

# EVALUATION OF STRUCTURAL EFFECTS FOR SOME ALKOXY MONOMERS IN UV CURABLE COATINGS

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## Introduction

Useful UV curable coatings are obtained by blending the appropriate oligomers, reactive diluents, photoinitiators and additives. Knowledge of how the chemistry of each of these components affects the coating properties is necessary and good introductory information on this subject is available in the literature.<sup>1,2</sup> In the course of our work we became interested in contributions of the acrylate reactive diluent component. Since the oligomers used in UV coatings are generally high in viscosity, the main function of the reactive diluent is to adjust the coating viscosity. In addition, reactive diluents are added to modify the physical properties of the coating. Monofunctional diluents tend to improve substrate wetting and have been known to decrease the curing rate while allowing an increase in the total double bond conversion. Coatings with high gloss and increased network flexibility but low surface hardness and scratch resistance have been obtained. For specific diluents it is necessary to develop additional relevant property data. This paper is concerned with our studies of some monofunctional acrylates containing alkoxy groups used as reactive diluents in UV curable coatings.

## Experimental

Oligomer 1 is a proprietary difunctional urethane acrylate oligomer. Oligomer 2 is a difunctional urethane acrylate oligomer prepared from PTHF 1000 (BASF), isophorone diisocyanate (Lyondell) and hydroxyethyl acrylate (Sartomer). Oligomer 3 is a difunctional urethane acrylate oligomer prepared from PTHF 650 (BASF), isophorone diisocyanate and hydroxyethyl acrylate. All the oligomers were prepared using known standard procedures.<sup>3</sup>

The diluents, EO<sub>4</sub> nonylphenol acrylate (SR 504), 2-phenoxyethyl acrylate (SR 339), Lauryl acrylate (SR 335), and EO<sub>4</sub> lauryl acrylate (CD 9075) were obtained from Sartomer; The diluent EO<sub>2</sub> phenol acrylate (Ebecryl 110) was obtained from Cytec Surface Specialties Inc.; The diluent PO<sub>2.5</sub> nonylphenol acrylate (Aronix M-117) was obtained from Toagosei Chemical Industry Co, Ltd. All were used as received. The diluent nonylphenol acrylate was synthesized from nonylphenol (GE Specialty Chemicals) and acryloyl chloride (Aldrich) using a typical Schotten-Baumann technique. The diluent PO<sub>6</sub> cresol acrylate was synthesized from propoxylated cresol (Milliken Chemicals) and acryloyl chloride using a typical Schotten-Baumann technique. Both were used as isolated without additional purification.

Lucirin TPO (2,4,6-trimethylbenzenediphenylphosphine oxide) was obtained from BASF and used as received.

Viscosities were run on a Physica Viscometer, Rheolab MC 10 using a Z3 cup with a shear rate of 50.3 reciprocal seconds.

Samples for testing were prepared on glass plates using 75  $\mu\text{m}$  (3.0 mil) Byrd film applicator. The films were then cured by exposure to UV light from a Fusion Systems model F450 curing unit with a 120 W/cm (300 W/in) "D" lamp. This unit was mounted on a variable speed conveyor (4 to 75 m/min; 13 to 225 ft/min) and was capable of delivering a energy density of 0.12 to 2.0 J/cm<sup>2</sup> in a single pass as measured with a UV Process Supply Compact Radiometer.

Tensile, elongation and modulus data were obtained using an Instron model 4201. Tensile specimens were prepared by cutting 1.25 cm (0.5 in) wide strips of the coatings (75  $\mu\text{m}$ ; 3.0 mil) cured on glass plates using 2 passes at 1 J/cm<sup>2</sup>. A 5.08 cm (2.0 in) gauge length was used with a crosshead speed of 2.54 cm (1.0 in) elongation per minute. The secant modulus at 2.5% elongation was recorded. A minimum of five tensile measurements was made for each sample.

Dynamic Mechanical Analysis experiments were performed on a Rheometrics Solids Analyzer RSA II at a frequency of 1.0 radian/second with measurements taken every 2° C. Films were prepared by the same method as for Instron testing and preheated at 80°C for 5 minutes.

## Results and Discussion

In order to obtain the desired structure-property information on acrylate diluents containing alkoxy groups in the molecule we chose eight different structures. These structures are shown in Table 1 and consisted of the acrylate moiety connected by the alkoxide moiety (X) to an aromatic/alkyl moiety (Y). The structures are arranged according to increasing molecular weight. In general, the structures varied according to the following; the type of alkoxide unit (ethylene oxide, propylene oxide) and amount (0 to 6 moles) of alkoxylation, the presence or absence of a phenyl group, the presence and type of an alkyl group. Most of the diluents used were available commercially but nonylphenol acrylate (Monomer D) and the PO<sub>6</sub> cresol acrylate (Monomer H) were synthesized from the appropriate hydroxyl compound and acryloyl chloride using the Schotten-Baumann technique.

