COMPARISON of PERFORMANCE of ACRYLATE and METHACRYLATE ALIPHATIC URETHANES

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INTRODUCTION

Historically acrylate functionality is preferred over methacrylate functionality in Ultraviolet Light (UV) and Electron Beam (EB) cured coatings due to its much faster cure speed. Methacrylate radicals are more stable than acrylate radicals and, therefore, slower to propagate than acrylate radicals. However, polymers constructed of methacrylate backbones have some distinct advantages over polymers assembled from acrylates. Methacrylate polymers tend to have higher glass transition (Tg) temperatures, improved impact resistance, and exhibit better weathering than their acrylate analogs.

For some applications, such as automotive finishes, these physical properties may be more important than the speed of cure. UV curing of automotive finishes, whether based on methacrylates or acrylates will dramatically reduce the time required for other conventional systems currently used in that industry. This paper will compare and contrast the performance properties of methacrylate versus acrylate functional aliphatic urethanes. Oligomers of similar structure were synthesized incorporating either an acrylate or methacrylate functional group. The physical, and cured properties of these products were evaluated. Studies on service life predictability have begun.

RAW MATERIALS AND FORMULATIONS

Four different oligomers were synthesized for this study. Two products were either tetrafunctional acrylate or methacrylate and were comprised of an aliphatic isocyanate and alkyl polyol. The other two products were either hexafunctional acrylate or methacrylate materials and were synthesized from a polyester polyol and an aliphatic isocyanate.

Each of the oligomers was then diluted to a workable viscosity with 1,6-Hexanediol Diacrylate (HDODA). HDODA was chosen due to its excellent weathering properties, outstanding diluency, and relatively benign impact on other properties. The photoinitiator was 1-hydroxy-cyclohexylphenyl-ketone at the 2 phr level and was selected due to its excellent performance in long-term weathering. Table I exhibits the formulations tested in this study.

Table I: Formulations

	A	B	C	D
Tetrafunctional Urethane Acrylate	70			
Tetrafunctional Urethane Methacrylate		70		
Hexafunctional Urethane Acrylate			70	
Hexafunctional Urethane Methacrylate				70
1,6-Hexanediol Diacrylate	30	30	30	30
1-hydroxy-cyclohexylphenyl-ketone	2 phr	2 phr	2 phr	2 phr

SAMPLE PREPARATION

Samples for impact, and scratch resistance testing were prepared on ACT® cold rolled steel, (B1000 P 60 DIW: polish) panels. Samples for accelerated weathering were prepared on powder coated (super durable white powder coating) 3" x 6" aluminum panels. The plain aluminum panels were electrostatically sprayed with powder coating and then thermally cured prior to coating with test formulations. A #5 wound wire bar was used to apply the liquid coating to the panels. Each panel was then cured with a total UV irradiation of between 1767 and 2930 mJ/cm² depending upon the test. Final cured coating thicknesses were found to be 0.005 inches thick +/- 5%. For a given test, UV dosage was kept constant, irrespective of the individual chemistries.

Tensile samples were prepared by drawing down a 0.005 inch thick layer of the formulation to be tested on an uncoated polyester sheet. A second polyester sheet was then placed in contact with the top surface of the coating and the laminate structure partially cured via UV light. Straight edge samples were cut from the laminate structure. After the samples were cut they were then exposed to the full energy density of UV light. The polyester sheeting was then removed and the samples were conditioned for 24 hours in a constant temperature (21° C) and humidity (50 % RH) room before testing.

APPLICATIONS INSTRUMENTATION/ EQUIPMENT
- Tensile and elongation: Instron, model 4467
- Impact testing: Byk Gardner Impact Tester (equipped with a 2 pound weighted rod)
- Steel Wool Scratch
- Accelerated weathering – Q-Panel QUV/se - UV – A bulbs (340 nm)
- Coating Color changes: Byk Gardner Color Guide with the geometry of 45/ 0, D65 (daylight – northern exposure) illuminant and a 10° observer.
- Coating Gloss: Byk Gardner micro–TRI-gloss meter
- Coating Thickness: Gardco Minitest 100-N
- Curing Equipment: Fusion EPIQ 6000 UV, 2 600-watts/inch power, H lamps
- Irradiation energy density measurement: IL 390c Light Bug

ACCELERATED WEATHERING: PROPERTIES MEASURED AND TEST PROCEDURES

- ASTM D 4587 Procedure "E" – 8 h UV/ 60ºC light followed by 4 h con/ 50º conforming to the procedure section of Practice G 53
- Color values - L*, a*, b*, (CIELAB) ΔE reported.
- 20°/ 60° gloss
- Visual inspection (ASTM D714/ D660) - used as reference as to the type of coating defect observed. The legend for observations will be noted on the individual charts.
- Readings were conducted approximately every 250 hours of total exposure time after the initial 100 hours time frame.

