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Abstract

Hydrophilic polyurethane polymers are important materials in the optical and medical device industries due to their anti-fog properties and biocompatibility. The ability of some to be dispersible or even soluble in water has also led to their extensive use in other fields, such as wood coatings. This paper will explore the properties of several urethane acrylate oligomers with hydrophilic moieties. The effect of the structure and concentration of such moieties on various coating properties such as scratch and chemical resistance will be investigated.

Introduction

The UV-ink and coatings industries are increasingly using waterborne polyurethane polymers as solutions to various problems with formulated products.^{1,2} The ability to use water in the place of flammable solvents as diluents increases the many environmental advantages a product may already have by being used in a UV-curable system.¹ Reactive diluent monomers, which can possibly damage substrates or have hazards of their own, can also be replaced by water.¹

Typically, waterborne polyurethane polymers are prepared through the inclusion of a hydrophilic (water-loving) moiety within the polymeric structure.¹ Unfortunately, this modification has been shown to have a negative impact on the polymer's physical properties including water sensitivity and chemical resistance.^{1,3} Stability of the water diluted polymer is also usually a concern requiring the use of neutralizers, co-solvents, or a specific level of water dilution limiting the options of the formulator.^{1,3} Previously, we reported on a class of water dilutable oligomers that did not have these disadvantages.⁴ These oligomers could be diluted into a water emulsion at any concentration without additives and had good physical properties. The remainder of this paper will further explore these oligomers and their properties.

Experimental

All oligomers were analyzed with gel permeation chromatography (GPC) using a Polymer Labs PL-GPC 50 equipped with RI detector and mixed D-columns. Formulations were mixed using a FlackTek DAC 150.1 FVZ SpeedMixer at 3000 rpm for 2.5 minutes.

Viscosities were measured at 25 °C using a Brookfield CAP 2000+ viscometer with CAP 2 Spindle. Fineness of dispersion was measured using a Hegman grind gauge in accordance with ASTM Method D 1210. Surface tension of water emulsions was estimated using the capillary rise method in ambient conditions with water as a reference (71.8 dynes/cm). Emulsion stability was measured by monitoring the condition of the emulsion in a sealed, graduated 20-mL glass vial over time.

Ambient drying times were measured by monitoring weight loss over time of a thin coating of emulsion in an uncovered, aluminum pan. Accelerated drying time was measured at 90 °C using an Ohaus MB45 moisture balance.

Formulations were cured in the air using a Fusion 300 processor with a D-bulb. Two passes under the lamp at a conveyor speed of 20 ft/min were performed for all cure experiments. Unless noted, the materials cured were dried films of undiluted oligomer with 2.0% photoinitiator added. The methods for determining the mechanical and physical properties of cured materials have been described in detail elsewhere.⁵

Abrasion resistance was tested using falling sand in accordance with ASTM Method D 968. Chemical resistance to solvent was determined in a manner based on ASTM Method D 5402 using methyl ethyl ketone (MEK), acetone, and water as solvents. A maximum of 200 solvent double-rubs were performed. Chemical resistance to common acids, bases, or staining materials was determined in a manner based on ASTM Method D 1308 with a 1.0 mil coating being applied to a stainless steel substrate. The test areas were covered and the materials allowed to sit for a maximum 4 hours after which the coating was examined for any defect in color, gloss, or integrity. Coatings tested for solvent and chemical resistance were prepared from formulations of oligomer diluted with 50.0% isobornyl acrylate (IBOA) and 2.0% photoinitiator.

For the purposes of testing the adhesion to various substrates, oligomers were also formulated with 50.0% IBOA and 2.0% photoinitiator. Adhesion was tested in accordance with ASTM Method B 2197.

Results and Discussion

Description of Oligomer Structure

The Oligomers A-D described below consist of a highly branched, hydrophobic core with covalently attached, dangling hydrophilic moieties as seen in Figure 1. Using **A** as a reference in describing the structural differences between them, **B** has more hydrophilic moieties, **C** has hydrophilic moieties of larger size, and Oligomer **D** has smaller moieties and in a different position in the oligomeric chain. Figure 2 reports these differences in tabular form as well as giving other characteristics that may affect the oligomer performance. For example, the functionality and relative concentration of acrylate groups would control the crosslink density of the final cured material and therefore its strength and resistance.^{1,3}

