OXETANES: CURING PROPERTIES IN PHOTO-CATIONIC POLYMERIZATION

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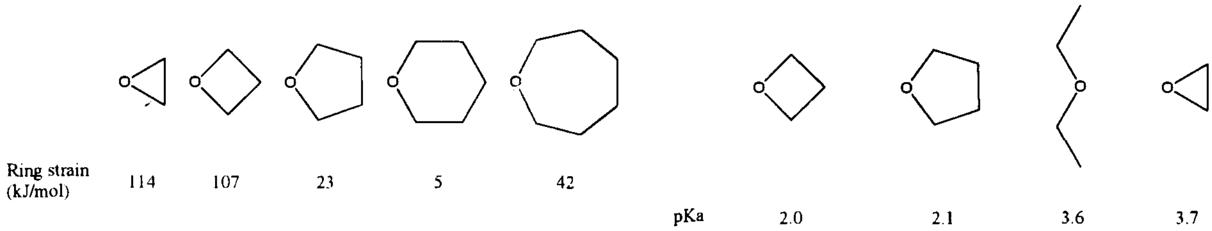
ABSTRACT

Novel mono- and di-functional oxetane monomers are evaluated for photo-cationic curing system in the formulation with cycloaliphatic diepoxide monomer. The viscosity of the formulations were reduced effectively keeping high surface cure rate as epoxide alone. Difunctional oxetanes exhibited improved solvent resistance.

I INTRODUCTION

In the photoinitiated cationic polymerization, many different types of monomers and oligomers have been examined and used [1]. In particular, the photopolymerization of epoxides gives coatings a high thermal capability, excellent adhesion and good chemical resistance. Although photo-polymerized epoxy coatings are known for their high performance, commercially available epoxides, such as bis-phenol-A-diglycidyl ether, undergo photoinitiated cationic polymerization at rather slow rates.

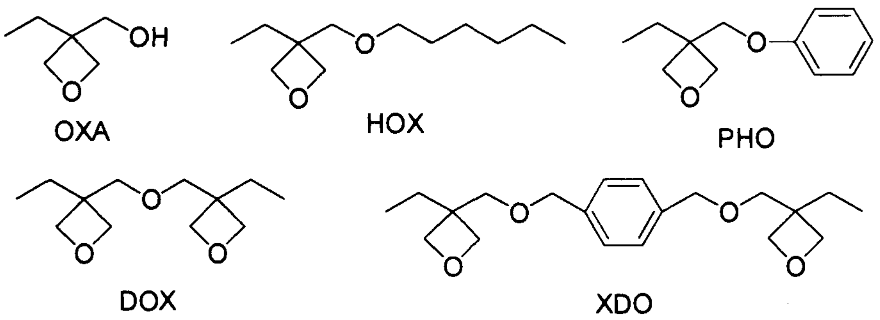


Scheme 1: Ring-strains and Basicities of Cyclic Ethers

Three major factors contribute to the reactivity of cyclic ethers during cationic ring-opening polymerization [2]. These are: the basicity, the ring strain and steric factors. It is interesting to compare these factors for two classes of cyclic ethers; oxetanes and epoxides. For example, the ring strain of ethylene oxide has been calculated to be 114 kJ/mol while that for oxetane is 107 kJ/mol [3]. At the same time, the pKa for these two ethers is 3.7 and 2.02, respectively [4-5]. Since the mechanism of the cationic ring-opening polymerization of cyclic ethers involves an SN 2 displacement, the steric requirements of these two monomer types are nearly identical. Thus, while both cyclic ethers have similar steric factors and ring strains, the basicity of oxetane is considerably greater than for ethylene oxide. This latter parameter should, therefore, dominate by making the oxetanes more reactive than epoxides during the photoinitiated cationic ring-opening polymerizations.

Previously, the curing property of oxetane monomer in photoinitiated cationic polymerization was investigated in comparison with the epoxy monomer [6]. Through real time FT-IR measurements, the oxetane monomer was proved to possess different polymerization character from epoxides toward photoinitiated cationic polymerization. Although rather long induction period compared with epoxide was seen in the early stage of oxetane polymerization, after that stage polymerization underwent smoothly until high conversion of monomer. In the formulation with epoxy monomer, oxetane exhibited fairly fast polymerization. Employing the computational study, the acceleration mechanism of oxetane polymerization was explained by the fast initiation of epoxide through S_N1 ring opening of oxirane ring.