Model formulations having a constant composition were prepared containing 40.0% by weight of each of the monomeric diluents, 11.4% of EO<sub>4</sub> nonylphenol acrylate, 45.6% of a difunctional urethane acrylate oligomer (Oligomer 1) and 3.0% of Lucirin TPO as the photoinitiator. These formulations and their viscosities are shown in Table 2. The table is organized with the monomers in increasing molecular weights. This means that as the formulation number increases the total double bond concentration decreases from 0.31 to 0.17 eq/100g. All the model formulations were clear solutions and had viscosities ranging from 1.9 to 11.7 Pa·s at 25° C. The viscosity was not related to the molecular weight of the alkoxy acrylate but seemed to increase as the amount of ethoxylation increased. Thus, the lauryl acrylate (Monomer C) diluent produced the lowest coating viscosity while the EO<sub>4</sub> nonylphenol acrylate diluent (Monomer G) gave the highest viscosity.

The results of the curing studies on these formulations are summarized in Table 3. Using 3 mil films, the cure speed of each formulation was measured by determination of the energy density required to obtain 95% of the ultimate modulus. The cure speed of the formulations varied from 0.18 to 0.56 J/cm<sup>2</sup>. A lower value indicates faster cure and is desirable. These cure speed values could be correlated with two features. First it was evident that the presence of the propylene oxide moiety instead of ethylene oxide moiety produced a lower dosage required to attain 95% of the ultimate modulus and, thus, was faster curing. Second, a linear relationship between viscosity and cure speed with an R<sup>2</sup> = 0.97 was found. Thus, as the viscosity of the formulation increased, the coating also cured faster. The cure speed did not correlate with molecular weight of the diluent and must therefore be affected by the structure of the diluent.

Table 1. Monofunctional acrylate structures used in model formulations.

$\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{X}-\text{Y}$			
Monomer	Mol Wt (g/mol)	X	Y
A	192	$\text{CH}_2-\text{CH}_2-\text{O}$	Phenyl
B	236	$-(\text{CH}_2-\text{CH}_2-\text{O})_2-$	Phenyl
C	240	nil	$\text{C}_{12}\text{H}_{25}$
D	274	nil	$\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19}$
E	416	$-(\text{CH}_2-\text{CH}_2-\text{O})_4-$	$\text{C}_{12}\text{H}_{25}$
F	436	$-(\text{CH}_2-\overset{\text{CH}_3}{\text{CH}}-\text{O})_{2.5}-$	$\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19}$
G	450	$-(\text{CH}_2-\text{CH}_2-\text{O})_4-$	$\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19}$
H	481	$-(\text{CH}_2-\overset{\text{CH}_3}{\text{CH}}-\text{O})_6-$	$\text{C}_6\text{H}_4-\text{CH}_3$

Table 2. Model formulations used to test structural variables in alkoxyated monofunctional acrylate diluents.

Component Description	Desig.	1	2	3	4	5	6	7	8
Prop. Oligomer MW = 4900	Oligomer 1	45.6	45.6	45.6	45.6	45.6	45.6	45.6	45.6
EO <sub>4</sub> Nonylphenol Acrylate	Diluent	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4
2-Phenoxyethyl Acrylate	Monomer A	40.0							
EO <sub>2</sub> Phenol Acrylate	Monomer B		40.0						
Lauryl Acrylate	Monomer C			40.0					
Nonylphenol Acrylate	Monomer D				40.0				
EO <sub>4</sub> Lauryl Acrylate	Monomer E					40.0			
PO <sub>2.5</sub> Nonylphenol Acrylate	Monomer F						40.0		
EO <sub>4</sub> Nonylphenol Acrylate	Monomer G							40.0	
PO <sub>6</sub> Cresol Acrylate	Monomer H								40.0
Lucirin TPO <sup>a</sup>	Photoinitiator	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total Double Bond Conc. (eq/100g)		0.31	0.26	0.26	0.24	0.19	0.18	0.18	0.17
Viscosity @ 25°C (Pa·s) <sup>b</sup>		4.0	5.1	1.9	NR <sup>c</sup>	3.9	11.7	10.8	NR

a. 2,4,6-trimethylbenzenediphenylphosphine oxide

b. Physica Viscometer, Rheolab MC 10, Z3 cup, 50.3 s<sup>-1</sup>

c. NR = not run

\* Content of each component is weight percent

The physical and thermal mechanical properties of each formulation were also measured on 3 mil films. Analysis of the physical properties showed that the tensile strength ranged from 0.5 to 2.0 MPa, the modulus ranged from 1.0 to 1.8 MPa and the equilibrium modulus ranged from 0.9 to 1.6 MPa. The lowest value in all three cases was obtained with Monomer C. These strength values were not related to the molecular weight of the monomer. The elongation values ranged from 124 to 310%. The highest value was obtained with Monomer D, which did not have an alkoxy moiety. The glass transition temperatures, which ranged from  $-42$  to  $-2$  °C, were measured using the  $\text{Tan } \delta_{\text{max}}$  from the DMA. Monomer C had the lowest value.

