Kinetics of Anhydride Curing of Epoxy : Effect of Chain Length of Anhydride

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에폭시 무수화물 경화의 동력학적 연구: 무수화물의 사슬 길이 효과

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ABSTRACT : The curing kinetics of epoxy resins with 3 different kinds of alkenylsuccinic anhydride (ASA) having C-8, C-12, and C-16 pendant side chain length with two different catalysts was studied by using differential scanning calorimetry (DSC). Nonisothermal and isoconversional method has been used for characterizing the effect of the pendant side chain length in the curing process. Results of nonisothermal method showed that there was no significant difference in the effect of the pendant side chain length of ASA. But isoconversional analysis showed that the value of the activation energy for the initiation reaction of C-8, C-12, and C-16 were 61.7~57.7 kJ/mol, 63.0~57.3 kJ/mol, and 130.4~94.2 kJ/mol, respectively, depending on the catalyst used. The values of activation energy for the initiation is different as reported value of 20 kJ/mol which indicating the difference in the effect of the pendant side chain length of ASA in the initial stage of the reaction.

요 약 : 시차열분석계(DSC)를 이용하여 달린(pendant) 탄소카본길이가 8(C-8), 12(C-12), 16(C-16) 인 3 가지 종류의 무수화물(ASA)과 두 가지 촉매를 이용한 에폭시 수지의 경화 동력학을 연구 하였다. 비등온(Nonisothermal)과 등전환(Isoconversional)법을 사용하였다. 비등온법의 결과는 무 수화물의 달린 카본길이에 따른 결과에는 큰 차이가 없었다. 그러나 등전환법에서는 촉매사용에 따라 개시반응의 활성화 에너지가 C-8, C-12, 그리고 C-16 의 경우 각각 61.7~57.7 kJ/mol, 63.0~57.3 kJ/mol, 그리고 130.4 kJ/mol~94.2 kJ/mol 이었다. 보고된 개시반응의 활성화에너지 20 kJ/mol 과 다른 것은 무수화물의 달린 탄소길이에 따른 효과로 해석된다.

Keywords : epoxy, anhydride, isoconversional, kinetics, curing

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Ⅰ. Introduction

Acid anhydrides are the one of the most commercially important curing agent for epoxy resins. Anhydride/epoxy resins are used in many structural and non-surface coating applications. A catalyst used in most epoxy/anhydride cured system is a tertiary amine to minimize the etherification reaction between the epoxy group and the hydroxyl group.

The mechanisms and kinetics of the curing reaction of epoxy resins with anhydride have been proposed and analyzed by several investigators. But the curing kinetics of epoxy resins with anhydride is not easily elucidated because the chemistry of epoxy curing is rather complex and not completely understood. Most authors agree that the mechanism of the reaction is initiated by anionic one. Fisher[1] proposed the formation of anion from the reaction between anhydride and tertiary amine. Tanaka and Kakiuchi[2]

proposed anion formation between epoxide and tertiary amine, whereas Fedtke and Mirsojew[2] reported chemically bounding of tertiary amine to epoxide. Trappe et al.[3] refined that the mechanism of the reaction of the epoxy/anhydride/tertiary amine systems by two steps. 1) Initiation by a tertiary amine and epoxy monomer to form the alcoholate anion through the interaction of the tertiary amine with an epoxy. 2) Propagation by an alcoholate anion with anhydride. Recently Riccardi et al.[4] derived the simple model to explain the complex kinetic behavior of epoxy/anhydride system by using the chain-wise mechanism of the copolymerization of epoxides with anhydride. From above investigations, it can be stated that the reaction is initiated by the interaction of tertiary amine with anhydride or epoxy to form the anion and propagation proceeds via two reactions involving acylation and esterification in sequence.[5]