Based on the above results, a series of mono- and di-functional oxetane monomers, possessing one or two oxetanyl group in the molecule, have been synthesized in our laboratory. This paper details the evaluation of three monofunctional oxetane monomers and two difunctional monomers listed below for performance UV cationic cure system.



Scheme 2: Mono- and di-functional oxetane monomers

II EXPERIMENTAL

Raw Materials

The oxetane monomers used throughout this study were synthesized from OXA or 3-ethyl-3-chloromethyl-oxetane through phase-transfer reaction. Cycloaliphatic diepoxide monomer (UVR-6110) and the sulfonium salt cationic photoinitiator (UVI-6990) used in the formulation were obtained from Union Carbide Co.

Test Methods

The formulations were prepared by mixing the monomers and UVR-6110 with UVI-6990 in an amber vials. The viscosity of monomers and their formulations was measured at 25°C using Brookfield viscometer. A uniform coating of the desired coating thickness was applied to the TFS test panel using a #4 bar applicator. The liquid coating was cured with 80 W/cm of high pressure Hg lamp. Samples for the acetone resistance were cured at 10m/min. conveyor speed.

Tack-free time was defined as the maximum conveyor speed which can be used to produce a coating that is dry to the touch immediately after UV exposure. The acetone resistance of the coatings was defined as the maximum number of rubs with cotton ball impregnated with acetone until the coating starts to be destroyed.

III RESULTS

Typical Properties of the Monomers

Some typical properties of oxetane monomers are listed in Table I. Among the mono-functional monomers, HOX possessing long alkyl side chain showed the lowest viscosity and specific gravity. The slightly high viscosity of OXA can be explained by the hydrogen bonding of hydroxy methyl group in the molecule. The simplest di-functional monomer, DOX, exhibited rather low viscosity and specific gravity compared with XDO with xylene moiety in the molecule. Each of the monomers shown in Table I was found to be completely miscible with UVR-6110. All the monomers listed were AMES Test negative.

Table I Typical Properties of Oxetane Monomers

Monomers	Viscosity cps @ 25°C	Specific Gravity @ 25°C	Compatibility with UVR-6110	AMES Test
OXA	22	1.024	OK	negative
PHO	14	1.046	OK	negative
HOX	4	0.899	OK	negative
XDO	150-170	1.068	OK	negative
DOX	13	0.999	OK	negative

Viscosity and Curing Properties of Oxetanes Formulations

All the oxetane monomers were evaluated using 2-factor mixture studies in combination with cycloaliphatic epoxide (UVR-6110). Each formulation also contained 3 phr (parts per hundred resin) sulfonium salt photoinitiator (UVI-6990). In the formulation of OXA, di-functional (XDO) was also used to enhance the cure rate.

(Formulations with monofunctional oxetanes)

The formulations for the study with monofunctional oxetanes (OXA, PHO and HOX) were shown in Table II. The viscosity of the formulation exhibited a decrease as the amount of monomer is increased. In the formulation of OXA, the viscosity reached almost half of epoxy monomer alone with 15 wt.% of addition. Among these three monomers examined, HOX with long alkyl side chain exhibited the lowest viscosity.

In the formulation of OXA, the cure rate was decreased with more than 20 wt.% of OXA addition. In the cationic ring opening polymerization, hydroxy functional materials such as alcohol is known to work as chain transfer agent. OXA possess not only oxetane ring which undergoes cationic polymerization but also hydroxy methyl group. With lower concentration of OXA in the formulation, the hydroxy group should work as chain transfer site and accelerate the cure rate. The higher content of hydroxy group in the formulation should lead to small polymer chain length and a resulting decrease in cure rate. Another possibility for the decrease in the cure rate is explained by the unreacted hydroxy group remained in the coating, which should work as some kind of tackifier. For the other two monomers, even with 30wt.% of addition, no decrease in the cure rate was found.

Table II Formulation of Monofunctional Oxetanes and Epoxy Monomer[1)]

UVR-6110[2)]	Monomers		Viscosity (cps at 25°C)	Cure Rate[3)] (m/min.)
100	-	-	380	>50
90	OXA	10	214	>50
85	OXA	15	170	>50
80	OXA	20	138	30
75	OXA	25	112	10
70	OXA	30	93	5
70	PHO	30	122	>50
70	HOX	30	44	>50

1) 3 parts of UVI-6990 (Union Carbide Co.) was added as photoinitiator

2) Cycloaliphatic epoxy monomer, available from Union Carbide Co.