Table 3. Properties of the cured films from the model formulations.

Formulation Number	1	2	3	4	5	6	7	8
<b>Structural Feature:</b>								
Alkoxylation	EO-1	EO-2	No	No	EO-4	PO-2.5	EO-4	PO-6
Phenyl	Yes	Yes	No	Yes	No	Yes	Yes	Yes
Hydrocarbon	No	No	C-12	C-9	C-12	C-9	C-9	C-1
Cure Speed: energy density @ 95% Modulus ( $\text{J}/\text{cm}^2$ )	0.29	0.41	0.56	0.54	0.42	0.18	0.24	0.24
<b>Physical Properties:<sup>a</sup></b>								
Tensile strength (MPa)	1.1	0.9	0.5	2.0	0.8	1.0	0.8	1.4
Elongation (%)	144	124	105	310	169	129	125	166
Modulus (MPa)	1.8	1.7	1.0	1.2	1.2	1.6	1.4	1.6
$\text{Tan } \delta_{\text{max}}$ (°C)	-2	-18	-32	-9	-42	-26	-32	NR
$E_o$ (MPa)	1.4	1.6	0.9	1.2	1.1	1.4	1.3	NR

- a. Cure energy density  $1 \text{ J}/\text{cm}^2$  under  $\text{N}_2$  for a 3 mil film on glass.  
b. NR = not run.

Our interest in the cure speed prompted us to test monomers F and G with two other oligomers. The results are shown in Table 4. In all three oligomers the viscosity, tensile strength, percent elongation and modulus are higher for Monomer F. In Oligomers 1 and 2 the cure speed is faster with Monomer F.

## Conclusions

The effect on the coating properties of some structural variables of eight alkoxy acrylate monomers used as diluents in UV curable coatings was studied. All of the model formulations were clear and had viscosities ranging from 1.9 to 11.7 Pa·s at 25° C. Cure speed, film properties and thermal mechanical properties were measured. Although general relationships between the structural variations and the properties measured were difficult to discern, the following observations can be made; lauryl acrylate produced the greatest reduction in coating viscosity, the absence of alkoxy groups resulted in higher elongation, a correlation was found between coating viscosity and cure speed and the propylene oxide (PO) group gave faster cure than the ethylene oxide (EO) group. The latter conclusion was also found to be true in testing with a second difunctional urethane acrylate oligomer.

Table 4. Testing of cure speed<sup>a</sup> in other oligomers.

Component Description	Designation	Mole Wt (g/mol)	9	10	11	12
H-I-[PTHF 1000]-I-H	Oligomer 2	1676	60.0	60.0		
H-I-[PTHF 650]-I-H	Oligomer 3	1326			60.0	60.0
PO <sub>2.5</sub> Nonylphenol Acrylate	Monomer F	436	37.0		37.0	
EO <sub>4</sub> Nonylphenol Acrylate	Monomer G	450		37.0		37.0
Lucirin TPO <sup>b</sup>	PhotoInit.		3.0	3.0	3.0	3.0
Total			100.0	100.0	100.0	100.0
Total Double Bond Conc. (eq/100g)			0.16	0.15	0.18	0.17
Viscosity @ 25°C (Pa·s) <sup>c</sup>			9.8	7.1	15.0	10.2
Cure Speed: Energy density @ 95% Modulus (J/cm <sup>2</sup> )			0.13	0.20	0.19	0.10
<b>Physical Properties:</b> <sup>d</sup>						
Tensile strength (MPa)			2.5	1.7	4.9	3.1
Elongation (%)			74	54	75	59
Modulus (MPa)			5.0	4.2	8.8	6.3
Tan δ <sub>max</sub> (°C)			-3	-12	13	5
E <sub>o</sub> (MPa)			5.8	4.4	7.5	7.9

a. Average of two runs.

b. Physica Viscometer, Rheolab MC 10, Z3 cup, 50.3 s<sup>-1</sup>

c. 2,4,6-trimethylbenzenediphenylphosphine oxide

d. Cure energy density 1 J/cm<sup>2</sup> under N<sub>2</sub> for a 3 mil film on glass.

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