

# Multifunctional UV curable Oligomers for Hard Optical Coating

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## **Abstract**

Hard, optical clear, protective UV curable top coats are necessary for a variety of demanding applications in the automotive, aviation, electronics and scientific instrumentation markets. Coatings with special properties, such as antifog, conductivity, anti-Newton ring, antiglare performance, are highly sought-after products. However, due to limited choices of oligomers, current coatings cannot easily meet customers' varied demands. Oligomers with low functionality may hardly meet scratch (mar) resistance or hardness specifications. Some coatings can only be applied as very thin films due to brittleness. Furthermore, chemical resistance, antifog, antistatic and antiglare properties all require artful formulation choices between monomers, oligomers, additives, photo-initiators and diluents. Lack of functionalized oligomers often restrict the creative venues for multipurpose applications. New oligomers have been developed that can solve problems like these. This presentation will discuss new polyurethane acrylate oligomers being developed using grafting and block copolymerization that, under adequate formulation, provide excellent optical properties while presenting great toughness after UV curing. Raw materials with different characteristics of hydrophilicity, hydrophobicity, conductivity, elasticity, mechanical properties, and/or formulation compatibility are selected in obtaining oligomers of desired properties. Oligomers targeting for antifog applications, glass adhesion, and soft touch application, will be discussed. Specifically, antifog coatings for Polycarbonate (PC) substrate has been evaluated extensively for performance against many real life use conditions. Some formulations were compared against other commercial products in the market place.

## **Introduction**

In modern society, more and more advanced products often require outstanding materials not only for its bulk properties, but also improved surface properties. Polymeric materials, for example, found widespread applications due to easy processing, cost-effectiveness and versatile properties. However, its surface characteristics at times cannot meet all the requirements of designated applications. There can be a set of special surface requirements, such as hydrophilicity, hydrophobicity, amphiphilic, conductivity, transparency, thermal, mechanical, and chemical resistance, and biological characteristics not found in the bulk materials for semiconductor, domestic, military, optical, medical, mechanical, environmental applications. Surface modification through coating is desirable if not a dominant way to give a satisfactory solution. In some applications, such as semiconductor, optical or medical applications, the surface characteristics of materials largely determine their utility and reliability. In biomedical applications for example, the bodily response to foreign material, and thus biocompatibility, is governed by surface interactions.

UV/EB curable coatings provide the versatility for fast processing that can complete the curing process in a few seconds, for environmentally friendly applications that can essentially eliminate solvent usage. UV as a "cold" energy source allows curing occur at low temperature. The "architectural" design is formed through chemical reaction of applied components, thus better performance due to the vast combination of monomers and oligomers. Some of these advantages are very beneficial to special coatings, such as optical coatings, for which polyurethane acrylates have been one of the key materials. Polyurethane's mechanical properties, wide range of hardness, high bearing capacity, flexibility, abrasion and weather resistance, adhesion, and low cost, can be exploited through creative chemistry for performance coating

hardly matched in any other material. However, due to limited choices of oligomers, current coatings cannot easily meet customers' varied demands. For example, scratch (mar) resistance properties or hardness cannot meet specifications due to low (meth)acrylate functionality of the oligomers. Chemical resistance, antifog, antistatic and antiglare properties all require artful formulation choices between monomers, oligomers, additives, photo-initiators and/or solvents.<sup>1,2</sup> Formulations have to offer a variety of different performance characteristics while reducing factors that may impact the desired function negatively. Use of an antifog optical coating formulation as an example, it needs to provide coating adhesion to substrate, appropriate mechanical properties that can resist scratch damage, antifog properties, while minimizing those factors that decrease transparency and color. Simply trying to mix monomers that are far away in properties may be unable to achieve the desired performances as phase separation and/or formula instability can be too much to overcome for a good formula.

Lack of functionalized oligomers often restrict for multipurpose applications. Through precision functionalization of polyurethane acrylates that enables flexible solutions towards targeted applications, many new oligomers were explored. Derivation of multifunctional oligomer can be obtained either through synthesis or chemical modification of preexisting polymers/oligomers. Star shaped oligomer, and/or dendrimer, can be a desirable candidate. Star shaped oligomers or dendrimers usually have significantly lower viscosity than its linear chain counterparts, and low viscosity is one important parameter for coating application, which at times has to be realized by the addition of solvents at the cost of environment pollution and process complications. Also, multiple functions can be easily derived from a dendrimer than linear counterparts,<sup>3</sup> which have to go multiple reaction steps to reach the final point where the dendrimers are.

