“Radiation Curable Components and Their use in Hard, Scratch Resistant Coating Applications”

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Abstract: Hard, scratch resistant, acrylate-based components are used in coatings for plastic substrates in a broad range of applications, from electronics, communications, semiconductor and data storage to optics, automotive, aerospace, and medical devices. Just as the applications are wide and diverse the variety of plastics that may be used has increased over time, and now includes materials such as polyethylene teraphthalate (PET), poly (methyl methacrylate) (PMMA), and polycarbonate (PC).

This paper describes a range of high functionality UV-curable products, including both 100% solids oligomers and waterborne polyurethane dispersions, which can be formulated for excellent scratch and abrasion properties as well as weathering performance, supporting their use in exterior coating applications.

Introduction: UV-curable materials, both 100% solids and polyurethane dispersions, have excellent utility in the design of hard, abrasion-resistant coatings. This paper explores these materials in typical hard coat formulations and details their performance in terms of abrasion resistance and weathering performance.

Description of Materials Evaluated

Highly Functional Urethanes: The materials investigated are aliphatic urethane acrylates (UA) having a polyester backbone structure. This type of oligomer has long been recognized as having a chemical structure that exhibits excellent durability when subjected to harsh environmental exposure, in either naturally occurring or accelerated weathering conditions. A higher cross link density generally increases a coating's hardness and scratch resistance. Thus the oligomers selected for this study range in acrylate functionality from 6 to 9 units per molecule and, for the purpose of this work, are identified as UA6, UAF6, UALT6 and UA9.

Waterborne Oligomers: Data is also presented for a family of UV-curable polyurethane dispersions, providing a comparison of physical property as it relates to wear resistance performance. These dispersions are identified as PUD 1, PUD 2, and PUD 3 in this paper.

Section 1: Urethane Acrylate Hard Coats

The first part of this investigation focuses on a series of highly functional aliphatic urethanes and assesses their protective coating properties on a variety of substrates. The following table provides a brief description of the oligomers and their attributes.

Oligomers Tested

Product Code	Acrylate Functionality	Attribute
UA6	6	Fast curing with proven weathering performance.
UAF6	6	More flexible with improved resiliency.
UALT6	6	Higher Mw with lower toxicity.
UA9	9	Very fast curing with enhanced stain resistance.
EA2	2	Lower cost with good chemical resistance.

Tabered Haze Testing: Initially the performance of the neat oligomers was quantified by tabered haze testing, which assesses the effect of surface abrasion, using a Taber wheel, on the change in haze for a clear coating. A description of the application conditions and performance results is provided in Figure 1.

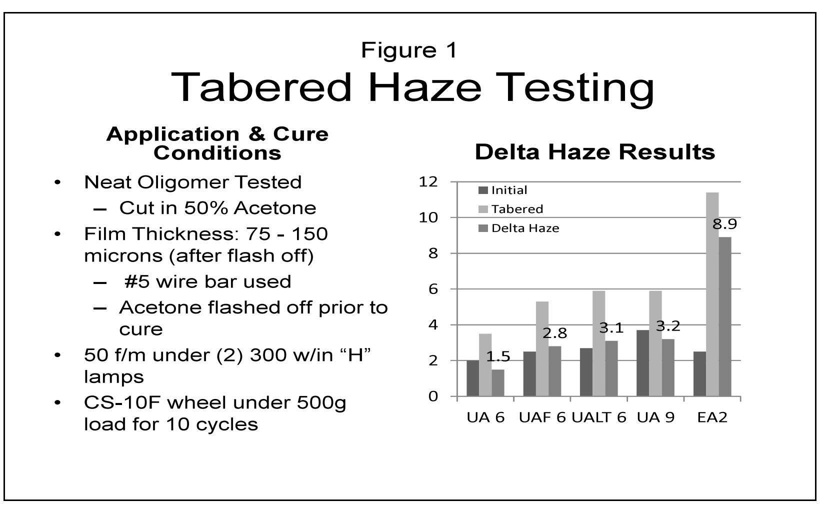


Figure 1

As these oligomers vary widely in viscosity, acetone was added to each to allow good control of film thickness. A photoinitiator (PI) was added to allow for UV curing. Each mixture was applied to a transparent substrate and UV-cured after removal of the solvent, yielding a dry film thickness of 75 microns. An epoxy acrylate (EA2) oligomer was also tested for comparative purposes.

