Chemical Resistance of Oligomeric Acrylates

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ABSTRACT
Chemical resistance of a series of UV cured oligomeric acrylate-based coatings was evaluated. Acids, bases, organic solvents, and industrial fluids were employed in the study. Gloss, yellowing index, tensile strength, and tensile elongation were measured at different time intervals and related to the backbone structures of these oligomers.

INTRODUCTION
UV curing involves the rapid polymerization of acrylic monomers and oligomers in the presence of photo-active initiators. In most cases, the monomers and oligomers are multifunctional in nature, resulting in the formation of a highly crosslinked thermoset polymeric film. Compared to thermoplastic polymers, which are often used in solvent-based coating applications, the UV cured thermoset films offer distinct advantages such as chemical resistance, high gloss, dimensional stability and mechanical integrity.

This new technology is quickly expanding into a wide spectrum of industrial sectors and replacing the out-dated solvent-based process. Coatings with improved chemical resistance and other desired properties are being required to survive and function in harsh environments such as automotive, marine, and aeronautical applications.

A generally accepted view in the radcure (UV/EB) industry is that for any parent resin (oligomer), i.e., epoxy, urethane, polyester, silicone, acrylated acrylics etc., the typical properties of the parent backbone are more or less carried through to the radiation curable analogue1. In this study, oligomers account for more than eighty percent of the overall formulation, thus the film properties are largely determined by the oligomer used.

Previous investigation by others has shown that oligomers based on polybutadiene have exceptional resistance to hydrolysis, but oxidative stability was identified as a deficiency. Polyether based oligomers afforded coatings with fair oxidative and hydrolytic stability. Polyester based oligomers provided good oxidation resistance but poor hydrolytic stability2.

Results of recent work from this lab have revealed that aliphatic urethane acrylates are the best oligomers in the 3000 hours QUV accelerated weathering test. Whereas in the QUV chamber, short wavelength UV and high humidity are the major degradation factors, the oligomers are expected to behave differently in a chemical exposure environment. Based on the results from this chemical resistance study and the ongoing weathering study, oligomers with superior chemical and weathering resistance will be identified. The findings will also help design novel oligomers with higher performance properties for demanding environments.

This work is only an initial investigation of the influence of the structures of seven selected oligomers on the chemical resistance of UV cured coatings. The effect of monomers, photoinitiators, and additives, as well as adhesion and temperature, will be the topic of future presentations.

EXPERIMENTAL
Formulation and Materials
Seven oligomers were used in this study. The general back-bone structure and physical properties of these oligomers are listed in Table 1.
Table 1 Structure and Physical Properties of Oligomers

<table>
<thead>
<tr>
<th>Group</th>
<th>Oligomer</th>
<th>Backbone</th>
<th>MW M=1,000</th>
<th>Viscosity @ 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group I</td>
<td>CN964</td>
<td>Ester</td>
<td>1.6-1.8M</td>
<td>21,000</td>
</tr>
<tr>
<td>Group II</td>
<td>CN966</td>
<td>Ester</td>
<td>5.4-5.6M</td>
<td>70,000</td>
</tr>
<tr>
<td>Group III</td>
<td>CN981</td>
<td>Ester/Ether</td>
<td>-</td>
<td>10,000</td>
</tr>
<tr>
<td></td>
<td>CN982</td>
<td>Ester/Ether</td>
<td>1.6-1.8M</td>
<td>9,375</td>
</tr>
<tr>
<td></td>
<td>CN986</td>
<td>Ether</td>
<td>1.6-1.8M</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>Pro1154</td>
<td>Ether</td>
<td>5.4-5.6M</td>
<td>26,500</td>
</tr>
<tr>
<td></td>
<td>CN301</td>
<td>PBD</td>
<td>-</td>
<td>4,175</td>
</tr>
</tbody>
</table>

1 All oligomers are aliphatic urethane acrylates (AUA) except CN301.
2 CN301 is polybutadiene dimethacrylate (PBDMA).

The typical formulation for all oligomers studied is as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligomer</td>
<td>80%</td>
</tr>
<tr>
<td>Monomer</td>
<td>20%</td>
</tr>
<tr>
<td>Photoinitiator</td>
<td>5% (on resin)</td>
</tr>
</tbody>
</table>

The monomer used is HDDA, hexanediol diacrylate. The photoinitiator is Esacure® KIP100F®, oligo[2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone]. This is an α-hydroxy-acetophenone type unimolecular photo-initiator. All materials are commercially available from Sartomer Company.