3) Coated on TFS with a #4 bar and cured with 80 W/cm of high pressure Hg lamp.

(Formulation with difunctional oxetanes)

The formulations with difunctional oxetanes (XDO and DOX) were listed in Table III. While the formulation with XDO exhibited rather small decrease in the viscosity, DOX reduced the viscosity effectively. In the combination of XDO with OXA, the viscosity of the formulation was also low. This viscosity reduction could be advantageous for some application methods. Each formulation showed very fast surface cure (cure rate). In the formulation of OXA and XDO, even with 30 wt.% of OXA the cure rate was enhanced over 50 m/min.

For the cationic curing system using epoxy monomers, it is well known that the post cure is required for the complete cure of the coating. UVR-6110 alone exhibited very poor acetone resistance until 24 hours. Addition of oxetane monomers improved the acetone resistance even 10 minutes. Higher amount of oxetane content increased the acetone resistance. The improvement effect could be explained by the fast generation of crosslinked network of oxetanes accelerated by epoxide. The higher acetone resistance of DOX formulation could be explained by the lower weight per oxetane of DOX, which resulted in shorter length of crosslinks i.e. stronger network.

Table III Formulation of Difunctional Oxetanes with Epoxy Monomer[1]

UVR-6110[2]	XDO	DOX	OXA	Viscosity (cps at 25°C)	Cure Rate[3] (m/min.)
100	-	-	-	381	>50
80	20	-	-	339	>50
60	40	-	-	304	>50
80	-	20	-	154	>50
60	-	40	-	109	>50
70	10	-	20	134	>50
50	30	-	20	128	>50
60	10	-	30	96	>50
40	30	-	30	93	>50

1) 3 parts of UVI-6990 (Union Carbide Co.) was added as photoinitiator

2) Cycloaliphatic epoxy monomer, available from Union Carbide Co.

3) Coated on TFS with a #4 bar and cured with 80 W/cm of high pressure Hg lamp

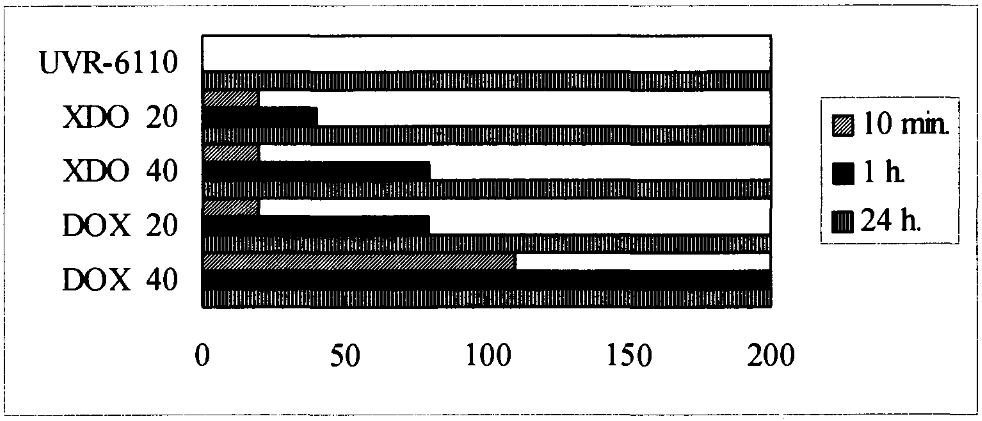


Figure 1 Acetone Resistance vs. Time

IV. CONCLUSION

Oxetanes are effective reactive monomers for photo-cationic curing system. All the monomers were completely miscible with UVR-6110 and AMES Test negative. In the formulation with monofunctional oxetanes, the viscosity of the formulations were reduced effectively. HOX with long alkyl side chain exhibited the lowest viscosity keeping the surface cure rate high.

In the difunctional oxetanes formulation, DOX alone and the combination of XDO with OXA gave the low viscosity formulations with fast surface cure rate. Addition of difunctional oxetane monomers improved the acetone resistance. Higher amount of oxetane content increased the acetone resistance.

As investigated in this study, mono- or di-functional oxetane monomers provide cationic UV-curing formulations of epoxide with fast cure rate and low viscosity. This viscosity reduction could be advantageous for some application methods such as coating industry.

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