

Curing Properties of Cycloaliphatic Epoxides Derivatives: Formulations of 3-Ethyl-3-Hydroxymethyl-Oxetane

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Introduction

UV-cationic-curing, based on the photo-generation of acid by and consecutive cationic polymerization, was first proposed in 1970's (1). Since then, wide variety of cationically polymerizable monomers such as epoxides and vinyl ether derivatives have been investigated (2). 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.

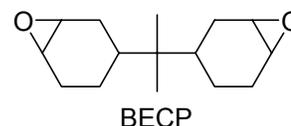
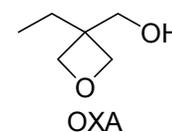
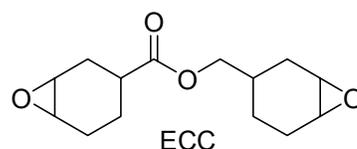
One approach was addition of alcoholic compounds. Crivello first studied the positive effect of alcohol on cure rate in UV-cationic polymerization of ECC (3). In an industrial application, formulation of polyether- or polycaprolactone-polyols is widely used as effective method to improve the curing rate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

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 ($pK_a = 2.02$) (5). In the UV cationic polymerization, oxetane derivatives were found to exhibit quite different polymerization characteristics from those for epoxides (6). 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 (7). In these formulations, the hydroxy unit in OXA should work as a chain transfer agent in the formulation and form a cross-linked network. Because of hydrophilic nature of OXA, relatively high amount of water will permeate into the formulation under humid conditions. The effect of water should be very important issue for the formulations, but not studied experimentally so far.

To clarify the water effect in the photo-cationic curing system, the consequence of contaminated water on the curing properties of OXA and epoxides formulations was carried out and the roll of hydroxy groups in water and/or OXA was also investigated (8). In the study, the positive effect of water for ECC alone formulations was found, while adequate amount of OXA addition exhibited very high reactivity regardless both coating thickness and amount of contaminated water. These results strongly suggest that a different, not simple chain transfer, interaction of hydroxy group and active species should occur in the ECC formulations and water migration from the surface should have a big effect on the curing rate.

As a continuing work, in this study, the reactivity ECC alone and OXA formulations was studied using realtime dynamic rheological analysis method and the effect of atmospheric water i.e. humid on the photo-cationic polymerization was also investigated. To clarify the effect of ester group on the cationic polymerization, di-functional cycloaliphatic epoxide,

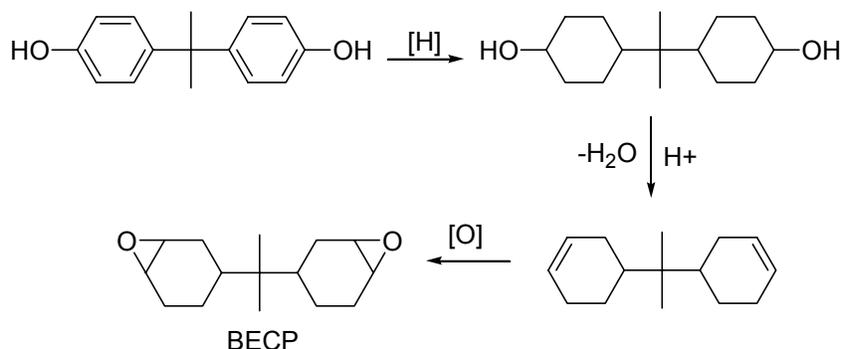


2,2-bis-(3,4-epoxycyclohexyl)-propane (BCEP), having no ester linkage was synthesized and evaluated.

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 (BCEP) was synthesized from hydrogenated bis-phenol A according the scheme shown below.



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 an dry air atmosphere at 40°C. The light intensity was adjusted to 2.5 mW/cm² 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 (9).

The viscoelasticity of the sample during the cationic polymerization was measured at 40°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/cm² 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/cm². 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.

Through Cure Energy (T.C.E.) measurements under varied humidity (30, 50 or 70%RH)

To establish constant humidity conditions, UV irradiator unit consisting of one microwave powered F-450 fitted with an H-bulb (Fusion UV Systems) was set in a booth covered with plastic films, which is connected to humidifier (Apiste, PAU-920S-HC). The atmosphere in the booth was controlled to 30, 50 or 70%RH at 28 to 30 °C by the humidifier. The formulated liquid sample was coated on a steel test panel using bar applicator (#3 or #20) and kept in the booth for 5 min. before UV irradiation. In this study, to eliminate the post-cure effect during the curing process, using static UV irradiator with timer, Through Cure Energy (T.C.E.), which was defined as the minimum energy to produce a complete cure immediately after UV exposure, was used. Qualitative cure to through-cure was determined by thumb twist test.