PROCESSING AND CURE

Cure speed was defined as the UV energy density required to produce a mar resistant surface. Table II displays the cure speed and the glass transition temperature (Tg) of the un-cured oligomers used in the formulations of Table I.

Table II: Minimum Energy Density Required to Obtain a Mar Resistant Surface Along with the Tg of the Base Oligomer for Each Formulation

Formulation	Functionality	Functional Group	Cure Speed (mJ/cm^2)	Tg of Oligomer (^oC)
A	Tetra	Acrylate	385	-37
B	Tetra	Methacrylate	587	-2
C	Hexa	Acrylate	706	-42
D	Hexa	Methacrylate	2100	-25

The tetrafunctional urethane acrylate (formula A) exhibited the fastest cure response requiring less than 400 mJ/cm^2 of energy to obtain a mar resistant surface. Curiously, both tetrafunctional materials exhibited faster cure speed samples than either of the hexafunctional materials. This seems counter intuitive until one investigates the Tg of the uncured base oligomers (last column of Table II). From these data it can be seen that the urethane oligomers based on the hydrocarbon polyol (formulas A and B) have a higher Tg than the corresponding urethanes based on the polyester polyol (formulas C and D). Thus, these materials will reach a lower degree of conversion during the cure cycle before they vitrify and become mar resistant. Thus, formula A, based on the tetrafunctional urethane acrylate with a Tg of $–37^o$ C, effectively shows increased cure speed when compared to formula C, which contains a $–42^o$ C Tg base oligomer. In fact the formula based on the tetrafunctional methacrylate oligomer with a Tg of only $–2^o$ C effectively exhibits higher cure speed than the hexafunctional acrylate oligomer based formula C with a Tg of $–42^o$ C.

INSTRON

Table II displays tensile data for formulations A, B, C and D cured at two different energy densities: 1760 mJ/cm^2 and 3500 mJ/cm^2.

Table III: Tensile Data for Formulations of Table I at Two Energy Densities

	A		B		C		D	
Energy Density (mJ/cm²)	1760	3500	1760	3500	1760	3500	1760	3500
Tensile (psi)	3681	4691	7369	5005	983	X	440	1818
Elongation (%)	8.0	5.8	4.4	2.6	0.3	X	0.3	0.6
Young's Modulus (kpsi)	99	141	243	206	286	X	271	288
Toughness (lbs.)	207	180	197	75	2	X	1	6

These data clearly indicate that both the acrylate and the methacrylate oligomers continued to crosslink as additional energy was imparted to them. In the case of the tetrafunctional acrylate, the tensile strength and Young's modulus increased while elongation decreased. There was relatively little change in the toughness of this material as measured by the area under the stress - strain curve. For the tetrafunctional methacrylate the elongation was reduced to a level where accurate tensile strength measurements become difficult by this test. The hexafunctional materials, whether acrylate or methacrylate, were extremely brittle in nature. The hexafunctional acrylate was so brittle at the high energy density exposure, that it's physical properties could not be measured. In general, formulations B, C, and D were so brittle that any microscopic flaw on the edges of the sample is sufficient to create a crack causing premature fracture of the sample. Thus it is difficult to confirm if the mechanical properties shown in Table III for these materials are intrinsic to their molecular structures, to the polymer network that has formed, or simply a practical limitation of the test procedure used to make these measurements.

DIRECT/ REVERSE IMPACT

Coatings for automotive applications need some degree of impact resistance. In general, increasing the crosslink density of the film decreases its impact resistance. In bulk polymers it is well established that methacrylates are far more impact resistant than acrylates. However it is not well understood if this will carry over to thin films.