Wet Film Preparation
The 5 mil wet films were cast on mill finished aluminum Q-panels by using zero drawdown rods with double tapes. Great care was taken to obtain films with uniform thickness. This is very important because film thickness is a very critical factor in determining a coating’s performance.

UV Curing System
A Fusion Model F440 UV curing unit was used. For gloss and yellowing measurements, 5 mil samples were cured by passing one 300 W/in “D” lamp followed by one 400 W/in “H” lamp at a conveyor speed of 50 fps (feet per minute). Each sample was exposed twice using this curing condition. For mechanical property measurements, 5 mil wet films were cast on aluminum Q-panels and initially cured under one 300 W/in “H” lamp at 200 fps. The semi-cured films were then cut into 0.5 inch wide strips. Finally, fully cured films were obtained by passing the strips under one 300 W/in “D” lamp followed by one 400 W/in “H” lamp at a conveyor speed of 50 fps. Again, a total of two passes was used.

Prior to testing, all the coated panels were stored in the dark after curing for 3 days. This was done to ensure a uniform environmental history.

Chemical Resistance Test
The test procedure followed ASTM method D 1308-79. Chemical reagents were as follows:

- 50% H₂SO₄
- 10% H₂SO₄
- 50% NaOH
- 10% NaOH
- Ethanol
- Toluene
- Skydrol, 5B-GL
- Tap water

Skydrol is a proprietary fire resistant hydraulic fluid which is formulated by Monsanto Company. Chemically, Skydrol belongs to the phosphate ester group and has performance additives.

For gloss and yellowing measurements, the covered spot method was used. The test was conducted at 23 ± 2°C and 50±5% relative humidity. A 5-mL pipet graduated in 0.1 mL was used to pipet onto the horizontal UV coated aluminum panel 1 mL of the reagents. The reagent was immediately covered with a watch glass. After an interval, the spot was wiped and washed clean and examined immediately. The
intervals used in this study were 1, 8, 24, and 120 hours.

For tensile measurement, film strips were fully immersed in the testing reagents in an amber bottle. The strips were exposed using the same intervals as those for the covered spot test. The strips were washed and dried before testing.

Gloss Measurement
60° gloss was measured using a Micro-Tri-Glossmeter from BYK-Gardner.

Yellowing Measurement
The yellowing property of a film is expressed by a yellow index which is calculated by the following equation:

\[ \text{YI} = \frac{(1.28 \times X - 1.06 \times Z)}{Y} \times 100 \]

where X, Y, and Z are the tristimulus coordinates. The values for X, Y, and Z were obtained from a Hewlett Packard 8452-A Diode Array UV-Vis Spectrometer equipped with a Reflectance Spectroscopy Accessory from LapSphere. The UV-Vis is operated by a Window Color software program which gives Tristimulus, Hunter Lab, CIELAB, and POLAR Coordinates.

Mechanical Properties Test
Tensile strength, elongation, and tensile modulus were determined with a Thwing-Albert tensile tester with a strain rate of 0.5 in/min. For each sample, at least 5 specimens were tested and an average value was reported.

RESULTS AND DISCUSSION

Oligomers: the Structural Aspects
As shown in Table 1, all oligomers are aliphatic urethane acrylates (AUA) except CN301.

The aliphatic urethane acrylates can be further divided into three different groups based on the structure of the polyol utilized to synthesize the acrylate oligomer.

