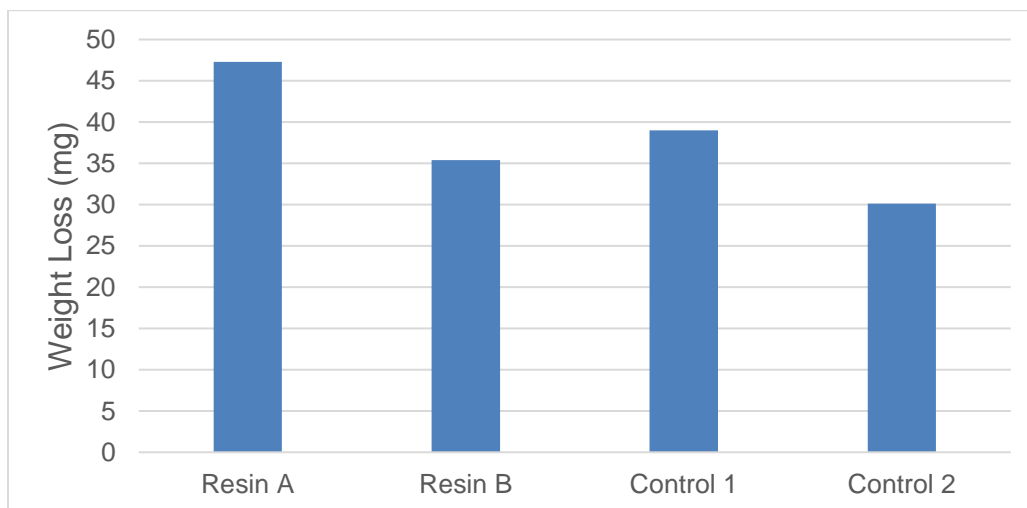


Figure 8. Weight loss of the coatings after 500 cycles of Taber abrasion test

As seen in Figure 8, the coating with Resin A had more weight loss than other PUDs, which is the opposite result of the scratch resistance test. In contrast, the coating with Resin B that contains the hard segment in the main chain showed better resistance to abrasion.

3.5 Matting efficiency

In many floor and furniture coating applications, flat sheens are desirable, as they give a natural look to wood substrates. The formulations listed in Table 4 contain 2% of silica matting agent, which is designed to achieve low gloss. The 20 degree and 60 degree gloss of the coatings were measured by BYK-Gardner Gloss Meter. Coatings were applied onto LENETA cards and UV cured with dry film thickness of 1.2 mil.

As shown in Figure 9, coatings with Resin B, Control 1 and Control 2 had similar behaviors in gloss, which is below 3 sheens at 20 degree and below 15 sheens at 60 degree. The coating with Resin A, however, appeared to have more than 30 sheens on 60 degree gloss and 5 sheens on 20 degree gloss. One of the possible reasons is the extra crosslinking contributed by the reactive diluents causing shrinkage of the coating, which ultimately affects the distribution of the matting agent.