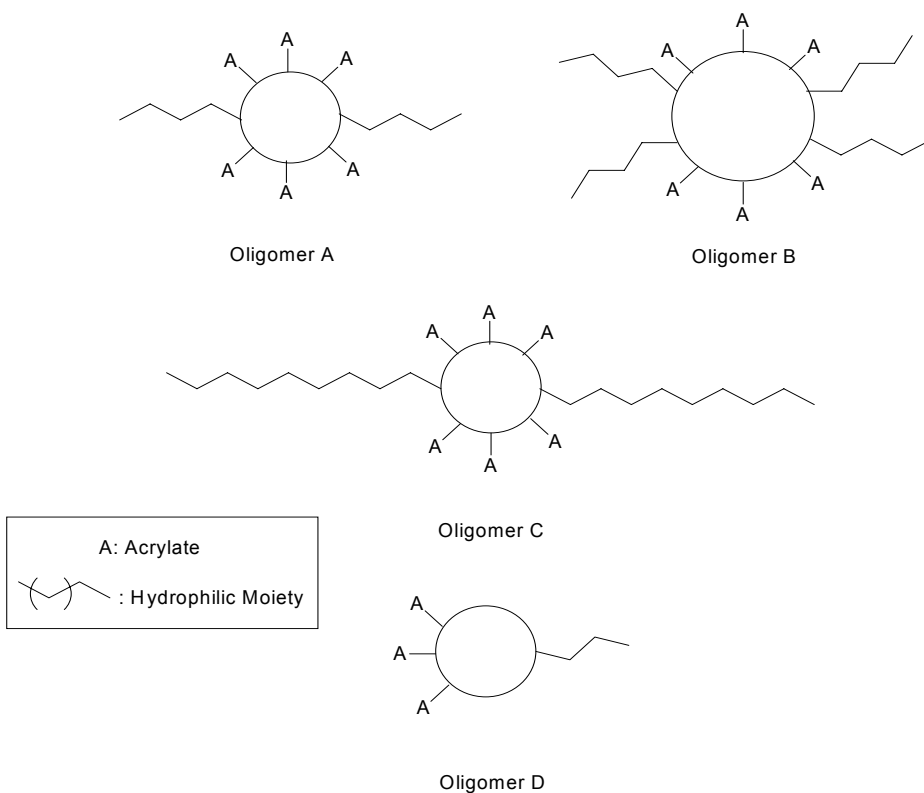


Figure 1: General Scheme of Oligomers A-D

Oligomer	Hydrophilic Moiety Size	Functionality	Acrylate Wt%:Hydrophilic Wt%	Position
A	Medium	6	2 : 1	Pendant
B	Medium	6	1 : 1	Pendant
C	High	6	1.3 : 1	Pendant
D	Low	3	1.5 : 1	Terminal

Figure 2: Further Description of Oligomers A-D

Oligomer Properties in Water Emulsion

Viscosity and Stability

The properties of the oligomer/water emulsion are essentially controlled by the oligomer's overall hydrophilicity. In general, the greater the hydrophilicity of the oligomer, the greater the viscosity and stability of the emulsion will be due the formation of smaller, finer particles of emulsified oligomer.^{1,3} Particle sizes are typically on a nanometer scale.³ Hydrophilicity also plays a significant role in the emulsions surface tension which affects pigment and substrate wettability characteristics.^{1,3}

Viscosity and stability data is found in Figure 3. Stability data was documented at the time when the emulsion first started to shows signs of separation or instability and the time when half the volume of the emulsion had separated into two distinct layers. Figure

4 presents the surface tension and fineness of dispersion for the oligomers in 50% water emulsions.

All oligomers show substantially lower viscosities than standard waterborne polyurethane materials in their undiluted form and the addition of just 10% water to the oligomer reduces the viscosity by over 50% in all cases. This property should allow formulators to potentially receive the oligomer in a high percent solids form giving greater leeway in formulation options and also reducing costs. Oligomer dilutions become usable in spray applications at 50% water dilutions.

As expected from the particle sizes, **A** and **B** have similar viscosities and **C** has the highest viscosity when diluted with 50% water. Based on its viscosity, **D** should be expected to have a similar particle size as **C** although it does not. Likely, the particle size giving rise to the higher viscosity of **D** is lower than the μm scale used in the test.

Oligomer	Viscosity (cP)			50% Water Stability	
	Undiluted	10% Water	50% Water	First Separation	50% Separation
A	8350	3150	60	1 day	4 days
B	2845	1450	70	<1 hour	3 hours
C	6735	3015	170	1 days	>14 days
D	5687	2285	120	12 day	>14days

Figure 3: Oligomer Viscosity and Stability

The smaller particle size is also indicative of increased stability as is illustrated by **D** and **C** in that order being the most stable. The larger particle sizes of **A** and **B** result in decreased stability. The surface tensions of the various oligomer emulsions directly follow this same trend with smaller particle sizes leading to lower surface tension.