Results and Discussion

Real-Time Dynamic Rheological Analysis (DRA)

Realtime DRA for ECC alone and 20% of OXA formulations (1 to 5 % of PI) were carried out with continuous irradiation of UV light (10mW/cm² at 365nm) and the gap for the measurement was set to 50µm. The results were shown in Figure 1 and 2. While the ECC alone formulations resulted in slow increase of storage modulus even with high amount of PI, cure rate increase was found for the 20% of OXA formulations and with only 2% of PI addition the final modulus reached the same value as high amount of PI formulations.

To determine the effect of added OXA amount, the realtime DRA measurement was performed using varied OXA (0 to 20%) formulations with 3% of PI and the results were exhibited in Figure 3. Even 5% of OXA addition gave an enhanced cure rate and higher amount resulted in higher reactivity.

To evaluate the minimum energy to complete the curing reactions, short time UV irradiation was carried out. As a typical result, results for ECC/OXA/PI=80/20/3 formulation were summarized in Figure 4. With only 10 seconds irradiation i.e. 100mj/cm², the storage modulus increased even after

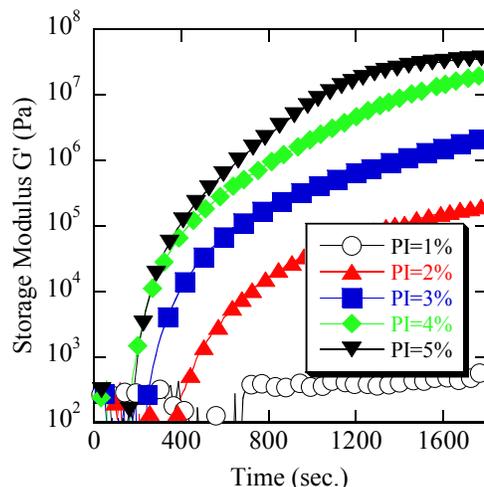


Figure 1 Real-time DRA measurement for ECC with 1 to 5% of PI (Irrad.=10mW/cm² at 30°C)

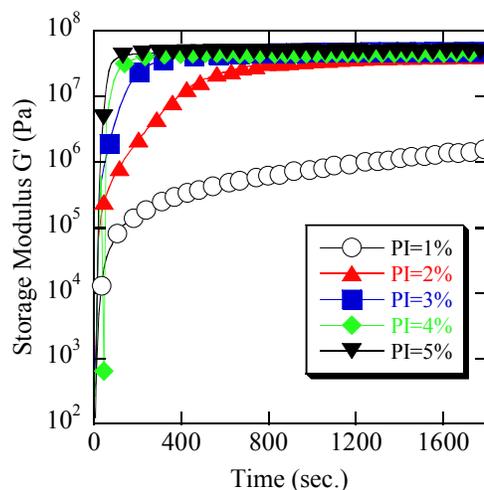


Figure 2 Real-time DRA measurement for ECC/OXA=80/20 with 1 to 5% of PI (Irrad.=10mW/cm² at 30°C)

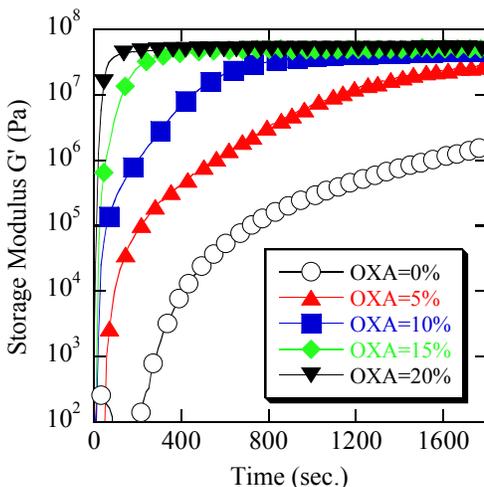


Figure 3 Real-time DRA measurement for ECC/OXA formulations with 3% of PI (Irrad.=10mW/cm² at 30°C)

short time UV irradiation and final storage modulus reached almost the same value as that of continuous irradiation. The minimum cure energies for the formulations mentioned above were listed in Table 1. For ECC formulations with 5% addition of PI, after 30 min standing the final modulus reached almost the same value as continuous irradiation. Only 5% of OXA addition (No.13 in table 1, 3% of PI) required the same energy as No.5 to complete the polymerization.

