

# Curing Properties of Cycloaliphatic Epoxy Derivatives

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## Introduction

UV-cationic-curing, based on the photo-generation of acid and consecutive cationic polymerization, was first proposed in 1970's<sup>1)</sup>. Since then, wide variety of cationically polymerizable monomers, such as epoxides and vinyl ether derivatives, has been investigated<sup>2)</sup>. Among these, formulations based on cycloaliphatic epoxy resins (such as 3,4-epoxycyclohexyl-3',4'-epoxy cyclohexane-carboxylate: ECC) are known to give cured coatings with high thermal capability, excellent adhesion and good chemical resistance. The curing rate of ECC is rather high, but still much lower than that for radical ones. Thus, it has been desired to develop novel cationic formulations keeping the good performance capabilities, while at the same time possessing higher reactivity competitive with radical system.

One approach was addition of alcoholic compounds. Crivello first studied the positive effect of alcohol on cure rate in UV-cationic polymerization of ECC<sup>3)</sup>. In an industrial application, formulation of polyether- or polycaprolactone-polyols is widely used as effective method to improve the curing rate and modify the cured coating property<sup>4)</sup>.

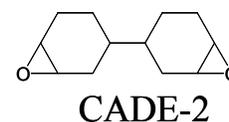
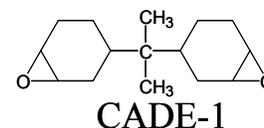
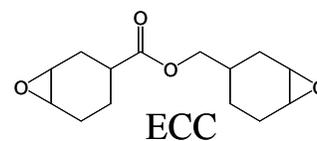
Another approach proposed by our laboratory is an introduction of a four membered cyclic ether; Oxetane, possessing rather high ring strain energy (107 kJ/mol) and basicity ( $\text{pK}_a = 2.02$ )<sup>5)</sup>. In the UV cationic polymerization, oxetane derivatives were found to exhibit quite different polymerization characteristics from those for epoxides<sup>6)</sup>. In spite of rather slow initiation, propagation of oxetane polymerization proceeded smoothly until high conversion of oxetane ring and gave higher molecular weight polymer. In the formulation with epoxy monomer, the slow initiation of oxetane monomer was improved drastically and exhibited fairly fast polymerization.

We have already demonstrated that 3-ethyl-3-hydroxymethyloxetane (OXA), possessing oxetane ring and methylol group in the molecule, effectively increase the curing rate of ECC<sup>7)</sup>. In these formulations, the hydroxy unit in OXA should work as a chain transfer agent in the formulation and form a cross-linked network. During the research, we also investigated the effect of ester group in ECC molecule. The basicity of the oxygen in alcohol or water should be lower than that for in the cyclic

ethers, especially for oxetanes or cyclohexene oxide possessing rather high basicity. The proton affinity of the carbonyl group in the ester unit is enough high to interact with oxonium cation. Crivello had pointed out the possibility of ester group participation in a ring-opening reaction previously<sup>8)</sup>.

To clarify the effect of ester group on the cationic polymerization, di-functional cycloaliphatic epoxide, 2,2-bis-(3,4-epoxycyclohexyl)-propane (CADE-1), having no ester linkage was synthesized and evaluated. In contrast to ECC curing, BECP possessing no ester unit exhibited higher reactivity compared with ECC in the real time DRA measurement and T.C.E. was not affected by atmospheric humidity and exhibited rather high reactivity.

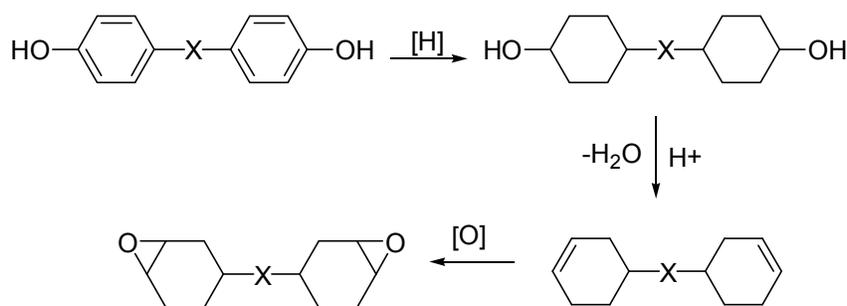
As a continuing work, in this study, the reactivity of di-functional cycloaliphatic epoxide (CADE-1 and 2) was studied using real time dynamic rheological analysis method and the effect of atmospheric water i.e. humid on the photo-cationic polymerization was also investigated.