Samples for both direct and reverse impact were exposed to approximately 2930 mJ/cm². This level is not optimized for each formulation but allowed for direct comparison. After curing, each of the test samples were allowed to remain overnight under constant temperature and humidity (22º C and 50% RH) prior to testing. Failure is typically reported as the force required to either crack the coating (star or halo shaped fractures) or to delaminate the coating from the substrate (in this case, cold rolled steel).
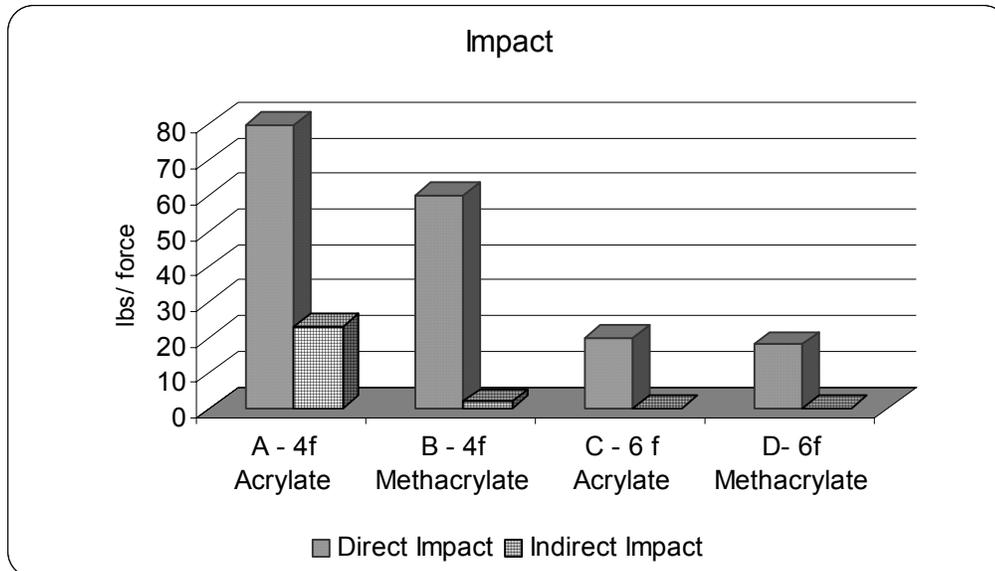
Figure 1: Impact Resistance

Figure 1 exhibits the force to failure for direct and reverse impact on the four formulations tested. Here again formulas based on the tetrafunctional oligomers out performed formulas based on the hexafunctional oligomers. The acrylated materials outperformed their methacrylated counter parts as well. DMA data (not shown here) indicate the formulations based on the hexafunctional oligomers were much more highly crosslinked, and in fact did not show a distinct Tg. These impact data, when considered with DMA data and the tensile data of Table III, suggest that the impact resistance of these films was directly dependent upon the ultimate elongation of these formulations and was not influenced by nature of the reacting double bond. In other words, the methacrylate group did not improve the impact resistance of these cured films.

STEEL WOOL SCRATCH
For some end use markets, surface hardness and resistance to scratch is of the utmost importance in the final film. Samples were drawn down and cured on cold roll steel to approximately 0.5 mil in thickness and cured with approximately 2930 mJ/cm² energy density. After curing, each test sample was allowed to remain overnight under constant temperature and humidity (22º C and 50% RH) prior to testing.

The test method involved wrapping the rounded end of a 2-pound balpeen hammer with 0000 steel wool. The steel wool wrapped hammer is allowed to rest its weight on the cured film and slowly moved across the surface of the film. A complete back and forth motion is counted as a single double rub. The back and forth movement continues until either scratches or a haze is observed.
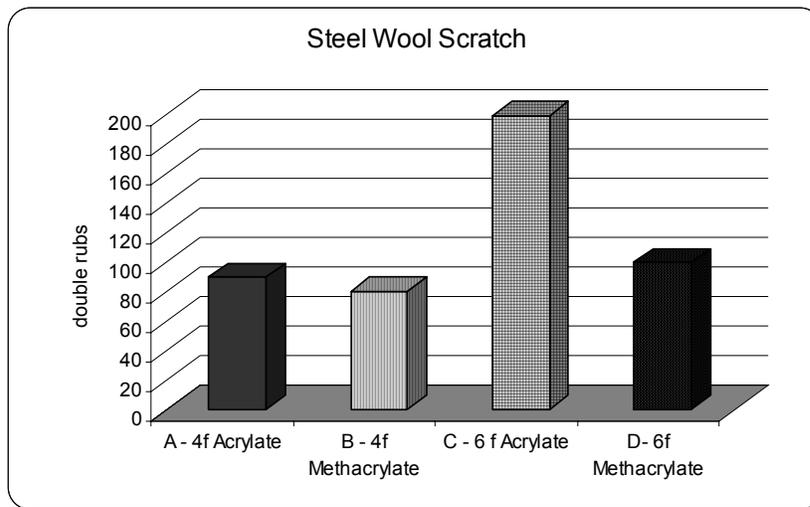
Figure 2: Steel Wool Scratch