One straightforward way for modification of dendrimeric raw materials can be done by converting unfunctional groups to hetero functional groups, as illustrated in Figure 1. Specifically for this study, branched or dendrimeric raw materials with hydroxyl functional groups have been converted to multifunctional UV curable polyurethane acrylate oligomers by reacting the hydroxyl groups with heterofunctional isocyanates.<sup>4,5</sup> In this study, new polyurethane acrylate oligomers that provide excellent optical properties while presenting great toughness after UV curing were developed using grafting and block copolymerization. The choice of different raw materials, such as highly functional monomers and polyols, will impact their structure and properties, i.e., number of functionality, hydrophilicity, flexibility of molecules, on performance of final coating as reported. Exploration of some application of the developed oligomers in antifog, glass adhesion antifog, and soft touch coatings were made.

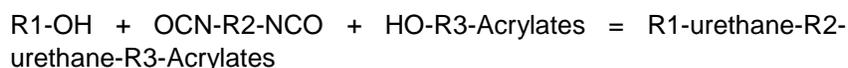
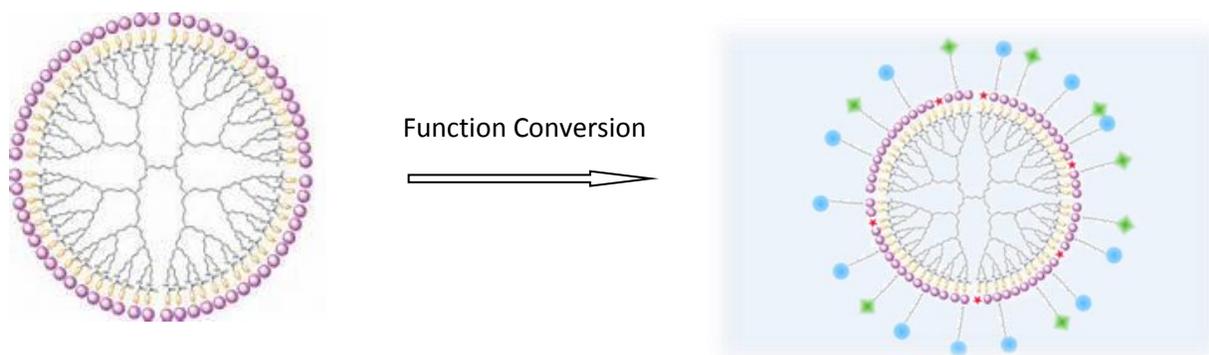


Figure 1. Conversion of hydroxyl dendrimer to multifunctional dendrimers

## **Oligomer Synthesis and Development**

Polyether polyols, polyester polyols, branched polyols, and dendrimeric polyols tested were from Perstorp Group, Panolam, Dow Chemical, Momentive, and Cray Valley. Heterofunctional monomers that include at least a hydroxyl group and an acrylate group were from Kowa, Bayer, and Sartomer. Multifunctional isocyanates tested were from Momentive, Kowa, Duranate (Asahi Kasei), Vencorex (Chemical Marketing Concepts Europe Ind.), and Vestanat (Evonik).

FTIR was measured using Perkin Elmer Spectrum 100 (Perkin Elmer). Viscosity was measured by a Brookfield viscometer RVF 100 (Brookfield). Molecular weight was evaluated by a gel permeation chromatography, PL-GPC-50.

Typical synthesis of UV cure oligomer for Antifog application: Isophorone diisocyanate was allowed to react with branched polyether polyol in a glass container under constant stirring at 70 °C for two hours with catalyst tin octoate. Stoichiometry was controlled to allow a half of the isocyanate to be reacted. Hydroxylfunctionalacrylates were further added to allow a half of the isocyanate to be reacted at 70 °C. Reaction process and final product was monitored by FTIR. Viscosity was measured by Brookfield viscometer, and molecular weight of the final product was evaluated by GPC (Agilent).

A dual cure glass adhesion oligomer combination for antifog application were made by the following reactions. Oligomer 1 is obtained by reacting isophorone diisocyanate with HEMA in a glass container under constant stirring at 70 °C for two hours with catalyst tin octoate. Stoichiometry will be controlled to allow a quarter mole equivalent of the isocyanate to be reacted. Subsequently, polyether polyol of a quarter mole equivalent of isocyanate was further added to the mixture for another two hours of reaction. Dendrimeric polyol was then added, and reaction was carried out at 80 °C for four hours. Stoichiometry was controlled in such a way that appropriate viscosity product was obtained. Reaction extent and final product were monitored by FTIR. Viscosity and GPC.