1.Initiation by formation of anion due to interaction of tertiary amine with anhydride or epoxy
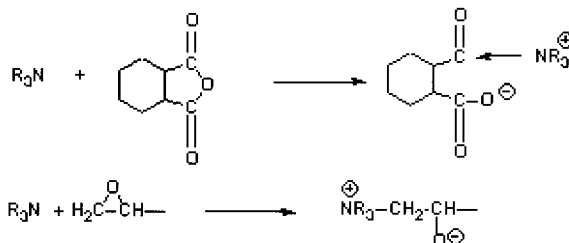
2. propagation via reactions involing acylation and esterification
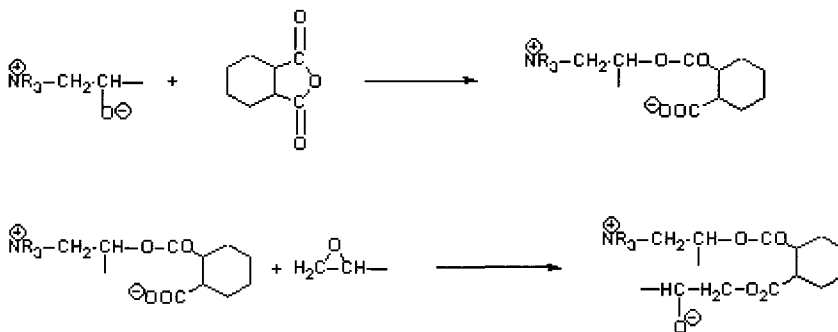
Scheme 1. Mechanism of the reaction of the epoxy/anhydride/tertiary amine systems.

Differential scanning calorimetry (DSC) is a convenient tool to study the kinetic behavior of crosslinking reaction of thermosetting systems such as epoxy and unsaturated polyester. According to the variation of temperature with time applied for measuring the thermogram, isothermal and nonisothermal method has been used for the estimation of single kinetic parameters such as activation energy and pre-exponential factor for the overall process.

There are several studies regarding the kinetic behavior of the epoxy/anhydride by using DSC. Chen et al.[6] characterize the curing behavior of bisphenol A epoxy and aryl phosphinate anhydride with benzyldimethylamine as catalyst. Under isothermal approach, the results show the autocatalytic behavior and two activation energies of 77~92 kJ/mol and 83~146 kJ/mol depending on the kinds of anhydride. Miranda et al.[7] studied the curing behavior of bisphenol A epoxy and three different cyclic anhydride with triethylamine as a catalyst. They found that the activation energies determined by single-rate method were range of 88~224 kJ/mol depending on the scanning rate and cyclic anhydrides. The activation energies determined by multiple scanning rate methods were range of 64~102 kJ/mol depending on the cyclic anhydride. From above single kinetic parameters of the overall process, they could not characterize the complicated reaction mechanism during crosslinking reaction.

Recently Vyazovkin et al.[8,9] studied the approach for isoconversional kinetic analysis that offers the effective activation energy at a given conversion. Analysis of the activation energy depending on conversion helps not only to disclose the complexity of a process but also to identify its kinetic scheme. Vyazovkin et al.[10] studied bisphenol A epoxy and hexahydro-4-methyl phthalic anhydride with N,N-dimethylbenzylamine as a catalyst. In this study, the isoconversional analysis has been applied to nonisothermal DSC data on the crosslinking reaction. The results show that the effective activation energy increases from 20 to 70 kJ/mol with increasing the

extent of conversion. They concluded that the increase of activation energies as a function of conversion suggests a mechanism of competing reactions of initiation and propagation during the extent of reaction.

In this study, we tried to evaluate the mechanism of the curing of the epoxy/anhydride/tertiary amine by using the estimation of single kinetic parameters such as activation energy and pre-exponential factor for the overall process. We applied single rate method of Barrett and the multiple scanning rate methods of Kissinger. Effective activation energy at given conversion was determined by using isoconversional analysis for characterizing the mechanism as a function of conversion.

In this experiment, we used the 3 different kinds of alkenylsuccinic anhydride, which have C-8, C-12, and C-16 pendant side chain length to study the effect of the formation of anion from the interaction of the tertiary amine with anhydride or epoxy in the initiation reaction.

Ⅱ. Experimental

Three kinds of alkenylsuccinic anhydrides, 2-octenyl succinic anhydride (C-8, OSA), 2- dodecenylsuccinic anhydride (C-12, DSA), and 2-hexadecenylsuccinic anhydride (C-16, HSA), were prepared by the ene synthesis. Detailed procedure for making alkenyl succinic anhydrides were referred by Jung et al.[11]

The liquid epoxy resin of diglycidyl ether of bisphenol A (DGEBA) (YD-115, epoxy equivalent weight of 194 g/epoxy, Kookto Chemical) was used after thoroughly drying. Stoichiometric epoxy/alkenylsuccinic anhydride (ASA) mixtures containing 0.1 phr diazobicyclo[2,2,2]octane (DABCO) or 2,4,6-tris(dimethylaminomethyl)phenol (TDMAMP) were used to cure the resin.