As Figure 2 illustrates, the hexafunctional urethane acrylate formula significantly out performs either of the tetrafunctional based formulas. The relatively low scratch resistance of the hexafunctional urethane methacrylate based formula D may be due to insufficient cure energy. The tensile data of Table III indicate that the full mechanical properties of this material were not developed even when cured with an energy density of 3500 mJ/cm^2.

ACCELERATED WEATHERING
Service life predictability is yet another of the many key determining factors used in various end use applications. Multiple sample specimens (three each) of the four formulations were drawn down onto white, thermal cured powder coated aluminum panels at the approximate cured film thickness of 0.5 mil and cured with approximately 2930 mJ/cm² energy density. After initial readings were conducted, the samples were placed under QUV A (340 nm) accelerated exposure conditions. The exposure cycle was set to be 8-hours light at 60º C followed by 4-hours of darkness with condensation at 50º C.   The three main categories recorded were
- Color (L*, a*, b*)
- Gloss (20º and 60º)
- Visual degradation

The samples were exposed for up to 5000 hours of total exposure time.

COLOR (Δb)
Initial color change at the point of cure is important in some end markets, but for the sake of this evaluation, the initial readings for establishment of baseline numbers was completed 24 hours after cure and just prior to placement into the accelerated QUV equipment. The exposure series was begun at the start of the light cycle. By doing so, the sample specimens were exposed to a consistent

source of heat and light prior to any exposure to the effects of humidity on the films.

Upon investigation of the overall change in color of these cured films with QUVA exposure, changes in the b* value were by far the greatest contributor. Therefore Δb* is shown in Figure 3.
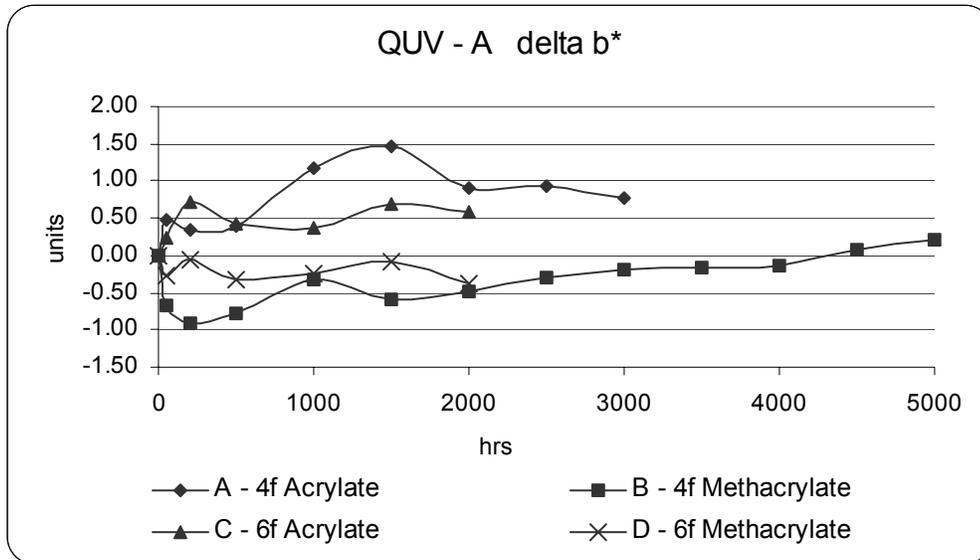

Figure 3: QUV – A, Δb*

The data of Figure 3 indicate a significant performance difference between the acrylate based oligomers and the methacrylate based oligomers, despite the structural differences in other components of their structure (polyester versus hydrocarbon). Both methacrylate based oligomers undergo significant photobleaching upon exposure to UV, whereas both acrylates show an initial increase in color followed by either stable color or very slow increases in color.