CN981 and CN982 (Group II) are aliphatic urethane acrylates, with ester/ether polyol as the backbone. Extended with branched polyester polyol, CN964 and CN966 (Group I) have identical stoichiometries with the exception of the polyester polyol molecular weight. CN986 and PRO1154 (Group III) can be identified as an oligomer group where the backbone is pure polyether. CN986 is characterized as strong and tough. PRO1154 imparts extreme flexibility to the film.

\[ \text{I: Polyester Aliphatic Urethane Acrylate (AUA)} \]

\[ \text{Group II: Polyester/ether Aliphatic Urethane Acrylate (AUA)} \]

CN301 is a polybutadiene terminated with methacrylates (PBDMA). With the high hydrophobicity of the polybutadiene chain, CN301 is expected to exhibit exceptional resistance to acids and bases.

\[ \text{Group III: Polyether Aliphatic Urethane Acrylate (AUA)} \]

Polybutadiene Dimethacrylate (PBDMA)
Among these three groups of oligomers, CN982, CN964, and CN986 have different polyol backbones, but the molecular weight of the polyol are the same. This provides a good base to study the influence of polyol structure on the coatings properties.

For all the formulations tested in this study, the oligomer is the only variable. The properties measured should be characteristic of the specific oligomer.

**Acid Resistance**

Both highly concentrated (50%) and diluted (10%) sulfuric acid were used to test acid resistance. The chance for a coating to encounter 50% sulfuric acid in its service life is probably extremely rare. Thus, 50% sulfuric acid is only used in this study to demonstrate the ultimate performance of the coatings.

**Figure 1. Effect of sulfuric acid on tensile strength of polyester AUA**

Figures 1-6 plot tensile strength and elongation vs. time for these seven oligomers after exposure to both 10% and 50% sulfuric acid. The general observation is that all oligomers perform well in 10% sulfuric acid. In 50% sulfuric acid, however, a dramatic reduction in tensile strength and tensile elongation was detected for all oligomers except CN301, the polybutadiene dimethacrylate.
Further examination reveals that Group III oligomers with pure ether backbones, i.e., CN986 and PRO1154, suffered the most in tensile reduction. CN964 and CN966 (Group I), the oligomers with pure ester backbones, had the least reduction whereas the mixed ester/ether backbone oligomers (Group II) lay somewhere between the I and III groups. This conclusion would be more valid if one compares CN964, CN982, and CN986 which have the same molecular weight but different polyol backbones.

It is highly possible that in the presence of this powerful oxidizing acid (50% H₂SO₄) the labile hydrogens along the ether and ester backbone have been oxidized. The oxidation and consequent reactions may have resulted in the partial breakage of the polymer network structure, which was reflected by the reduction in both tensile strength and elongation of the coatings.

**Figure 5. Effect of sulfuric acid on elongation of polyester/ether AUA**

The α hydrogen in an ether is more prone to oxidation than the hydrogen in an ester. Thus, the oligomers with the most ether linkages suffered more from oxidation. This was confirmed by the fact that CN986 and PRO1154 (Group III) started yellowing after only one hour immersion in 50% sulfuric acid. The color development began after eight hours for CN981 and CN982 (Group II). Group III & II coatings broke after two and eight hours in a covered spot test, respectively. The test was stopped when a film was broken. The yellowing of CN964 and CN966 (Group I) was only observed in the later stage of the covered spot test (Figure 7).

The data also suggested that within the same oligomer group, the higher the molecular weight of the oligomer, the more the reduction in tensile strength and elongation. This can be easily explained by the difference in crosslink density and the number of oxidizable hydrogens. On a volume basis, a low molecular weight oligomer will have a higher acrylate concentration than its high molecular weight counterpart. As a result, a higher crosslink density was achieved for CN964 and CN986 in Group I and III, respectively. At the same time, CN964 and CN986 also possess less oxidizable hydrogens than CN966 and PRO1154, which have substantially longer ester and ether polyol backbones. Both factors also contributed to the more pronounced color development for CN966.
Excellent gloss and color retention were observed in 10% sulfuric acid as shown in Figures 9 & 10.

For CN301, excellent retention of tensile, elongation, gloss, and color were observed in both 10% and 50% sulfuric acid. The hydrophobic nature of the polybutadiene backbone is the major reason for the superior acid and oxidation resistance of this remarkable oligomer. The polybutadiene building block also makes this oligomer highly flexible (70% elongation with Tg of -70°C).

It is interesting to note that all the coatings had a very high initial gloss level. More importantly, for the oligomers (coatings) which did survive the test, the high gloss of the coatings was not affected by this oxidation process (Figure 8).