In the photo-initiated cationic polymerization, post-curing is very important nature, which means long-lasting polymerization after UV-irradiation as shown in Figure 4. In general, it is known to proceed even at room temperature and to be facilitated by heating the irradiated coatings. Utilizing DRA apparatus, one can follow the viscoelastic change for the irradiated sample even during post-cure heating, which should be very informative to investigate the reaction manner of the formulations.

Using No.3 and 8 formulations in Table 1, in-situ post-cure measurement was carried out according to the following sequence. UV was irradiated (100mW/cm² for 100sec.) and temperature was controlled to 30 °C for 15min including irradiation time, followed by heating (2 °C /min. up to 150 °C and kept 30min.) and cooling (2 °C /min.) to 30 °C. To detect proper response, the gap, which is equal to the sample thickness, was set to 500µm. Change in storage modulus for both samples was summarized in Figure 5 together with a temperature sequence. Modulus and Tanδ in cooling stage were shown in Figure 6.

For ECC (No.3), post-curing proceeded not only in 15 min. standing but also in heating stage until

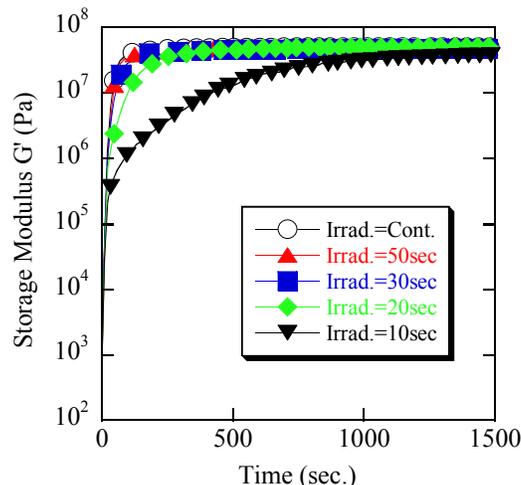


Figure 4 Real-time DRA measurement for ECC/OXA=80/20 formulation with 3% of PI (Irrad.=10mW/cm² at 30°C)

Table 1 Min. Energy for complete cure

R.N.	ECC	OXA	PI	Min. Energy (mj/cm ²)
1	100		1	>1000
2	100		2	>1000
3	100		3	>1000
4	100		4	>1000
5	100		5	300
6	80	20	1	>1000
7	80	20	2	150
8	80	20	3	100
9	80	20	4	100
10	80	20	5	200
11	85	15	3	150
12	90	10	3	250
13	95	5	3	300

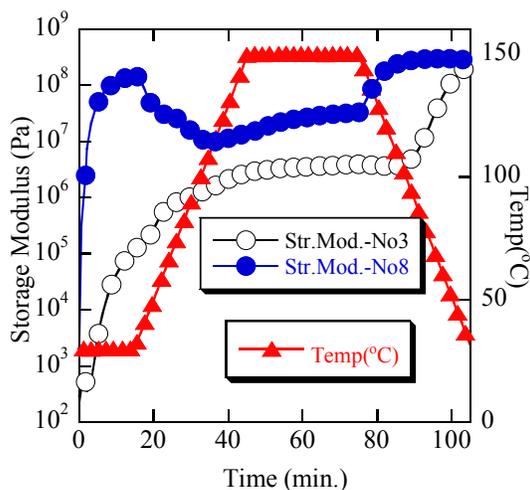


Figure 5 Post-cure measurement for No.3 and 8 in Table 1. (Irrad.=100mW/cm² for 100sec. at 30°C and heated to 150°C)