Oligomer 2 is obtained by reacting triisocyanate TPA-100 with polyester polyol in a glass container under constant stirring at 70 °C for two hours with the catalyst tin octoate. Stoichiometry was controlled to allow a third mole equivalent of the isocyanate to be reacted. Subsequently, a third mole equivalent of multifunctional hydroxyl acrylate and glass adhesion monomer, were further added to be reacted at 80 °C for two hours. Reaction extent and final product were monitored by FTIR. Viscosity and GPC.

Appropriate combination of Oligomer 1 and oligomer 2 was used as a basis for dual cure glass adhesion formulations.

Oligomer for Soft-touch application: Reaction of branched Polybutadiene polyol and polyG polyol with isophorone diisocyanate was carried out at 70 °C for two hours with the catalyst Tin Octoate. HEMA was then added to the mixture. Stoichiometry was controlled in such a way to get to an appropriate viscosity. Reaction extent and final product were monitored by FTIR. Viscosity and GPC.

## **Formulation, Coating and Curing**

Multifunctional UV curable oligomer(s) obtained above were mixed in a mixer with appropriate amounts of compliment oligomers, monomers, adhesion promoters, flow and leveling adhesives, and UV initiators. The mixture can further be diluted with suitable diluents under stirring depending on process application to adjust viscosity for better flow and leveling. The formulation can then be used to coat on substrates such as PC, PMMA, PET, or glass substrates under spray or dip coating processes. Spray was carried out using an EJM 208 spray nozzle. Dip coating was held at room temperature at the dipping speed of 2.54 cm/min. Upon drying at 40 °C for approximately 3 min, the coating was further cured under UV irradiation.

## **Coating Evaluation**

Adhesion - Surface adhesion was evaluated following the ASTM D-3359 cross-cut test.<sup>6</sup> A lattice pattern in the film was made using the appropriate tool with 1 mm spacing to cut into the coated portion. Brush in diagonal direction 5 times each, using a brush pen or tape over the cut and remove with Permacel tape. Examine the grid area and score the damage. When all the pattern are completely removed, a score of 0 is given. When none of the patter is removed, a score of 5 is given.

Adhesion after boiling water treatment was also tested by placing samples in a beaker with boiling water at 100 °C and make sure the coating is completely covered for 30 minutes. Air dry for two hours then perform the cross-hatch adhesion test.

Mechanical properties were evaluated by scratch and abrasion resistance tests, and surface hardness.

Scratch resistance test was carried out using Steel-wool test. Steel-wool rotary test representing severe scratching using a 1.25-square-inch #0000 steel-wool pad at 2 psi for five rotations.

Wear abrasion resistance tests were carried out using both Taber abrasion test and Bayer abrasion test. Taber Abrasion Resistance test was done following ASTM D-1044. CS10F wheels with 500g load was used. For abrasion resistance of transparent plastics and coatings, Bayer abrasion resistance test, was done following the Standard Oscillating Sand Test Method, ISO CD 15258, ASTM F735. This test method determines the resistance of transparent plastics and transparent coatings to surface abrasion using oscillating hard particles of defined size. Rigid specimens that are 100mm square and less than 12.5mm in thickness are mounted in a holder located in the bottom of a sand tray so the surface is flush within 1mm. The tray is filled to a uniform depth (e.g. 12.5mm) with a standardized abrasive media such as Kryptonite. A scotch-yoke drive system reciprocates the tray in a back-and-forth (to-and-fro) motion which causes the entire mass of the abrasive media to shift significantly within the tray. The oscillating movement of the abrasive media results in a random pattern of scratches to simulate everyday wear. Surface hardness was tested using a pencil hardness test with 750 g weight following ASTM 3363 (Mitsubishi Hi Uni pencils).

## **Optical Properties**

Optical properties were measured using Color Quest II. Impact of storage conditions - coated samples are generally stored after being masked by plastic films in a cold room before delivery. Changes of sample performances after these tests were used as an indicator for storage stability. In masking test, samples were masked by placing films on top of the sample, and stored for predetermined times. Subsequently, samples will be evaluated for adhesion, antifog, and optical performance changes.

## **Antifog Properties**

Many factors affect antifog properties, such as antifog enabler, the characteristics of oligomer, and the compliment components.<sup>7,8,9</sup> Antifog properties were first evaluated by both fogmaster/breath test and beaker test. In fogmaster/breath test, fogging source was provided by exhaling moisturized air by breath or fogmaster towards the sample surface. Record the start and ending of three phases of fogging on tested samples. The first phase of changes denotes loss of transmission yielding to an opaque film. The second phase of changes commences spotted film from large or small drops of water being formed that reduces transmission. The third phase change starts when clear water film that does not reduce transmission has been formed. In beaker antifog duration test, samples were placed in a beaker that is filled with 60 °C water up to 5cm from the top where the sample is placed. After proper sample conditioning and preparation as per ASTM D618-00, the sample is tested for antifog performance as well as adhesion.