Sample of approximately 10 mg was used in sealed pan for all experiments to prevent evaporation of reactants. A differential scanning calorimetry (DSC2010, TA Instrument) was used to moni-

2-octenylsuccinic anhydride (C-8, OSA)

2- dodecenylsuccinic anhydride (C-12, DSA)

2-hexadecenylsuccinic anhydride (C-16, HSA)
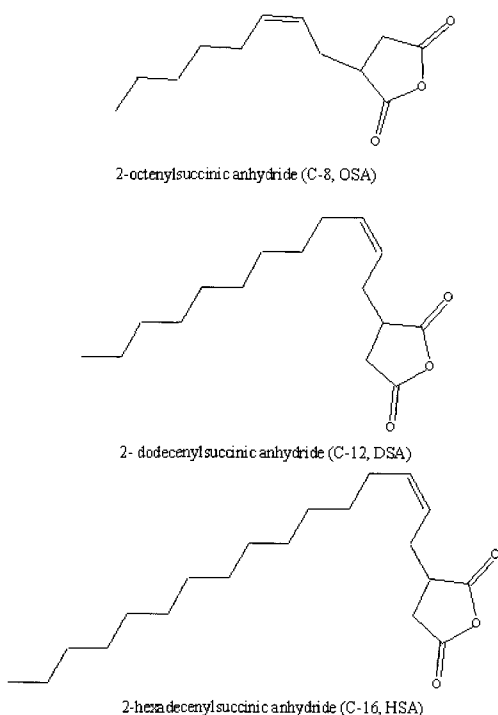
Scheme 2. Structures of the alkenylsuccinic anhydrides used in this study.

tor the reaction kinetics. The DSC enthalpy was calibrated using a high purity indium sample. High purity tin sample was also used to calibrate the temperature scale. Initial kinetic studies were performed in the scanning mode from room temperature to 250 ℃ at the rate of 2 ℃/min, 5 ℃/min, 10 ℃/min, and 20 ℃/min. The DSC cell was flushed with nitrogen at a flow rate of 50 ml/min.

For the kinetic analysis of experimental data, two methods were used for the calculation of the activation energy of the crosslinking reactions of the epoxy resin with the three different anhydrides. Activation energy was determined by applying the single rate method of Barrett[12] and the multiple scanning rate methods of Kissinger.[13]

Kinetic analysis of Barrett method was performed based on the DSC thermogram by assuming that the area under the curves is proportional to the extent of reaction. The conversions (α) of the crosslinking reaction at the time t was determined from the partial

area under a DSC thermogram up to time t, heat evolved up to that time (ΔH_t), divided by total area under the thermogram, overall heat of reaction (ΔH_r):

$$\alpha = \Delta H_t / \Delta H_r$$

The reaction rate (k) of the crosslinking reaction at the time t was also obtained from the following equation :

$$k = (dH_t / dt) / (\Delta H_r - (H_t))$$

where H_t is the heat evolved at time t.

Activation energy was determined from the slope of linearity in the plot of the reaction rate obtained from ln k versus 1/T.

The activation energy from Kissinger method was calculated from slope of the plot of ln (β/T_{max}^2) vs. T_{max}^{-1}, where β is a heating rate and T_{max} is a maximum temperature for DSC thermogram.

To perform isoconversional analysis, the original DSC data were transformed into the form α (conversion) vs. T_α (temperature at conversion α) for heating rate, β.

The effective activation energy at certain conversion α were calculated from the slope of the plot of ln (β/T_α^2) vs. T_α^{-1}
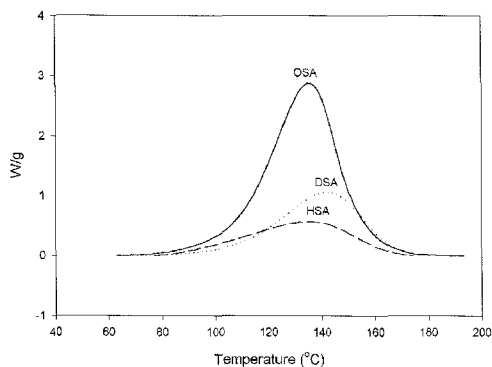
Ⅲ. Results and Discussion

Figure 1 and Figure 2 show the DSC thermogram for the reaction of the stoichiometric mixtures of bisphenol A epoxy resin, YD-115, with ASA in the presence of 0.1 phr of DABCO and TDMAMP as an initiator at a heating rate of 5 ℃/min.