The light transmission properties were then measured before and after Taber Testing. The decrease in percent of light transmission is reported as the Delta Haze. The results demonstrate a dramatic shortfall in abrasion resistance of the epoxy acrylate (EA2) as compared to the urethane acrylate (UA) family of oligomers. This result is due in part to the higher functionality of the urethane acrylates, which results in improved surface cure. However, better flexibility of the urethane acrylate materials is also is a contributing factor.

Other tests were conducted to quantify the hardness characteristics of each oligomer and results are listed in Table 1. The glass transition temperature (T_g) of a cured film is a fairly good indicator of hardness. Typically, a higher glass temperature yields a film with higher surface hardness. However, high hardness does not always equate to good abrasion resistance. The steel wool resistance data demonstrate this effect. Oligomers having lower T_g values passed the steel wool test while those with the higher T_g values failed.

Table 1

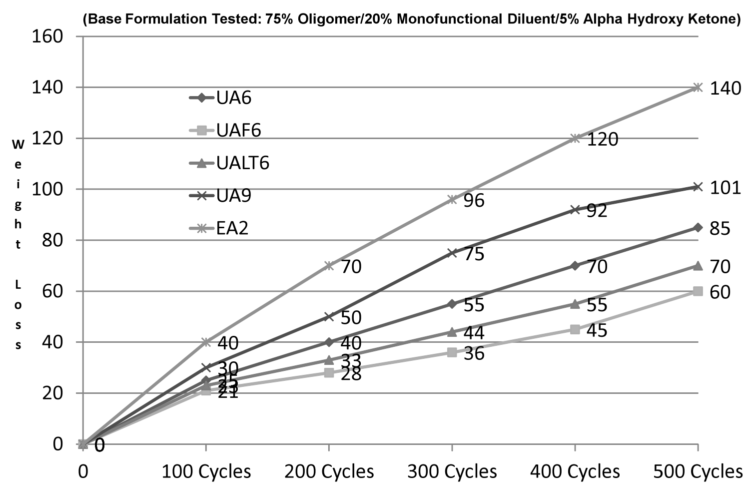
Characterization of “Neat” Oligomer Performance

Oligomer Identification	T_g by DMA, °C	Pencil Hardness	Konig Pendulum Hardness	0000 Steel Wool Resistance, 50 Cycles, 1.0 Kg Weight
UA 6	77.25	8H	116	Pass
UAF 6	74.41	7H	98	Pass
UALT 6	80.0	7H	103	Pass
UA9	135.0	7H	128	Fail
EA2	146.0	9H	138	Fail

Taber Testing by Weight Loss: Whereas the Tabered Haze Test quantifies surface scratch and abrasion resistance qualities of a coating or film, the Taber abrasion resistance test measures the bulk properties. The test is typically conducted on a thicker coating using a more aggressive Taber abrasion wheel (CS17 instead of CS10). The oligomers were tested in a formulation that included a low functionality monomer to better control film thickness and to improve ductile properties. Figure 2 summarizes the base formulation, the Taber test conditions, and the Taber weight loss results for each oligomer formulation. The tests were conducted on 50 micron thick cured films applied to aluminum test panels.

Again, poor abrasion resistance of the epoxy acrylate oligomer was noted, with a weight loss of 140 mg after 500 Taber cycles. By contrast, the urethane acrylate oligomers exhibited substantially lower weight loss. It is also noteworthy that the highest functionally oligomer (UA9) had poorer results than those having a functionality of 6. This would suggest that high hardness and crosslink density do not always drive good abrasion resistance because the resiliency and ductile properties of the cured film also influence the abrasion performance. In other words, the ability to resist abrasion is controlled both by hardness and lack of brittleness. This concept is also supported by the excellent performance of UAF6, which was chemically designed for enhanced flexibility.