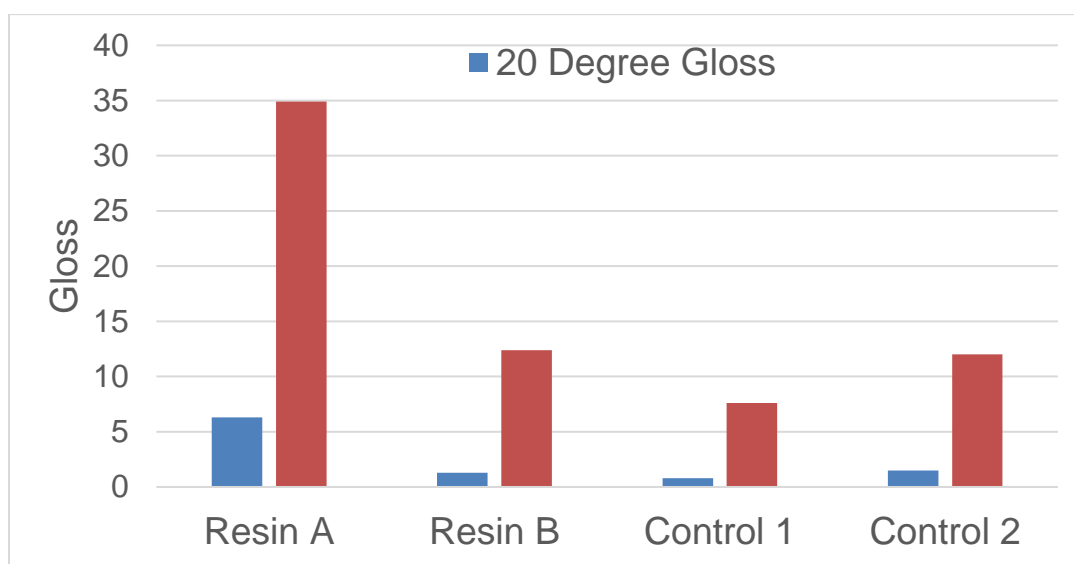


Figure 9. Gloss of the coatings

3.6 Weathering resistance

ASTM G154 test was used to evaluate weathering resistance of the coating. Coatings were drawn down on white aluminum panels, dried and UV cured with dry film thickness of 1.2 mil. Samples were then placed in a QUV Accelerated Weathering Tester under exposure of 0.55 W/m^2 , 351 nm UV light for 1000 hours. Color difference between the initial sample and weathered samples was measured to describe the weather resistance of the coatings. Coating formulations listed in Table 4 do not contain any UV absorbers or hindered amine light stabilizers (HALS).

As seen in Figure 10, ΔE of coating with Control 2 resin was above 30 after 1000 hours of UV exposure, which is much higher than the other resins. This is mainly because of the aromatic groups in the PUD backbone. Coatings with Resin A, Resin B and Control 1 had similar weathering resistance behavior. The ΔE of three resins was below three after 1000 hours of exposure; however, Resin A had the best resistance to UV with ΔE below 1.

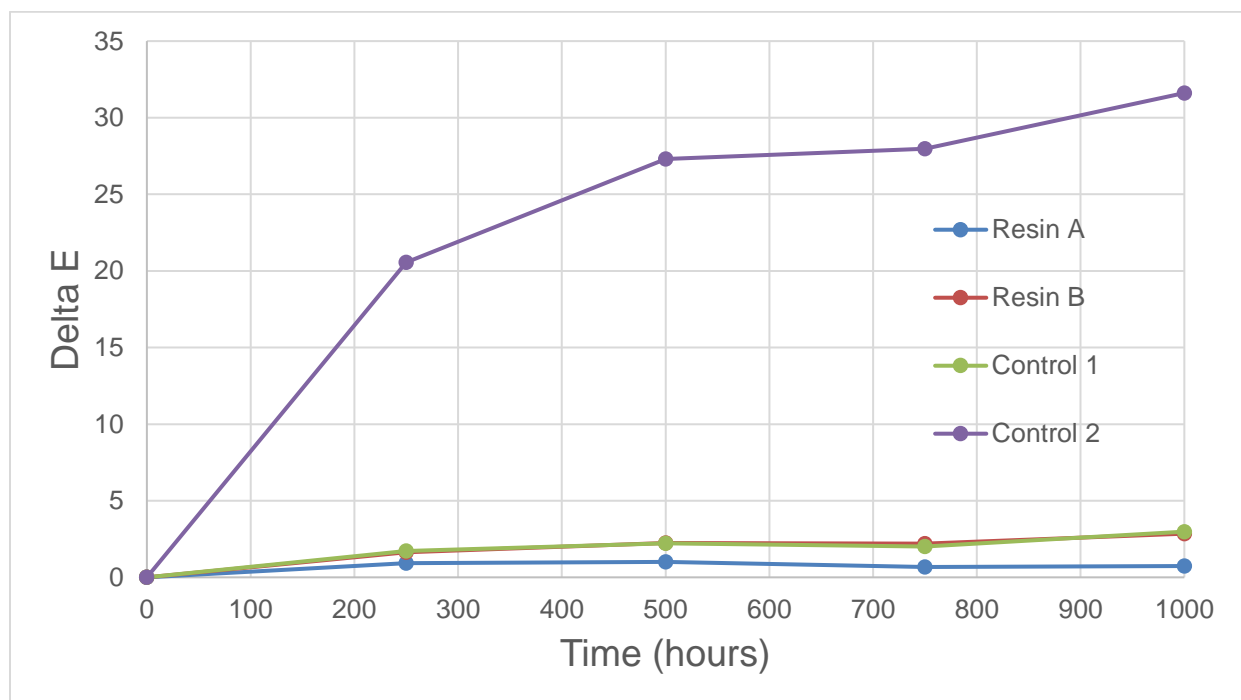


Figure 10. 1000 hours ASTM G154 weathering data

4. Conclusions

Achieving good chemical resistance, hardness and physical drying from a waterborne UV system is always a challenge. In this paper, two new resin approaches were introduced and compared with two commercially available waterborne UV resins. Resin A was an aliphatic polyurethane dispersion with acrylate functionality and contained UV-curable monomers. Resin B was also an acrylate functional aliphatic PUD, but with hard segment in the polymer chain and intrinsic dispersion agent. Control 1 resin was a commercial available aliphatic PUD acrylate, and Control 2 resin was an aromatic PUD acrylate. The two new resin approaches showed significant improvement in chemical resistance, hardness and physical drying as compared to the conventional UV-curable PUDs. Ultimately this makes the technologies an ideal fit for floor and furniture coatings, automotive interior coatings and pigmented coatings.

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