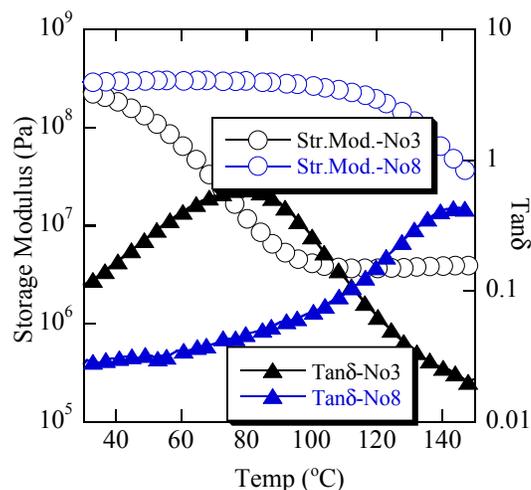


Figure 6 Real-time DRA measurement for formulation No.3 and 8 in Table 1. (During Cooling period from 150 to 30°C)

reached to 150 °C. With addition of OXA (No.8), storage modulus exceeded 10E+8 and reached to plateau during 30 °C stage, and in the early heating stage until 120 °C a decrease showing some relaxation mode followed by an increase at 150 °C. After post-curing, the temperature of $Tan\delta_{max}$ for No8 was about 150 °C, which was same level as post-cure temperature, while it was much lower (about 80 °C) for ECC alone. The higher $Tan\delta_{max}$ should be explained by higher cross-link density, which was generated through smooth propagation reaction.

The same measurement was performed for varied OXA content formulations (No.11, 12 and 13) and the results were shown in Figure 7. $Tan\delta_{max}$ temperature exhibited good correlation with OXA content added and higher amount of OXA resulted in higher transition temperature. These results suggested that some undesirable side reaction should occur in propagation stage for ECC polymerization, which could be compensated by OXA addition. The basicity of oxygen atom in cyclohexene oxide moiety was evaluated by computational chemistry in our lab and found to be rather high, which was almost comparable with that for oxetane's (10). Based on this calculation, the nature of reactive site should not be the reason for the side reaction.

Through Cure Energy Measurements

As noted in experimental part, the realtime DRA measurements were carried out under dry air, and sample thickness was set to 50 or 500µm to monitor adequate modulus change during cure. In the coating applications, the coating thickness is much

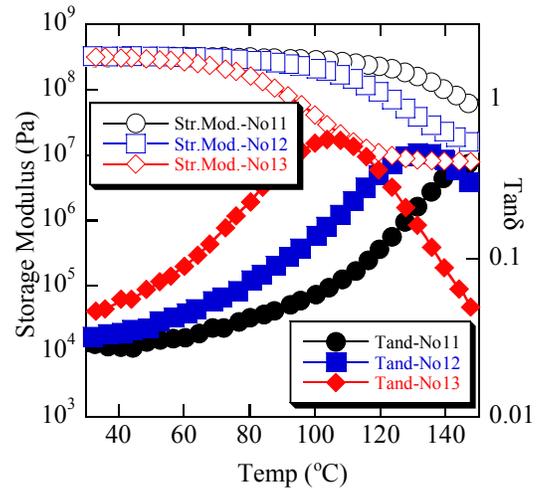


Figure 7 Real-time DRA measurement for formulation No.11, 12 and 13 in Table 1. (During Cooling period from 150 to 30°C)

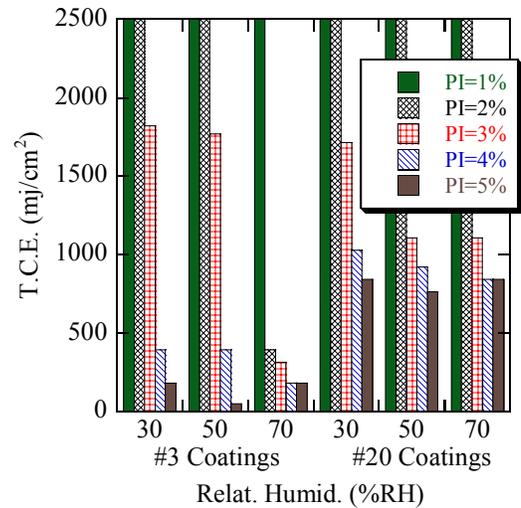


Figure 8 T.C.E. for No.1 to 5 formulations coated by #3 or #20 bar and cured under 30, 50 or 70%RH