Figure 2
Taber Abrasion Testing, CS17, 500g Load
Mg of Weight Loss per 100 Cycles



Weathering Resistance Testing: To be effective as a protective barrier a coating must have excellent scratch and abrasion resistance, and must not degrade when exposed to harsh environmental conditions. When high functionality oligomers are used for enhanced scratch resistance, cracking of the coatings may result, especially in thicker film sections. The UA oligomers were applied to a substrate at film thicknesses of 5, 10 and 15 microns. The cured samples were then subjected to accelerated laboratory weathering in a QUV® test chamber. The QUV test conditions were varied to include a cycle of 8 hours of UV radiation at 60°C, followed by 4 hours of dark condensation at 40°C. The test chamber was fitted with UVA 340 lamps. The UVA 340 lamp spectral output ranges from 300-400 nm and is centered at 340 nm. This lamp most closely replicates the emission spectrum of sunlight. Both the degree of yellowing and the gloss retention of the film were measured as functions of time and the results were recorded.

Since the UA oligomers tested have an aliphatic structure, no change in color or increased yellowness was detected with time. The gloss of each coating was also measured and differences were noted between the oligomers. In each case a loss of gloss was observed, which is due to micro-fracturing of the hard coat. The severity of fracturing is related to both acrylate functionality and film thickness. As oligomer functionality and the thickness of the coating are increased, the extent of fracturing increases. The exceptions to this are the oligomers that were modified to have improved flexibility in combination with high acrylate functionality, specifically UAF6 and UALT6.

No fracturing of the UALT6 oligomer was observed after 5000 hours of exposure at a 5 micron film thickness. Fracturing was noted after 1500 hours at a 10 micron thickness and after only 700 hours exposure at 15 microns. The UAF6 oligomer performed well regardless of film thickness and no fracturing was observed for any film thickness after 5000 hours of exposure, the full duration of the test. These results are shown in Figure 3.

Figure 3

Severity of Micro-Cracking as it Relates to Oligomer, Film Thickness & QUV Exposure

Oligomer& Film Thickness	0	100 Hours	300 Hours	500 Hours	700 Hours	1000 Hours	1500 Hours	2000 Hours	3000 Hours	4000 Hours	5000 Hours
UA 6 5 micron	Good	Good	Good	Slight	Slight	Slight	Slight	Severe	Severe	Severe	Severe
10 micron	Good	Good	Good	Slight	Slight	Slight	Severe	Severe	Severe	Severe	Severe
15 micron	Good	Good	Slight	Slight	Severe	Severe	Severe	Severe	Severe	Severe	Severe
UALT 6 5 micron	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Slight
10 micron	Good	Good	Good	Good	Good	Good	Slight	Severe	Severe	Severe	Severe
15 micron	Good	Good	Good	Good	Good	Slight	Severe	Severe	Severe	Severe	Severe
UAF 6 5 micron	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
10 micron	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
15 micron	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
UA 9 5 micron	Good	Good	Good	Good	Good	Slight	Severe	Severe	Severe	Severe	Severe
10 micron	Good	Good	Good	Good	Good	Slight	Slight	Severe	Severe	Severe	Severe
15 micron	Good	Good	Slight	Severe	Severe	Severe	Severe	Severe	Severe	Severe	Severe

Urethane Acrylate Hard Coat Summary: Aliphatic urethanes with high acrylate functionality result in cured films having excellent abrasion resistance properties. Higher functionality yields a higher crosslink density, which, in general, is desirable. However, the downside of increased crosslink density can be a decrease in abrasion resistance and an increase in micro-cracking of the cured film during weathering exposure, particularly when coating thickness exceeds 5 microns. These limitations can be controlled by modification of the backbone structure to impart increased flexibility or by the addition of lower functionality acrylates to the formulation to reduce crosslink density. These adjustments improve the ductile properties of the film making it more malleable, resulting in cured film with better abrasion resistance and a lower propensity for micro-cracking during weathering.