Antifog properties against freezing cycles were also tested. A two cycle test was applied to samples in this study. In the first cycle, the samples were placed in a freezer cooled to  $-15\text{ }^{\circ}\text{C}$ , for 45 minutes. Then the samples were removed from the freezer and checked for the three phases of fogging in room temperature. Record the time of the start and end of each phase that occurred. Subsequently, the sample was placed back into the freezer for another 15 minutes. The sample was then removed from the freezer and immediately placed over the beaker to perform the 2<sup>nd</sup> cycle beaker test at  $60\text{ }^{\circ}\text{C}$ . Record the times of three phases as before.

Chemical resistance tests were also performed. Cotton balls soaked in the corresponding chemicals are placed on top of coated substrate. Observe the sample constantly to see apparent loss of coating, loss of antifog properties, and the loss of integrity. Record the time.

Contact Angle tests provide a direct indication of surface tension<sup>10</sup> that correlates closely with antifog properties. Water contact angle was measured by placing a drop of deionized water onto the coated sample using a 20 gauge needle. The increase of the spreading diameter of the water drop as a reflection of the advancing angle was recorded over time.

Stability was characterized by performing the same set of tests being described above, at predetermined time intervals after stability treatment. The tested values will be compared against those being derived before stability treatment.

## **Results and Discussion**

### **Synthesis**

Highly branched oligomer, especially dendrimer, generally possess low viscosity than their linear counterparts. Most of the current commercial coating process requires flow characteristics to be in a desirable operating window. Dendrimeric oligomers demonstrate a new dimension in processability. Furthermore, curability, and therefore mechanical properties, i.e., hardness, highly correlate with functionality. By increasing functionality per chain, it would be more likely to reach hard, scratch resistant, chemical resistant, and abrasion resistant coatings. Using high functionalized monomer one may not easily get to desired properties as highly shrinkage during polymerization lead to stress formation that in turn will yield a brittle coating and crack. Because multifunctional oligomers can choose to include proadhesion segments as well as performance enforcing segments in the same chain, the coating performance using the developed oligomers over commercial counterparts was significant.

The derivation of quality multifunctional dendrimer depends on purity of reactants, reaction condition, stoichiometry, and sequence of feedstocks. High moisture level in raw materials, high reaction temperature, or inappropriate reactant ratio may also be detrimental against obtaining quality products in that premature gelling can occur during the reaction due to complication of side reactions of isocyanates. Inappropriate stoichiometry may also lead to products with inappropriate amount of functional groups for targeted applications. Reaction can be monitored kinetically by a number of techniques.

FTIR at different stages can be obtained to monitor reaction extent. Figure 2 is the FTIR that reflects the incomplete reaction mixture as well as the final product. The peak at  $2200\text{ cm}^{-1}$  on the left chart, and the lack thereof on the right chart showed the presence and disappearance of isocyanate groups in the samples.

Molecular weight of samples also change with reaction time. For multifunctional oligomers, multiple reaction steps are usually needed to get to the final product, which include a few different compounds that were generated at different stages. Figure 3 shows the GPC chart that reflects the molecular weight and molecular weight distribution of the sample.