Figure 1 and 2 show that as the pendant side chain length of the ASA increases the total heat evolution decreases. The tendency of the maximum heat evolution temperatures of the pendant side chain length of the ASA used was different depending on the catalysts used. This might indicate that the pendant side chain length of ASA affects the reactivity of
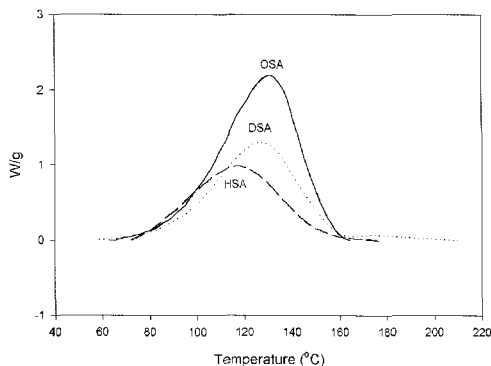
Figure 1. DSC thermogram for the reaction of the stoichiometric mixtures of bisphenol A epoxy resin, YD-115, with ASA in the presence of 0.1 phr of DABCO as an initiator at a heating rate of 5 ℃/min.

Figure 2. DSC thermogram for the reaction of the stoichiometric mixtures of bisphenol A epoxy resin, YD-115, with ASA in the presence of 0.1 phr of TDMAMP as an initiator at a heating rate of 5 ℃/min.

the ASA against epoxy group or catalyst.

In this work the Barrett and Kissinger methods were applied to determine the activation energies for the three systems studied at all measured temperature scanning rates.

Table 1 shows the activation energies obtained by using DABCO and TDMAMP as catalyst for the three systems. For the activation energies determined by Barrett method indicate that the activation energy is affected by the pendant side chain length of ASA and catalyst used. For the systems of HSA show lower values of the activation energy than

Table 1. Energies of Activation for the Reactions of YD115 with Three Different Anhydride in the Presence of DABCO and TDMAMP as Catalyst Determined by Barrett's Method and Kissinger's Method.

| Catalyst	Anhydride	Energy of activation (kJ/mol)				
		Barrett				Kissinger
		2 ℃	5 ℃	10 ℃	20 ℃	
DABCO	OSA	102.5	88.2	98.0	87.5	82.1
	DSA	78.3	84.1	80.5	82.5	58.8
	HSA	66.1	60.4	59.0	57.4	59.3
TDMAMP	OSA	93.4	94.0	103.7	88.4	61.9
	DSA	123.3	102.2	101.1	109.1	62.0
	HSA	66.1	85.3	83.8	73.3	63.4

those of other ASA used for both catalyst. For OSA and DSA, the values of activation energy are depends on the catalyst used. When DABCO is used as catalyst the system of DSA shows lower value of activation energy but when TDMAMP is used as catalyst the system of OSA shows lower value of activation energy. For the activation energies determined by Kissinger method indicated that when DABCO is used as catalyst the systems of OSA show higher value of the activation energy than the others. When TDMAMP is used as catalyst there was no effect of the pendant side chain length of ASA in the activation energy. This behavior suggests that the pendant side chain length of ASA affect the reactivity towards the crosslinking process.