## Experimental

### Materials

OXA used throughout this study were obtained from Toagosei Co. Ltd. ECC (UVR-6110) and PI (UVI-6992: Sulfonium salt with hexafluoro phosphate as counter anion) were obtained from Dow Chemical. 2,2-bis-(3,4-epoxycyclohexyl)-propane (CADE-1 and 2) was synthesized from hydrogenated bis-phenol A or biphenol according the scheme shown below.



CADE-1: X=C(CH<sub>3</sub>)<sub>2</sub>  
 CADE-2: X=none

### General Procedure

Atmospheric condition was roughly controlled between 30 to 40%RH (25°C) for all the formulating experiments. The content of water in the formulations were ensured to be less than 0.2 wt%

by Carl-Fischer type apparatus. The formulations were prepared by mixing monomers and PI in the desired composition at 40°C.

### Photo-DSC measurement

Heat of photo-polymerization was measured by DSC220C (Seiko Instruments Inc.) equipped with a UV-1 lighting unit (200 W Hg-Xe lamp, Seiko Instruments Inc.). Samples (about 1 mg) were applied to an aluminum pan and irradiated with UV light under a dry air atmosphere at 30 °C. The light intensity was adjusted to 2.5 mW/ cm<sup>2</sup> at 365nm using ND filter.

### Real-Time Dynamic Rheological Analysis (DRA)

Employing stress control Dynamic Spectrometer, we can irradiate UV light to the samples through quartz glass and measure the rheological properties during the photo-polymerization<sup>9)</sup>.

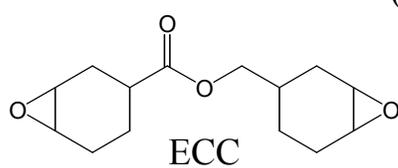
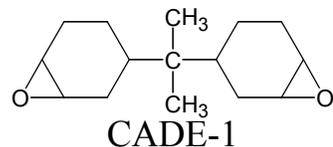
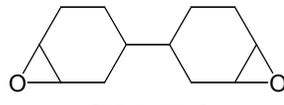
The viscoelasticity of the sample during the cationic polymerization was measured at 30 °C by the parallel plate (diameter=6mm) method using VAR-50 Viscoanalyser (Reologica Inst. A.B.) equipped with a UV irradiator (200 W Hg-Xe lamp, Hamamatsu). The gap, which is equal to the sample thickness, was set to 50µm. The irradiation intensity was adjusted to 10 mW/ cm<sup>2</sup> measured at 365nm using ND filter. Temperature in the measuring chamber was controlled to 30 °C by dry air, which was also used to eliminate the atmospheric water. Using computational feed back, the measurement was performed in strain control mode (0.5%) during the change of a sample from a liquid phase to a solid.

In the post-curing measurement, to ensure an adequate response, the gap was set to 500µm and UV irradiation was performed varied time with intensity of 100mW/ cm<sup>2</sup>. Including UV irradiation time, the sample was kept at 30 °C for 15min., the temperature was raised to 150 °C at 2 °C /min. rate and kept for 30min., finally cooled to 30 °C.

## Results and Discussion

### Monomer Properties

After distillation from reaction mixture, both CADE-1 and 2 was clear liquid. Viscosity of the monomers were measured and listed. CADE-1 possessing propylidene group between the cycloaliphatic units exhibited rather high viscosity compared with ECC. The viscosity of CADE-2 without linkage group was much lower than that for CADE-1. The details for the big difference in the viscosity among these monomers is still obscure,

	Viscosity (mPas at 25°C)
 ECC	400
 CADE-1	1000
 CADE-2	50

however, the interaction of CADE-2 molecule in the liquid stage should be much lower compared with CADE-1, which might be explained by conformer study.

### Photo-DSC Measurement

Exo-thermo during the ring opening polymerization of monomers was measured by Photo-DSC. The heat flow was summarized on Figure 1.

ECC possessing ester group resulted in low heat generation, which means low reactivity. CADE-2 exhibited much higher reactivity compared with ECC. The peak height of CADE-1 was almost the same as ECC. The low reaction rate for CADE-1 might be caused by its high viscosity, which resulted in lower mobility of the monomer.

### Real-Time Dynamic Rheological Analysis (DRA)

Real time DRA for cycloaliphatic epoxides were carried out with continuous irradiation of UV light (10mW/cm<sup>2</sup> at 365nm) and the gap for the measurement was set to 50μm. The results were shown in Figure 2.

While ECC resulted in slow increase of storage modulus, CADE-1 showed much faster cure rate. Low viscous CADE-2 exhibited the fastest increase of storage modulus among the monomers tested.

Taking account the result of Photo-DSC measurement, the lower reactivity of CADE-1 than expected should be caused its low mobility. To clarify this idea, OXA was formulated as diluting monomer to reduce the viscosity.