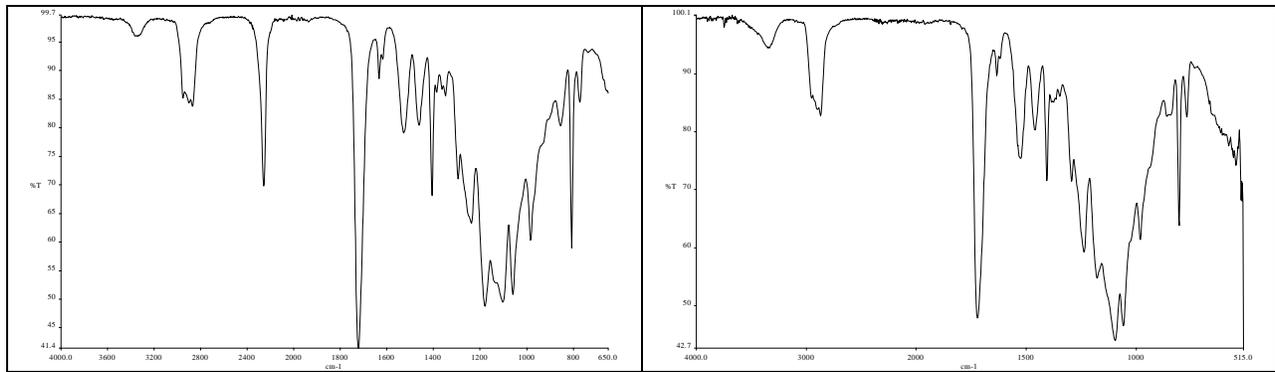


Figure 2. FTIR of a reaction mixture that includes branched polyester polyol, diisocyanates, hydroxyfunctionalacrylates at different reaction stages. The peak at 2200  $\text{cm}^{-1}$  on the left chart indicated unreacted isocyanates at an early stage of reaction, and the lack thereof on the right chart indicated the completion of urethane reaction.

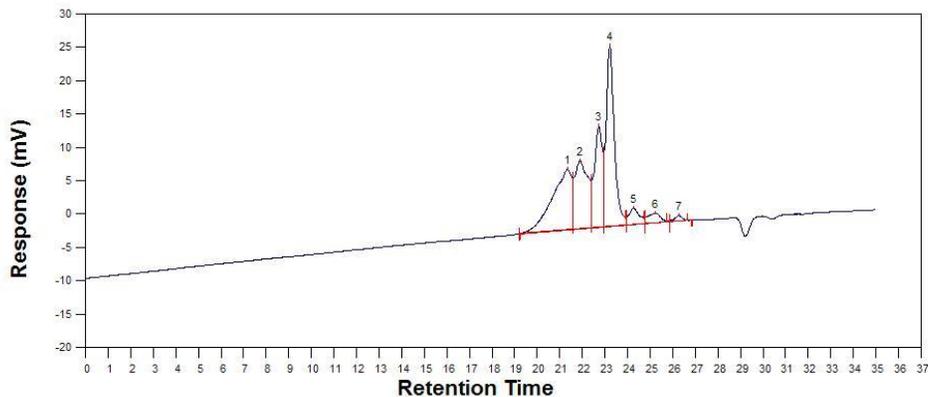


Figure 3. GPC of a reaction product that included polyester polyol, diisocyanates, hydroxyfunctionalacrylates. Multiple peaks reflects the presence of molecules of different molecular weight and chain connection.

Viscosity of samples were also monitored within a tight range as a spec for the final product.

The oligomers synthesized were used on a number of applications. In this study, the usefulness of oligomers in antifog coatings on PC and glass substrates, as well as soft touch application will be presented.

## Coating Formulation and Property Evaluation

### Antifog Coating

Antifog oligomers were mixed with a combination of acrylate monomers, antifog promoters, adhesion promoters, photo initiators, and solvent mixtures. Viscosity of formulations are 10 cP for spray coating, and 50 cP for dip coating. The substrate used for the antifog study were polycarbonate. Dip coating was used throughout this antifog application study. Coating samples were obtained by dipping at the speed of 2.5cm/min, a minute and a half drying at 30 °C, and UV curing at 700  $\text{mj}/\text{cm}^2$ . A number of formulations were examined for antifog performances. One formulation, 931-PC, gave satisfactory properties across the spectrum. The results for a subset of samples, 931-PC-1, 931-PC-2, and 931-PC-3, will be reported. The impact of components, UV dose and photo initiator was monitored by transparency, adhesion, and antifog properties. Final products for antifog applications need to be transparent. Noncoated PC substrate was used as control for the experiments.

A sequence of different antifog tests were used to examine the antifog properties of samples. First, fogmaster/breath test was applied to ensure antifog property. Sample should not generate noticeable fogging under the test condition. Both coated sample and the noncoated PC were tested, and it was found that 931-PC did not have any fogging under the test condition while the control substrate showed obvious fogging.

The more aggressive antifog tests were used to evaluate the quality of antifog coatings. Antifog beaker test (Table 1), and antifog duration test (Table 2), were carried out. Samples tested showed significant improvements over noncoated control samples.

Table 1. Antifog beaker test at 60 °C of 931-PC against PC control without antifog coating

Coating ID	Rainbow	Fogging
931-PC-3	30 seconds	No fog $\geq$ 30 minutes
Control	30 sec	Fog immediately

Table 2. Duration test of 931-PC samples against PC controls without antifog coating

Coating ID	Fog start (sec)	Fog end (sec)	Non-uniform film start (sec)	Non-uniform film end (sec)	Uniform film starts (sec)
931-PC-2	2-4	10-13	10-13	113-115	115
Control	Fogs immediately	60	60	120	120

Stability of samples against storage, such as masking, cleaning and freezer placement, were evaluated by examining the antifog three phase performance after predefined time intervals. For masking, samples are masked with different types of masking tape and checked for fogging after 3 and 6 months of masking times.