GLOSS/ PHYSICAL DEGRADATION
Another factor, which directly impacts the acceptance of a material, is the gloss retention over exposure time. Changes in gloss are typically the result of physical changes at the surface of the coating. Physical degradation includes not only cracking and delamination but also surface erosion over time.
Gloss measurements were made at a 60° angle and each panel was visually inspected for physical degradation. Figure 4 shows the gloss readings of the four formulations tested.
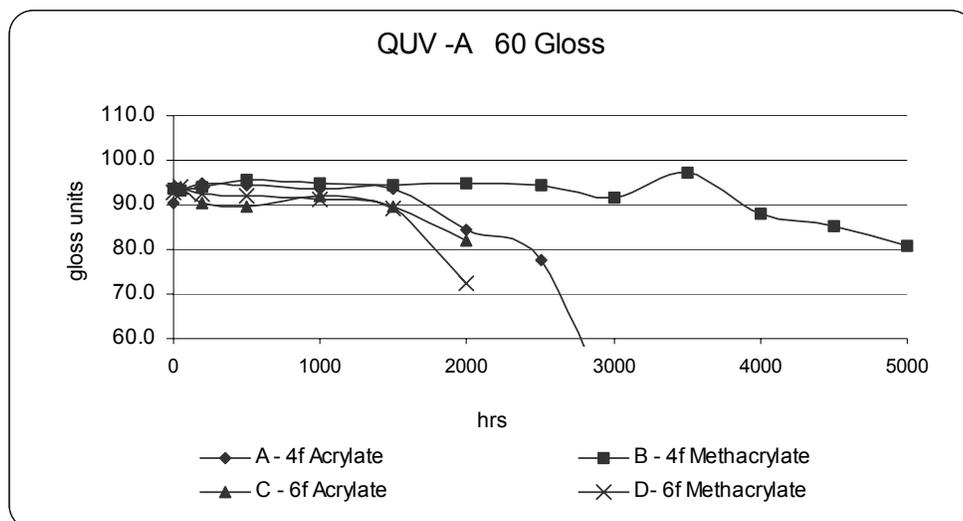
Figure 4: 60 ° Gloss

From Figure 4 one can see that only the tetrafunctional urethane methacrylate based formula B performed differently lasting the entire 5000 hours with about a 15 % drop in gloss. Even after 5000 hours, formula B maintained good film integrity. The primary form of film degradation noted for these samples was "crowfoot" or mosaic splits in the film's surface. Both hexafunctional samples faired poorly in this study. The performance of formula C based on the hexafunctional urethane acrylate was not surprising as this level of performance has been seen repeatedly in our laboratories. The high shrinkage and very high crosslink density of this material leads to high internal stresses that cause premature failure of films based on this product. In addition, the polyester nature of this oligomer almost certainly contributes to its poor weathering.

The poor performance of the hexafunctional urethane methacrylate (formula D) was somewhat unexpected and may be due once again, to the under cured state of this material. Testing is underway to evaluate the performance of this material based on higher cure energy.

CONCLUSIONS
Four urethane (meth)acrylate oligomers were tested for cure speed, basic mechanical, and physical properties, and accelerated weathering. The results paint a complex picture of the performance of such materials that at times defies conventional wisdom. Cure speed was shown to be highly dependent on the Tg of the uncured oligomer, not simply on the number of functional groups or the chemical nature (methacrylate or acrylate) of the functional group. Accurate mechanical data was difficult to obtain due to the high crosslink density and very brittle nature of all of these samples with exception of the tetrafunctional urethane acrylate.

The tetrafunctional urethane (meth)acrylates clearly out performed the hexafunctional materials in impact resistance. Though this is not surprising, the dependency of this property on the elongation properties of the film, and not whether they were acrylate or methacrylate functional, became apparent. Accelerated weathering showed some clear advantages for methacrylate based materials in color development, gloss measurements, and the related surface defect observations.

It is clear from the data in this study that additional testing of these materials is warranted as cure conditions did not always produce sufficiently cured films to make valid comparisons. Some potentially significant performance advantages could be obtained for specific applications by correctly engineering methacrylate functional urethane oligomers with the proper number of functional groups and other structural components.