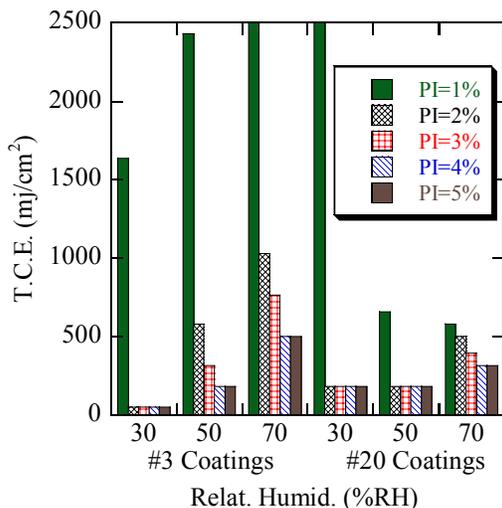


Figure 9 T.C.E. for No.6 to 10 ECC/OXA formulations coated by #3 or #20 bar and cured under 30, 50 or 70%RH

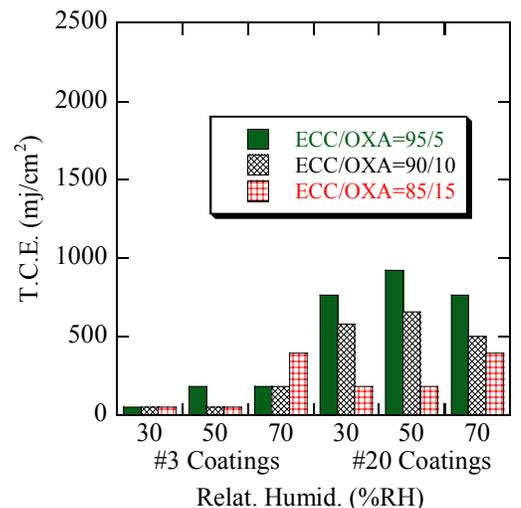


Figure 10 T.C.E. for No.11 to 13 ECC/OXA formulations coated by #3 or #20 bar and cured under 30, 50 or 70%RH

thinner and the atmospheric conditions, such as humidity, vary. Using humidity controller connected booth, UV-curing of samples, which were used above mentioned measurements, with different thickness under varied humidity were performed and the results were summarized in Figure 8 to 10.

For ECC alone formulations, excepting PI=1%, thicker coatings (#20) resulted in slower through-cure and higher amount of PI addition resulted in enhanced reactivity. It is noteworthy that the cure rate was increased under high humid condition and in 70%RH 2% of PI formulation gave cured coating by rather low energy.

On the other hand, OXA addition resulted in accelerated cure rate under low humidity compared with ECC alone both in thin and thick coatings, however higher amount of UV irradiation was required for high-humid condition. 10 to 15% of OXA exhibited high reactivity throughout the measurements.

The difference in the cured coating surface was also found for thick coatings, ECC alone resulted in twinkled surface but smooth for the OXA formulations. This surface roughness should be explained by an inhomogeneous cure rate between surface and inner area, which quickly cured layer of the surface was distorted by the stress caused from the shrinkage of slower inner cure. This fact suggested that some diffusion-controlled reaction during the propagation stage should contribute to the slower inner-cure. The water migration from the surface of the coating was suspected.

Recently two independent researches have studied on the effect of atmospheric water in the UV-cationic polymerization of ECC and, at least until some amount of atmospheric water, the polymerization rate acceleration of cyclohexene oxide unit was reported (11, 12). In their study, stabilization of proton around the active species (11) or the cage effect of water (12) were mainly discussed, but not an attention was paid for the ester group in ECC.

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 (13).

UV-Curing of BECP Formulations

To evaluate the effect of ester moiety in ECC,

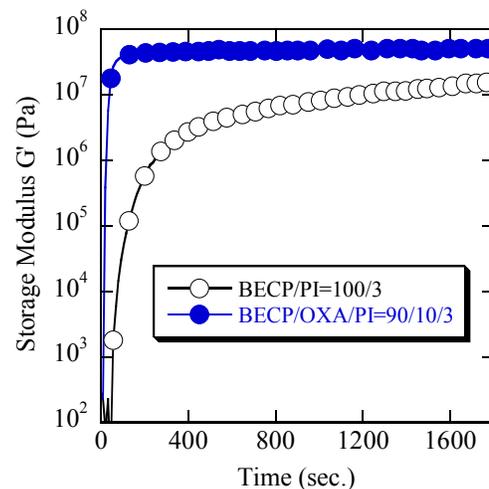


Figure 11 Real-time DRA measurement for BECP/OXA with 3% of PI (Irrad.=10mW/cm² at 30°C)