In cleaning test, samples were sprayed with Windex and then wiped clean with a dry scratch free rag. Antifog properties were tested by doing the beaker test at 60 °C. The test was repeated until the sample started to fog longer than three seconds. Table 3 listed some results. The antifog property is sustainable against cleaning agents, suggesting the antifog enabler is taking effect on surface under the condition.

Table 3. Antifog performance of 931-PC-1 sustained 12 cycles of cleaning treatment

Coating ID	Before Test	Cycle 1-11	Cycle 12
931-PC-1	No fog 1-30 sec.	No fog 1-30 sec.	No fog 1-6 sec. (fail)
PC substrate	fail		

The Freezer test gives an indication of stability of antifog properties after cold temperature experience of the samples. The samples were placed in a freezer cooled to -15 °C for 45 minutes. Then the samples were removed from the freezer and checked for the three phases of fogging in room temperature for a 90 second or greater time period. Record the time of the start and end of the stages that are occurred. Subsequently, the sample was treated for a second time in freezer for 15 minutes. The samples were

then immediately transferred and placed over the beaker to perform the beaker test (60 °C) for 90 seconds or more. Record the times the three phases begin and end. Table 4 lists some of the results.

Table 4. Antifog performance of 931-PC-1 against Freezer test, in air or over beaker

Coating ID	Fog Start (sec)	Fog End (sec)	Non-uniform Film Start (sec)	Non-uniform Film End (sec)	Uniform Film Starts (sec)
931-PC-1 in air	3-6	41-43	41-43	96-98	96-98
931-PC-1 over beaker	2-5	8-18	8-18	30-33	30-33
Control	Fogs immediately	140	140	180	180

Haze, light transmittance, and the yellow index measurements were also performed on samples before and after high temperature treatments. Samples were placed in a preheated oven at 100 °C and left them at the temperature for five hours. After five hours, the samples were cooled down to room temperature for at least 2 hours, followed by the same optical tests. The tested values should be within the specified values, transmittance (95% from the original), Yellow Index (3% from the original) and Haze (5% from the original). Table 5 lists some of the values before and after the beaker treatment.

Table 5. Change of Haze, light transmittance, and yellow index upon high temperature treatment of sample 931-PC-1.

	Before Treatment	After Treatment	Gain
YI E (%)	0.74	0.83	12%
YI D (%)	0.88	0.98	10%
Haze (%)	0.22	0.24	8 %
Luminous transmission (%)	89.63	90.68	1 %
Adhesion (%)	Pass	Pass	No change
Antifog	No fog	No fog	No change

Three perfect scores have to be obtained for cross-cut adhesion test to indicate good adhesion (ASTM 3359). For antifog formulation, adhesion and hardness were kept in check closely as changes in the quantity of the antifog enabler noticeably impacted the adhesion and hardness of the formulation. Optimization was carried out to reach desired performance.

Surface tension measurement were made of the samples. As it is discussed in literature, antifog surfaces can be hydrophilic or hydrophobic,<sup>11,12,13</sup> and most of the antifog surfaces fell into these two categories. In this study, however, it is observed a dynamic change of surface tension with time. The advancing contact angle of antifog samples, as seen in Table 6, changed from 40° to 10° in a 4 seconds, while untreated PC surface showed a constant angle of 72°. It is also worthwhile to mention that the contact angle after a month's placement is 7°, indicating the long term stability of coating. Figure 4 shows the area or a water droplet coverage over time. Within a few seconds, the droplet spread quickly on the antifog surface,

reaching a plateau in three minutes. At the end of the observation, the water drop almost disappeared, indicating an extremely hydrophilic surface.

The contact angle is dominated by the interaction of  $\gamma_{sg}$ ,  $\gamma_{sl}$ , and  $\gamma_{lg}$ , according to the following relationship,  $\gamma_{lv} \cos\theta_Y = \gamma_{sv} - \gamma_{sl}$  (1.1) where  $\gamma_{lv}$ ,  $\gamma_{sv}$ , and  $\gamma_{sl}$  represent the liquid-vapor, solid-vapor, and solid-liquid interfacial tensions, respectively, and  $\theta_Y$  is the contact angle (Figure 5). Equation (1.1) is usually referred to as Young's equation, and  $\theta_Y$  is Young's contact angle. Because  $\gamma_{sg}$  will not change over time, it should be the  $\gamma_{lg}$  and  $\gamma_{sl}$  that provide changes of tension. One important reason can be that some surface ligands may have rearranged over time due to the exposure to water, that lead to a more hydrophilic surface. More studies are underway to understand the structure-property relationship, and make more suitable products for customers.