**Figure 7. Effect of 50% sulfuric acid on the yellowing of AUA and PBDMA**

![Figure 7](image)

**Figure 8. Effect of 50% sulfuric acid on Gloss of AUA and PBDMA**

![Figure 8](image)

**Figure 9. Effect of 10% sulfuric acid on Gloss of AUA and PBDMA**

![Figure 9](image)

**Figure 10. Effect of 10% sulfuric acid on yellowing of AUA and PBDMA**

![Figure 10](image)

**Figure 11. Effect of NaOH on tensile strength of polyester AUA**

![Figure 11](image)
Base Resistance
All oligomers were quite resistant to base. In 10% and 50% sodium hydroxide solutions, all the coatings retained their original tensile, color, and gloss. Again, CN301 kept its tensile properties fairly constant while other oligomers exhibited observable fluctuations during the course of the 5-day test. Figures 11-16 show the impact on tensile strength and elongation with time. Figures 17 & 18 show the color and gloss change after exposure to 50% sodium hydroxide solution.
Solvent Resistance
As shown in Figures 19–24, all oligomers behaved similarly in ethanol and toluene. The initial conclusion is that the ether backbone provides better solvent resistance. This is evident when the tensiles and elongations of oligomers with the same molecular weight (CN964, CN982, and CN986) are compared. Group I and II oligomers were swelled and plasticized by the small solvent molecules. This contributed to a significant reduction in tensile strength. However, the tensile elongation of the coatings remained almost unchanged even after 5 days of immersion.

It is interesting to note that the tensile strength of CN966, with a higher polyester molecular weight, was barely affected by the solvents, while CN964 experienced a dramatic reduction. However, both CN964 and CN966 retained a constant elongation. The reason for this unusual behavior remains unclear.

Again, the oligomer with the best property retention was CN301.
Skydrol and Water Resistance

Figures 25-30 illustrate the response of the coatings based on seven oligomers to water and Skydrol.

Water resistance of all the oligomers was generally good, which is probably due to the high crosslink density of the UV cured coatings. However, variation in tensile properties did occur for certain oligomers such as CN986 and PRO1154. It is proposed that the hydrophilicity of the pure polyether backbone renders the coatings interactive with water. After long exposure, water might function as a plasticizer. Overall, no detectable damage was done to the coatings.
An aviation hydraulic fluid, Skydrol seems to have a very high penetrating power. All oligomers suffered tensile and elongation reduction after being immersed in this fluid. Most of the films were obviously weak and showed significant swelling after being taken out of the Skydrol. Among the seven oligomers, CN981 and CN982 were the most resistant to Skydrol’s attack.
In Skydrol, CN964, CN981, and CN982 were the only oligomers that survived the 5-day covered spot test. All others simply delaminated and peeled off the aluminum panels. For the coatings that did survive, gloss and color were retained (Figure 31 and 32).

After exposure to water, only a minor change was observed in gloss and color. This is shown in Figures 33 & 34.
CONCLUSIONS
Overall, UV cured coatings based on the oligomers studied show great promise for chemical resistance. The high crosslink density of these coatings protected them from chemical degradation. Resistance of a coating to certain chemicals is largely controlled by the structural nature of the oligomer backbone.

Polybutadiene has been identified as the best oligomer in terms of resistance to strong acids, bases, and organic solvents. 50% sulfuric acid caused damage to most oligomers. The effect of 10% sulfuric acid, as well as 10% and 50% sodium hydroxide on all the coatings was minimal. Polyether-based oligomers, as well as polybutadiene dimethacrylate were superior in solvent resistance. All oligomers exhibited good water resistance. Skydrol seems to penetrate almost any coating.

Work is underway to further investigate the actual failure mechanism of UV cured coatings following exposure to strong chemicals.

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REFERENCES


KEYWORDS
UV curing, Chemical resistance, Acid resistance, Base resistance, Skydrol resistance, Water resistance, Oligomeric acrylates, Aliphatic urethane acrylates, Polybutadiene dimethacrylate, Gloss, Yellow index, Tensile strength, Tensile elongation