Section 2: Substrate Weathering Protection

Protection of the Coated Substrate: An important attribute of a barrier coating is the ability to prevent degradation of the end product onto which the coating is applied. To examine this feature a scratch resistant hard coat was applied to a polyester (PET) film and exposed in the QUV for 2000 hours. Where noted a light stabilizer was added to the hard coat formulation. The difference between this testing and the previous weathering data is that ΔE is tracked with QUV exposure instead of degree of yellowness (YI). This is a measurement of the total color change. The readings were taken on 250 micron thick PET with and without the hard coat applied. In this way the degradation of the PET can be monitored and compared to the coated stock to demonstrate the effectiveness of the coating for protecting the PET substrate. The base formulation and the cure and application parameters are detailed in Figure 4. An explanation of the ΔE test method is shown in Figure 5.

Figure 4

Weathering Resistance on Polyester Film

ΔE and Gloss Loss as it Relates to QUV Exposure

Base Formulation

75% UAF 6
22% Flexible Monofunctional Acrylate
10% Low Surface Tension Monofunctional Acrylate
3% Irgacure 184

- 820 cps @ 25C

Cure & Application Parameters

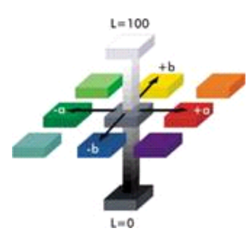
(2) 400 W/in "H" Lamps
Line Speed 50 F/M
Power Puck,1.8 J/CM^2
Film thickness 5-7 microns

- # 4 wire bar

Figure 5

Test Method Employed

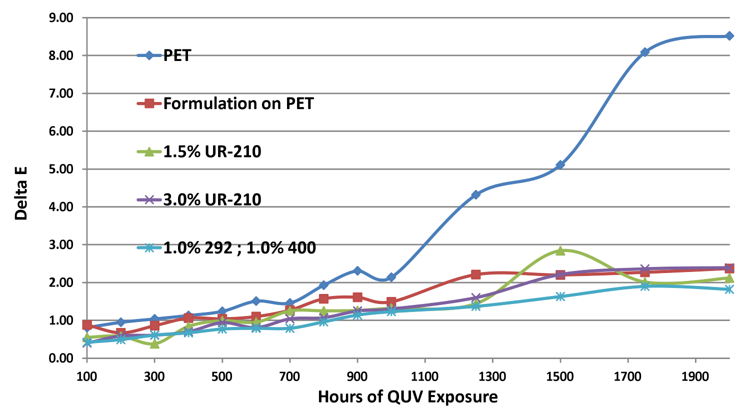
- BYK Color-Guide Sphere
  - CIE Lab
  - YE313-98
  - D65/10
- Readings taken on coated 5 mil thick PET placed over a white background for measurement
- ΔE is measure of overall color change



$$\Delta E = \sqrt{(L2 - L1)^2 + (A2 - A1)^2 + (B2 - B1)^2}$$

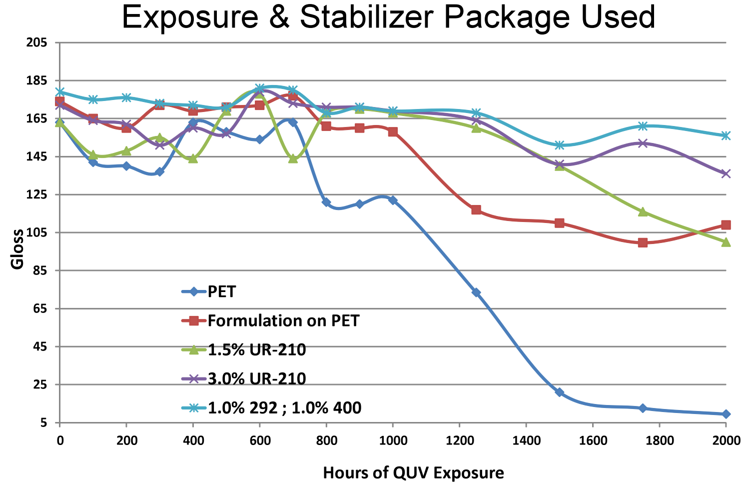
ΔE Test Results: The coated PET samples performed well during this testing regardless of the level or type of added light stabilizer. All of the coated PET samples had a maximum ΔE of approximately 2.0 after 2000 hours of QVU exposure. By contrast, the ΔE of the uncoated PET sample was 4.5 after 1300 hours and reached a value of 8.5 after 2000 hours of exposure, which indicates significant discoloration. The detailed results are presented in Figure 6.