Figures 3 and 4 show the effects of reaction rate as a function of the extent of reaction when DABCO and TDMAMP are used as catalyst. These figures indicate that the effects of reaction rate as a function of the extent of reaction shows the similar pattern in both catalysts. In the early stage of the extent of reaction, HSA shows the higher rate of reaction but after about 0.2 of the extent of reaction HSA shows lower rate of reaction. OSA and DSA shows similar rate of reaction all the extent of reaction range.
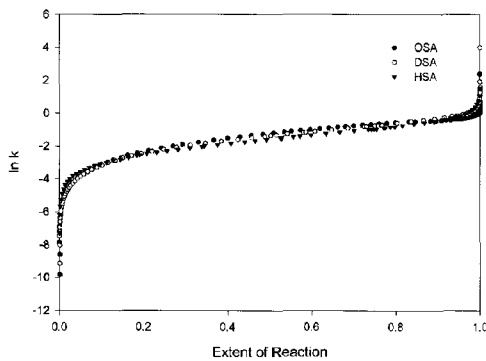
Figures 5 and 6 show the change of reaction rate as a function of the temperature when DABCO and
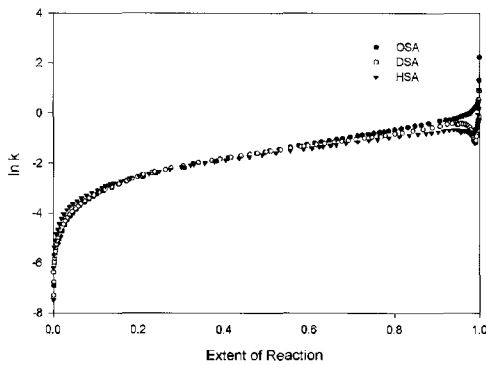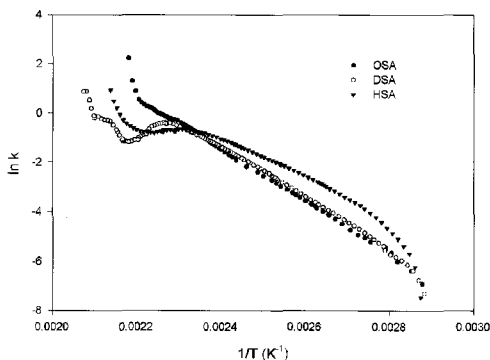
Figure 3. Effects of reaction rate as a function of the extent of reaction when DABCO is used as catalyst.
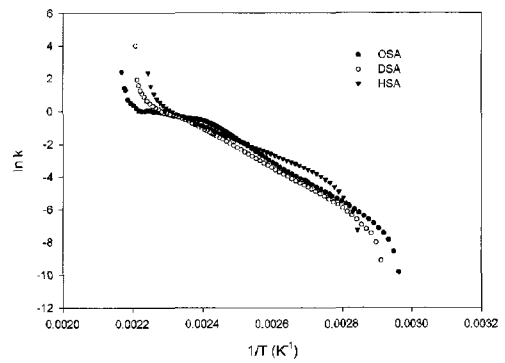
Figure 6. Effects of reaction rate as a function of the temperature when TDMAMP is used as catalyst.

Figure 4. Effects of reaction rate as a function of the extent of reaction when TDMAMP is used as catalyst.


Figure 5. Effects of reaction rate as a function of the temperature when DABCO is used as catalyst.

TDMAMP are used as catalyst. As shown in these figures, the change of reaction rate as a function of the temperature depends on the catalyst used in the system. When DABCO is used as catalyst HSA behaves differently from the systems cured with other ASA. At lower temperature, the reaction rate of the system cured with HSA is higher than the system cured with other ASA. But at higher temperature, the reactions rate of HSA decreases more than other reaction rate of ASA.

But when TDMAMP is used as catalyst there was no significant of the change of reaction rate with the temperature as a function of ASA used.

Figures 7 and 8 show the dependence of the activation energy characterized by isoconversional method on the extent of conversion for the epoxy cured with different ASA. These figures indicate that the dependency of the activation energy of the C-16 pendant side chain length of ASA (HSA) shows different comparing C-12 and C-8 pendant side chain length of ASA (DSA and OSA) as a function of the extent of conversion at both catalysts used. Assuming that the initial stages of epoxy/ anhydride cure are controlled by initiation, it shows that the activation energy of initiation varies with the pendant side chain length of alkenylsuccinic anhydride (ASA). The values of activation energy of initiation of HSA, DSA and OSA at both catalysts were 61.7~57.7 kJ/mol, 63.0~57.3 kJ/mol, and
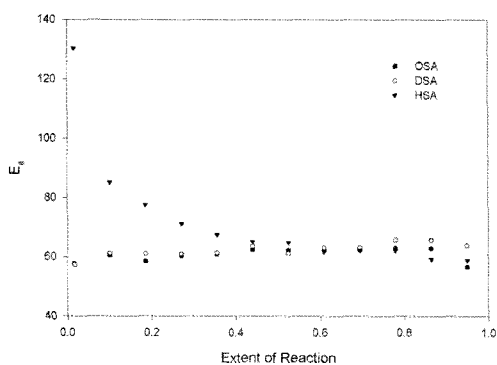
Figure 7. Effects of the activation energy as a function of the extent of conversion when DABCO is used as catalyst.
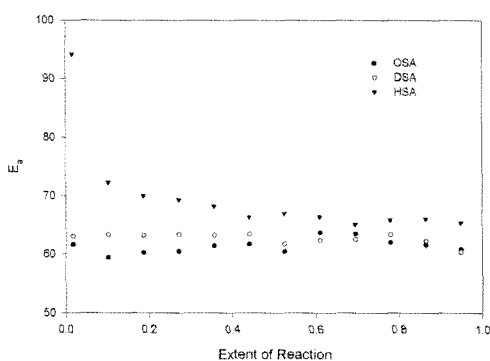
Figure 8. Effects of the activation energy as a function of the extent of conversion when TDMAMP is used as catalyst.