Oligomer	Surface Tension (dynes/cm)	Particle Size (μm)
A	59.02	25
B	70.12	30
C	61.73	<10
D	44.4	40

Figure 4: Surface Tension and Fineness of Dispersion of 50% Water Emulsions

The significantly higher stability of **D** is somewhat surprising given it has the smallest hydrophilic moiety. However, the terminal position of the moiety probably allows **D** to align itself much better into the typical surfactant head-tail formation making it the most hydrophilic. Conversely **B**, with all its many hydrophilic groups tightly, clustered next to each other, cannot attain that degree of alignment explaining its instability and lack of hydrophilicity. **A** and **C** are roughly in between with the **C** being more stable due its hydrophilic groups being large and farther from the hydrophobic core.

Drying Times

In practical use it is important to know how fast water can be evaporated from the applied coating so that it can be cured. This data is found in Figures 5 and 6 which track the water evaporation for the 50% water emulsions as measured as a loss in weight over time. Of course, the actual drying time of a waterborne coating will depend on a multitude of factors including the amount of water present, the thickness of the coating, and the relative humidity of the atmosphere where drying is taking place.

As shown there is little difference between the dry times of the oligomer emulsions when dried at ambient temperatures. All dried in approximately 3.5 hours. Under accelerated drying conditions there does seem to be a slight difference. **B** dried slightly slower than **A**. **C** and **D** dried at nearly the same rate which was faster than both **A** and **B**. However, the range of drying times under accelerated conditions was approximately 6-9 minutes which may or may not be significant in practical application.