Figure 3 shows the real time DRA results for CADE-1 with 10% addition of OXA formulations with continuous UV irradiation. CADE-1 exhibited faster increase in modulus compared with ECC and OXA addition accelerated the cure rate. Using short time irradiation method, the minimum UV dose for complete cure was >1000 (CADE-1 alone) or 250mj/cm<sup>2</sup> (10% OXA).

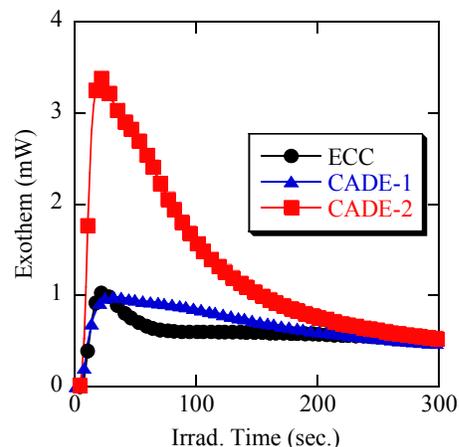


Figure 1 Photo-DSC measurement for ECC, CADE-1 and CADE-2

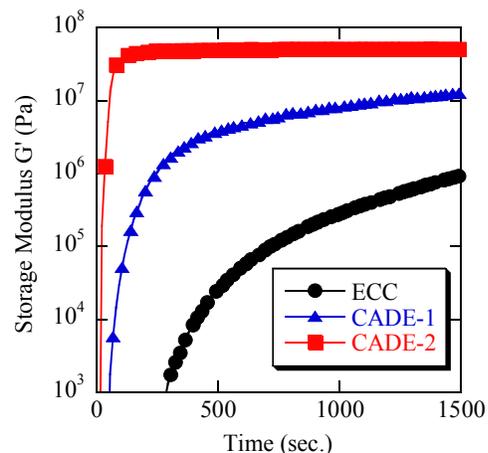


Figure 2 Real-time DRA measurement for ECC, CADE-1 and CADE-2

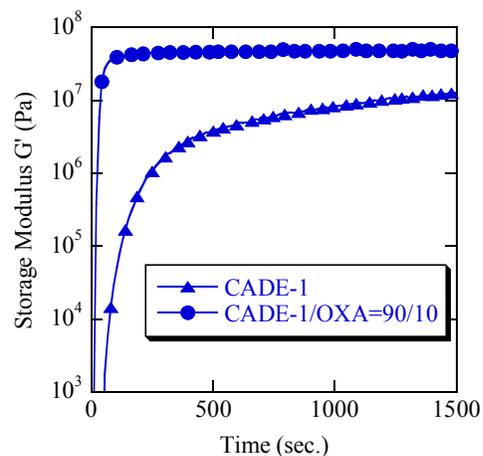


Figure 3 Real-time DRA measurement for ECC and CADE-1 with 10% of OXA

## Conclusions

In this study, the curing properties of cycloaliphatic epoxides derivatives, possessing no ester group (CADE-1 and 2), in the photo-initiated cationic polymerization were investigated. Using Photo-DSC and real time DRA method, reactivity comparison of them with ECC was conducted.

High curing rate of CADEs, especially for low viscous CADE-2, was confirmed. The curing rate of highly viscous CADE-1 was effectively accelerated by addition of OXA.

Although the detail mechanism for the curing properties of ECC is still obscure, one possibility should be the interaction of ester unit in the molecule. Farther investigation of the reaction manner of ECC in comparison with CADEs is progressing in our laboratory.

## Reference

- 1) J.V. Crivello, J.H.W. Lam, J. Polym. Sci. Polym.: Chem. Ed., 16, 2441 (1978)
- 2) J.V. Crivello, J.L. Lee, D.A. Conlon, J. Radat. Curing, 10(1), 6 (1983)
- 3) J.V. Crivello, D.A. Conlon, D.R. Olson, K.K. Webb, J. Radat. Curing, 10, 3 (1986)
- 4) J.W. Carter and J.K. Braddock, RadTech N.A. '94, 246 (1994)
- 5) A.S. Pell, G. Pilcher, Trans Faraday Soc., 61, 71 (1965)
- 6) H. Sasaki, J.M. Rudzinski, T. Kakuchi, J. Polym. Sci.: Part A, 33, 1807 (1995)
- 7) H. Sasaki, RadTech 2000, 61 (2000)
- 8) J.V. Crivello and U. Varlemann, ACS Symp. Ser., Vol. 673, Am. Chem. Soc., 82 (1997)
- 9) H. Sasaki, RadTech 2002, 64 (2002)