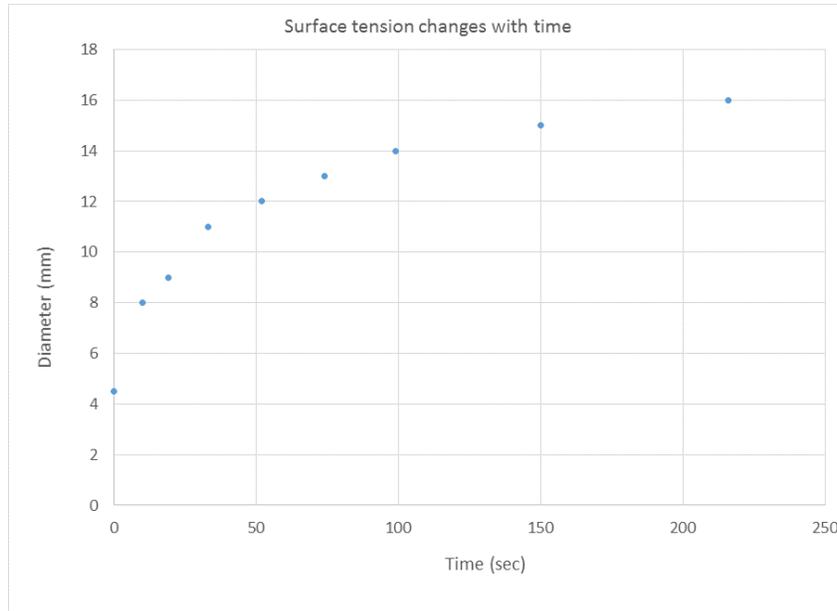


Figure 4. Water contact area change with time as a measure of surface tension for 931-PC.

Table 6 Changes of water contact angle ( $^{\circ}$ ) with time for sample 931-PC. Contact angle is lower for antifog samples, and the contact angle decreases quickly over time.

	1 sec	2 sec	3 sec	4 sec	30 days
931-PC	40	25	15	10	7
PC	72				

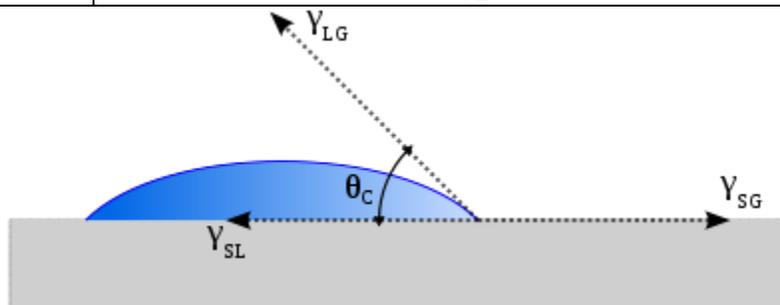


Figure 5. Surface tension is caused by the unbalanced forces of liquid molecules at the surface

Adhesion test was performed using cross-cut method. A score of 5, corresponding to 100% adhesion, would indicate a good adhesion and is denoted as "pass". Three passes have to be satisfied for a good coating. Adhesion tests of antifog samples prior and after 100 °C oven treatment were performed on samples. Adhesion after boiling was also tested for robustness of coating. All coated samples reported in this study showed good adhesion for PC. In general, addition of antifog enabling components to the formula impacts adhesion, most of the time inversely. Therefore, formulation is challenging in achieving desired performance. Adding heterofunctional oligomer should provide advantages in terms of performance, storage stability against phase separation, and easy processing.

Scratch resistance steel wool test, pencil hardness, Taber abrasion resistance tests were used to evaluate the quality of coating against potential wear forces. In scratch resistance tests, both the depth and the width of the scratches by steel wool were recorded and compared for scratch resistance. Pencil hardness has to be B or higher for qualification. In Taber abrasion resistance, haze gain and weight loss were used to evaluate abrasion resistance. Table 7 listed results of 931-PC.

Table 7. Haze level increase of antifog samples after 100 cycles and 500 cycles of abrasion resistance tests, respectively.

931-PC-2	after 100 cycles	after 500 cycles
Haze gain (%)	9.7%	31.5%

Bayer test was carried out using 500 g of Kryptonite with 600 cycles. Table listed the results of 931-PC-2. The Bayer ratio for 10-11 micron film thickness is 1.43.