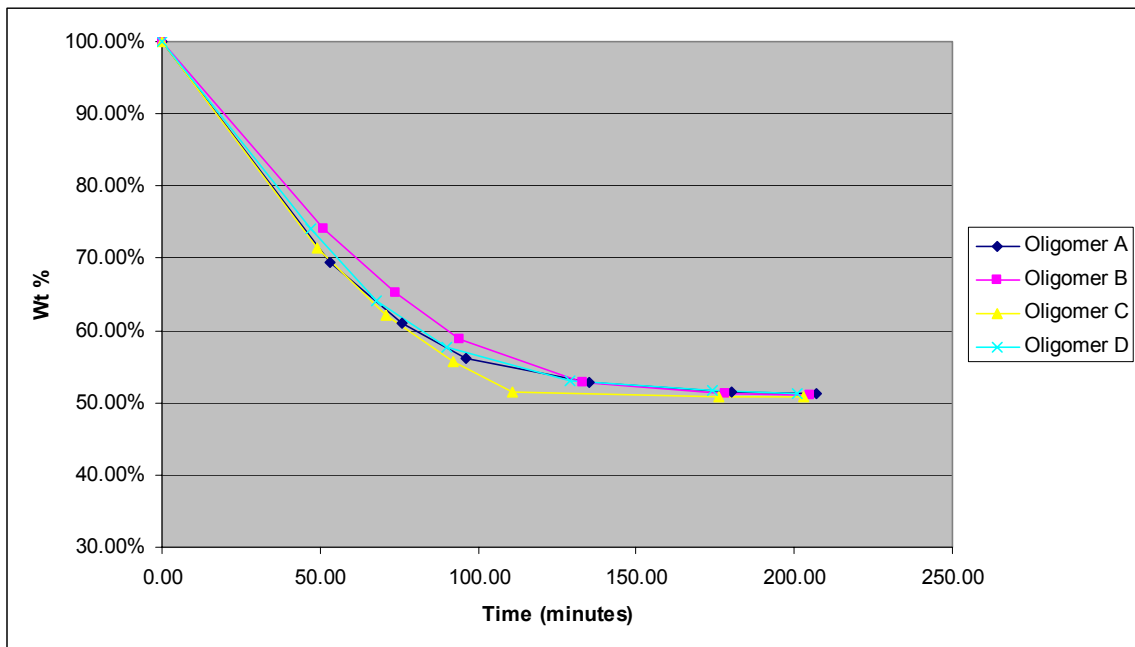


Figure 5: Drying Times at Ambient Temperature

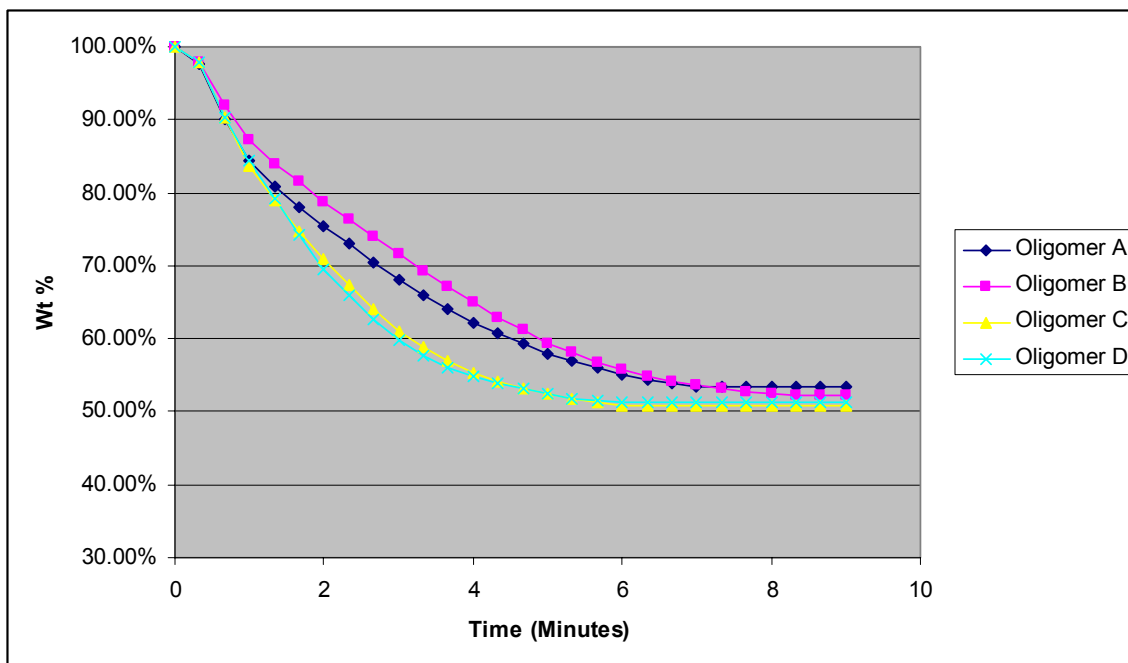


Figure 6: Accelerated Drying Times at 90 °C

Physical Properties

Tensile and Hardness Properties

The tensile and hardness properties of the oligomers are given in Figure 7. The higher crosslink density arising from high functionality and acrylate concentration of **A** clearly impart the greatest strength and hardness. **B** has the lowest acrylate concentration and therefore is the weakest and softest of the oligomers. **C** and **D** are very similar with differences in hardness resulting from **D**'s lower functionality.

Oligomer	Tensile Strength (psi)	% Elongation	Durometer Hardness	Pencil Hardness
A	4100	2	88D	5H
B	1800	3	73D	4B
C	3100	3	82D	5H
D	2900	2.5	81D	4B

Figure 7: Tensile and Hardness Properties

Abrasion, Solvent and Chemical Resistance

The abrasion, solvent and chemical resistance of the oligomers can be found in Figures 8, 9, and 10, respectively. As with the mechanical properties, the higher crosslink density of **A** results in superior resistance to all forms of weathering, especially resistance to solvents. **C** and **D** also have good resistance properties to a majority of exposure types. **B** had acceptable resistance to standard chemicals but poor resistance to abrasion and most solvents, again, due to its low crosslink density. All oligomers have substantial water resistance unlike standard waterborne materials.

Oligomer	Sand To Coating Failure (gal/mil)
A	12
B	< 2
C	10
D	10

Figure 8: Resistance to Abrasion

Oligomer	MEK Rubs	Acetone Rubs	Water Rubs
A	> 200	> 200	> 200
B	30	22	> 200
C	108	57	> 200
D	127	53	> 200

Figure 9: Resistance to Solvent

Oligomer	Draino	5.0% Acetic Acid	Iodine	Yellow Mustard	Ketchup	Coffee
A	5	3	4	4	4	4
B	5	1	3	1	2	4
C	5	2	2	2	3	5
D	5	2	2	3	3	5

Figure 10: Resistance to Chemicals. 5 = no effect on coating; 0 = coating was at least partially removed

Adhesion

Figure 11 presents adhesion data for the oligomers on various metal and plastic substrates. In general, **D** has the best adhesion to metals whereas **B** shows the best adhesion to plastics. **A** also has good overall adhesion properties across both type of substrates. The adhesiveness of **C** seems to be limited to very specific substrates. None of the oligomers adhered very well to glass.

Oligomer	Steel	Stainless Steel	Aluminum	ABS	Polycarbonate	Acrylic	Glass
A	3	3	2	5	3	0	0
B	1	1	3	5	4	4	1
C	2	3	1	5	0	0	0
D	3	4	2	5	0	0	0

Figure 11: Adhesion to Substrates. 5 = coating could not be removed; 0 = no effort required to remove coating

Conclusion

We have described four different oligomers containing hydrophilic moieties dangling from a hydrophobic polyurethane acrylate core. These oligomers show many advantages over standard waterborne materials including low viscosity and substantially increased levels of weathering resistance. However, each oligomer of this type should be evaluated on an individual basis as increasing the level of hydrophilic moieties can

negatively impact these properties without any counterbalancing increase in emulsion stability.

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OCWP002 5/2012

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