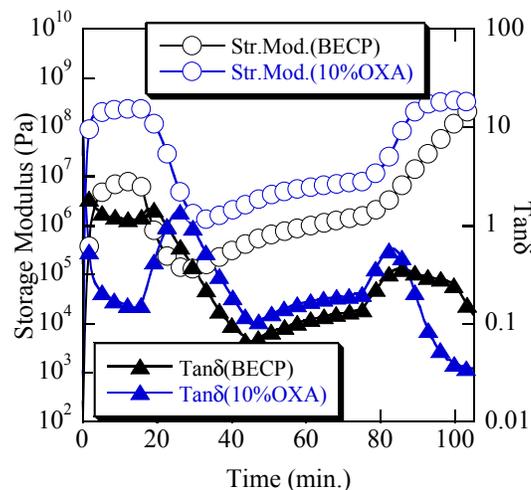


Figure 12 Real-time DRA measurement for formulation BECP and 10% OXA (Same conditions in Figure 5)

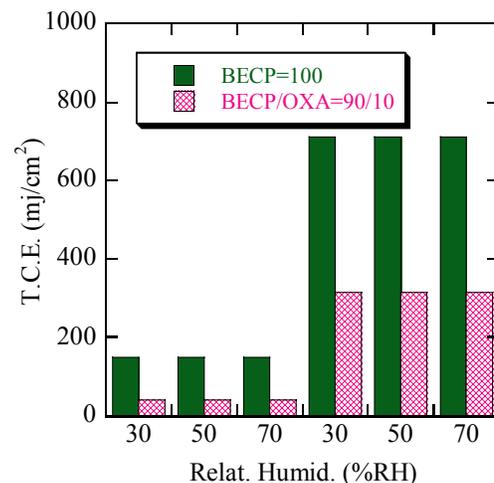


Figure 13 T.C.E. for BECP alone and 10% of OXA formulations with 3% PI coated by #3 or #20 bar and cured under 30, 50 or 70%RH

BECP possessing no ester unit in the molecule was synthesized and photo-polymerization was carried out. Experimental conditions for each measurement were the same as mentioned above

Figure 11 shows the realtime DRA results for BECP alone and 10% addition of OXA formulations with 3% of PI with continuous UV irradiation. BECP 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 (BECP alone) or 250mj/cm^2 (10% OXA).

Using the same sample, post-curing measurements were performed (Figure 12). For both formulations, storage modulus exhibited plateau during 30°C stage and $\tan\delta$ also reached almost constant, which means completion of curing at this temperature. In the early heating stage until 120°C modulus once decreased followed by an increase at 150°C .

Figure 13 exhibited the T.C.E. results. Differing from the ECC based formulations, the energy for through cure was not affected by atmospheric humidity and thicker coatings required higher energy to cure.

Detailed study on the reactivity of BECP, including PI concentration effect, cured coating properties and so on, is progressing in our laboratory and the latest result will be presented in the presentation.

Conclusions

In this study, the curing properties of ECC in the formulation with OXA were investigated.

First, using realtime DRA, reactivity comparison was conducted and slow polymerization of ECC alone formulation was effectively accelerated by OXA addition even with lower PI concentration. Minimum UV dose for complete cure was measured by short time UV irradiation and more than ten times lower energy was found enough for OXA formulations. In-situ post-cure measurement was also carried out and long-lasting and slow post-cure for ECC was found and addition of OXA resulted in completion of curing at 30° and much higher transition temperature, which exhibited good correlation with OXA content.

Secondly, to compare the performance as thinner coating application, T.C.E. was compared for each other with different thickness under varied humidity using humidity controller connected booth. Under dry conditions, ECC required high energy and thicker coatings resulted in slower through-cure, while the cure rate was increased under high humid condition. OXA addition resulted in accelerated cure rate under low humidity both in thin and thick coatings, however higher amount of UV irradiation was required for high-humid condition. The twinkled surface of ECC thick coating suggested an inhomogeneous cure rate between surface and inner area, which could be caused by some kind of diffusion-controlled reaction of water during the propagation stage.

Lastly, to evaluate the effect of ester moiety, photo-polymerization BECP possessing no ester unit was examined. In the realtime DRA, BECP exhibited higher reactivity compared with ECC and OXA addition accelerated the cure rate. In contrast to ECC curing, both formulations seemed to complete polymerization in less than 15min of post-curing. T.C.E. for both formulations were not affected by atmospheric humidity and exhibited rather high reactivity.

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