Sample hardness was tested using pencil hardness tests. A pencil hardness from B to H were obtained on PC samples that showed quality antifog performances in this study. Chemical resistance of coated and noncoated samples were compared for the length of time necessary to make noticeable changes on tested substrates. Table 8 lists some of the results. Coated samples did not make significant changes to substrate performance against most of the organic chemicals being tested. On the other hand, coated samples seem more susceptible under basic solutions, such as sodium hydroxide. The exact reason needs to be confirmed with more detailed study, but the hydrophilicity of the coating may have contributed to the easy penetration.

Finally, antifog performances of 931-PC, was compared against a commercially available antifog product. Table 9 lists some of the data obtained. It can be found that in general, 931-PC was noticeably better in performance than commercial samples in many categories. Especially in the areas of haziness, adhesion, and antifog performance against harsh environment such as water immersion, boiling and freezing, and antifog duration, 931-PC products showed significant improvements. For applications that require better hardness, toughness, and minimum thickness, other product formulations are feasible.

### **Glass Adhesion Antifog Coating**

Antifog formulations do not have sufficient adhesion onto glass without primers. Replacing components in the AF formulas, especially the highly ethoxylated oligomers, with glass adhesion components through simple formulation above would result in loss of antifog properties. An effort was made to develop two multifunctional oligomers, one with a glass adhesion promoter, and the other with an antifog promoter. The glass adhesion oligomer, oligomer 1, carries acrylate groups as well as hydroxyl groups, while the antifog oligomer, oligomer 2, carries acrylate groups as well as isocyanate groups. When being mixed together, the mixture will provide dual cure reaction mechanisms, UV cure and thermocure. This combination enables an elegant extension of formulation capabilities towards the required antifog properties. It is found that with the proper mixture that includes Oligomer 1, Oligomer 2, and antifog

enablers, formulations lead to coatings with better adhesion to glass while maintaining antifog performance. Extensive antifog evaluation is underway.

Table 8. Chemical Resistance of antifog treated PC substrate, 931-PC, and untreated PC substrate

	Uncoated	Coated
Distilled White Vinegar	2 minutes	10 minutes
Toluene	2 minutes	2 minutes
Acetone	2 minutes	2 minutes
Ethanol	< 30 minutes	< 30 minutes
28% Ammonia Hydroxide	2 minutes	8 minutes
10% Sodium Hydroxide	< 30 minutes	4 minutes
25% Sodium Hydroxide	< 30 minutes	2 minutes
10% Sulfuric Acid	< 30 minutes	18 minutes
IBIB	< 30 minutes	6 minutes
Butyl Acetate	2 minutes	4 minutes
MEK	4 minutes	2 minutes
MIBK	4 minutes	8 minutes
MIAC	2 minutes	2 minutes

### Soft Touch

Soft touch coatings are another area where UV-curable oligomers play a big role for function. In order to get soft touch performance, the final product needs to be soft, which means materials of high elasticity and low Young's modulus at the usage temperature have to be available. Materials that have these properties are mostly oligomers or polymers, such as natural rubber, PBD rubber, and silicones. UV curable soft touch formulation demand conversion of these existing oligomers to UV curable functional oligomers.

In this study, polybutadiene polyol was used as one key raw material to derive the final oligomer. PBD polyol of different molecular weight and functionality, in combination with other polyols, were used to develop proper oligomers.

Table 9. Comparison of antifog formulation 931-PC against commercially available product

	931 - PC	Commercial sample
Haze	0.15	1.23±0.63
Yellow Index	1.03	1.1±0.01
Transmittance. %	92.37	92.40±0.55
Adhesion, %	100	95±5
Thickness, mil	0.3	0.5
Scratch Resistance, psi	2 to 3	1 to 2
Pencil Hardness	HB	B
Breathing Test	Antifog	Antifog
Water Immersion Test, % adh.	100	< 50
Boiling Test, % adh.	100	failed
Fogging test, min w/o fogging	120	flash, 57
Freezer Test, % adhesion.	100	68±17

## Conclusions

Heterofunctional polyurethane acrylates have been developed based on highly branched polyol raw materials, including dendrimeric polyols. Raw materials with different characteristics, hydrophilicity, hydrophobicity, conductivity, elasticity, mechanical property, and/or formulation compatibility were selected in obtaining oligomers of desired properties. Thin film UV-curable oligomers targeting for antifog application, glass adhesion, and soft touch application, have been developed. Performance for some final coatings were presented. Specifically, antifog coatings for PC substrates were evaluated extensively for performance against many application scenarios, from masking, freezing, abrasion resistance, time degradation, high temperature stability, to longevity against water immersion. Some of the formulations were compared against commercial products, and found that many of the performance qualities were better than their commercially available counterparts.

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