Figure 6
ΔE Test Results as they Relate to QUV Exposure & Stabilizer Package Used



The gloss retention of the same PET films (coated and uncoated) was also monitored as a function of QUV exposure time. The effectiveness of the light stabilizers can be observed in Figure 7.

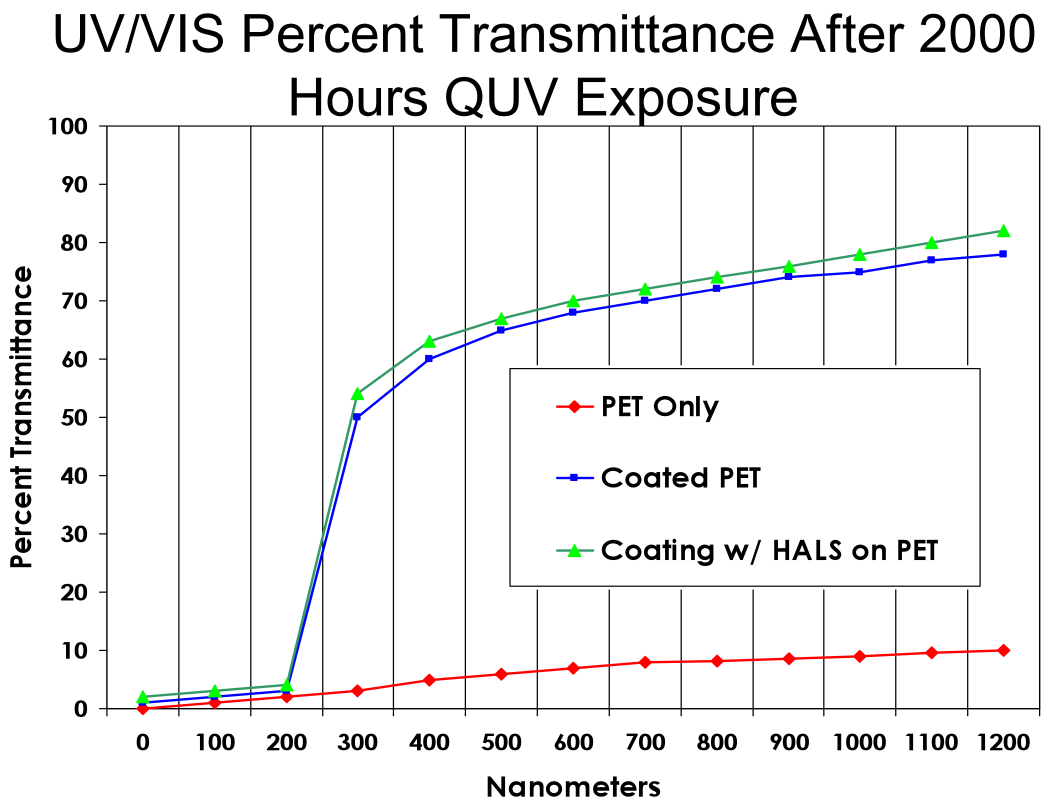
Figure 7
Gloss Retention @ 60 as it Relates to QUV Exposure & Stabilizer Package Used



The coated PET without light stabilizers showed gloss retention of 70% of its original value, while the PET coated with the light stabilizer containing formulation retained 86% of its initial gloss after exposure. Finally, the uncoated PET performed very poorly and maintained only 3% of its initial gloss value.

Substrate Protection: The light transmittance properties of uncoated PET and coated PET, with and without added hindered amine light stabilizer (HALS), were measured using UV/Vis as a function of time during 2000 hours of QUV exposure. The test results (see Figure 8) demonstrate the ability of the UV-cured coating formulation to protect the PET substrate from degradation. The protective properties are somewhat enhanced by the addition of a light stabilizer.

Figure 8



Substrate Performance Observations: Certain grades of PET will degrade when exposed to heat, light and moisture for extended periods. A properly formulated coating can lessen the degradation and provide a protective wear layer for the PET. The addition of HALS and light absorbers can further enhance protection.

Section 3: UV-Cured Polyurethane Dispersion Hard Coats

Waterborne Oligomer Testing: A series of UV-curable polyurethane dispersions (UV-PUD) was evaluated for scratch and abrasion resistance performance in a range of application-related tests. Table 2 lists the waterborne UV-PUD oligomers tested along with the corresponding liquid properties for each. The typical solids content for many UV-PUD materials on the market is 35% or less and typical viscosities are greater than 20 cps. It should be noted that the oligomers tested have an average solids content of 40% with a viscosity range of 8-15 cps. The higher solids content coupled with a lower viscosity offers more latitude in formulating industrial coatings.

Table 2

Product Designation	Percent Solids	Viscosity @ 25 C, cps	pH	Mean Particle Size (nm)
PUD 1	39-41	10-12	7.3 – 8.0	125
PUD 2	40-42	8 - 15	7.3 – 7.9	120
PUD 3	39-41	10-12	7.2 – 7.9	140
Control	35	20	8.0	<150

Application Properties of Waterborne UV-PUD Oligomers: Each of the UV-PUD oligomers was formulated using standard industry additives to give good film forming properties and was tested over a variety of applications parameters, including flexibility, hardness, abrasion resistance, stain resistance, water resistance, and weathering resistance. The solids content of each was adjusted to 35% to offer a consistent basis of comparison.

Each formulated UV-PUD oligomer was applied to the substrate at a wet film thickness of 150 microns, which resulted in a dry film thickness of approximately 50 microns. Laboratory drying procedures (30 minutes at room temperature followed by 30 minutes at 60°C) ensured that all water was removed before UV curing. Drying conditions for production situations would vary depending on the equipment used, but typically 10 minutes at temperature in the range of 50-60°C is sufficient.

Figure 9 shows the experimental approach used for each UV-PUD. A relative ranking of end-use performance for each of the properties tested is displayed as well. All of the oligomers performed well in the stain resistance, water resistance, and solvent resistance testing. The control UV-PUD (a widely used commercial UV-PUD product) was found to be lacking in flexibility and QUV yellowing resistance but was acceptable in terms of hardness and abrasion resistance.

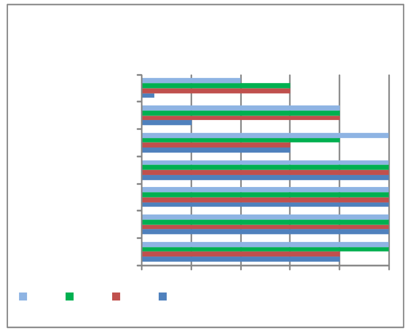
Figure 9

Waterborne Oligomer Testing

Formulating and Processing

- Formulation: UV-PUD diluted to 35% solids plus standard additives and photoinitiators
- Film Thickness: 150 microns wet/50-60 microns dry
- Substrates: Glass (hardness and tensile), Leneta charts (KCMA stain), aluminum panels (MEK resistance and Taber abrasion)
- Drying Conditions: 30 min @ 72ºF/50% RH, 30 min @ 60ºC
- Cure Conditions: 2 x 400 W/in. Hg lamps @ 50 ft/min

Feature Tested



The UV-PUD oligomers show excellent water resistance. For example, none of the cured films whitened after direct exposure to hot water. Also of note is that the QUV accelerated weathering results are comparable to those for an aliphatic urethane.

Surface Scratch Testing: Given that PUD 3 shows good abrasion resistance, stain resistance, and superior moisture resistance, it was chosen for comparison to the competitive control for surface scratch resistance.

Figure 10

Waterborne Oligomer Testing

Surface Scratch Testing

- Affix white abrasive pad to a mounting fixture having an area of 1 sq. in.
- Place 100g weight on top of mounting fixture.
- Slide weighted pad back and forth over the surface 50 times at each weight load.
- A back and forth motion constitutes one cycle.
- Measure gloss before and after abrading.
- Report gloss readings.

Gloss Retention

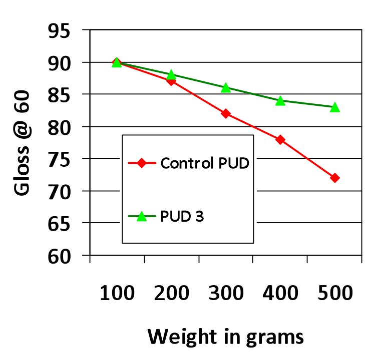
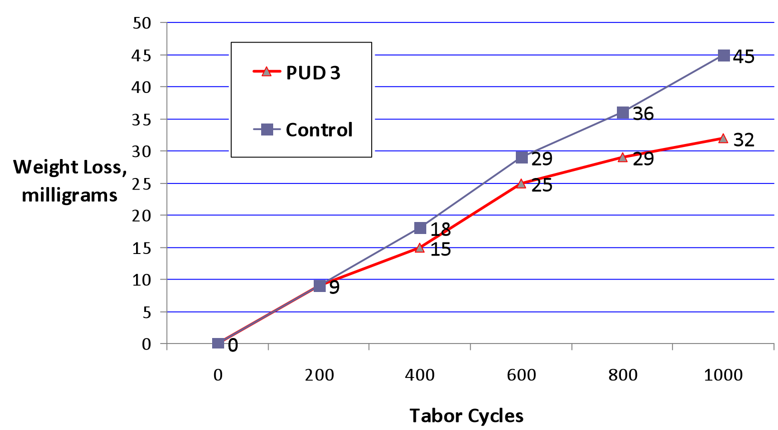


Figure 10 describes the surface scratch test method used. The gloss retention was measured for loads from 100 g to 500 g in 100 g increments. At each load the sample received 50 abrasion cycles with a white abrasive pad (3M ScotchBrite). The control material had much poorer resistance to abrasion and showed a much more significant loss in gloss than the PUD 3 sample. PUD 3 maintained a relatively high level of gloss for the duration of the test.

Abrasion Resistance: Whereas the surface scratch test provides information about the surface properties of the cured film, the Taber abrasion resistance test assesses the bulk abrasion resistance properties of the coating. PUD 3 and the control UV-PUD were tested by Taber abrasion using a CS17 Taber wheel, with weight loss measured every 200 cycles (up to 1000 cycles total). This protocol employs a much more aggressive abrasive medium compared to the abrasive pad used in the surface scratch test, which makes this test significantly harsher. Based on the weight loss results shown in Figure 11, PUD 3 is substantially more resistant to abrasive wear than the control material.

Figure 11

Tabor Abrasion Resistance, CS 17, 1000g Load



Summary

Scratch & Abrasion Resistance Observations:

1) Aliphatic urethanes with high acrylate functionality result in cured films having excellent abrasion resistant properties.

2) High oligomer functionality results in a high crosslink density, which increases hardness. However, depending on the flexibility of the formulated coatings, high functionality may result in micro-cracking of the cured film during weathering, particularly when coating thickness exceeds 5 microns.

3) Two approaches can be taken to improve film flexibility and ductile properties to improve abrasion resistance and address micro-cracking for high functionality oligomers:

   a. modification of the backbone structure to impart better flexibility and/or

   b. addition of lower functionality acrylates to the formulation to reduce film crosslink density.

Barrier Performance Observations:

1) Certain grades of PET will degrade when exposed to heat, light and moisture for extended periods.

2) A properly formulated UV coating can dramatically lessen the PET film degradation by providing a protective wear layer. This protective function can be applied to other substrates as well.

3) The addition of HALS and light absorbers to the UV coating can further enhance weathering protection.

Waterborne Oligomer Observations:

1) The family of UV-PUD materials examined in this paper offers a higher reactive solid content at a lower viscosity when compared to typical UV-PUDs on the market. These features provide greater formulating latitude for industrial coatings.

2) When compared to the control UV-PUD, enhanced surface scratch resistance, flexibility, yellowing upon QUV exposure, and abrasion resistance are noted for the UV-PUDs studies.

3) The UV-PUD oligomers show excellent water resistance. For example, no whitening of any of the cured films was noted after surface exposure to hot water.

4) The QUV accelerated weathering results for the UV-PUD oligomers are excellent; these materials have comparable weathering resistance to those of an aliphatic urethane.