130.4~94.2 kJ/mol, respectively. The values of activation energy of propagation were about 57.3~65 kJ/mol for 3 ASA at both catalysts.

Table 2 and Table 3 show the results of kinetic parameters as a function of the extent of reaction at both catalyst. These results indicate that the variations in the values of the collision frequency factor, A, are much greater than those in the Arrhenius activation energy, E_a, for HSA comparing to other ASA. These results reveal that the activation energy of initiation is affected by the pendant side chain length of alkenylsuccinic anhydride (ASA). Vyazovkin et al.[10] reported that the activation energy of reaction of epoxy/anhydride for the initiation is about 20 kJ/mol which is the activation energy for

Table 2. Kinetic Parameters for the Reactions of YD115 with Three Different Anhydride in the Presence of DABCO as Catalyst as a Function of the Extent of Reaction.

Extent of Reaction	OSA		DSA		HSA	
	$A \times 10^{-4}$	E_a	$A \times 10^{-4}$	E_a	$A \times 10^{-4}$	E_a
0.01	0.669	57.7	0.684	57.3	5×10^{10}	130.4
0.10	0.535	60.5	0.777	61.2	3147.3	85.1
0.19	0.186	58.5	0.471	61.1	151.7	77.6
0.27	0.247	60.4	0.334	61.0	13.95	71.3
0.36	0.225	61.0	0.289	61.3	3.139	67.5
0.44	0.273	62.4	0.449	63.6	1.177	65.0
0.53	0.231	62.4	0.188	61.3	0.854	64.8
0.61	0.196	62.4	0.268	63.2	0.274	61.7
0.70	0.166	62.4	0.225	63.2	0.258	62.3
0.78	0.162	63.0	0.367	65.7	0.190	62.1
0.86	0.129	63.0	0.283	65.8	0.062	59.2
0.95	0.015	56.7	0.109	63.9	0.035	58.9

Table 3. Kinetic Parameters for the Reactions of YD115 with Three Different Anhydride in the Presence of TDMAMP as Catalyst as a Function of the Extent of Reaction.

Extent of Reaction	OSA		DSA		HSA	
	$A \times 10^{-4}$	E_a	$A \times 10^{-4}$	E_a	$A \times 10^{-4}$	E_a
0.01	3.107	61.7	2.780	63.0	2×10^5	94.2
0.10	0.505	59.5	1.194	63.3	46.103	72.3
0.19	0.441	60.3	0.785	63.2	13.098	70.0
0.27	0.378	60.6	0.648	63.4	7.364	69.4
0.36	0.418	61.6	0.508	63.3	3.898	68.2
0.44	0.382	61.8	0.460	63.5	1.745	66.4
0.53	0.230	60.5	0.244	61.8	1.688	67.0
0.61	0.513	63.7	0.247	62.4	1.141	66.4
0.70	0.444	63.5	0.226	62.6	0.650	65.2
0.78	0.232	62.1	0.238	63.4	0.633	65.8
0.86	0.169	61.6	0.146	62.3	0.526	66.1
0.95	0.097	60.9	0.063	60.4	0.302	65.4

the formation of anion due to the interaction of tertiary amine with anhydride and that for propagation is about 70 kJ/mol. The activation

Table 4. T$_g$ Values of the ASA Themselves and Cured Materials and Density of Cured Materials.

ASA	T$_g$ (℃)*		Density (g/cm^3)**
	ASA themselves	Cured material	
OSA	-78	34	1.132
DSA	-25	24	1.103
HSA	15	10	1.072

* refered by reference [11]
** measured by method of ASTM D792-66

energy value of propagation of alkenylsuccinic anhydride (ASA) is similar to the reported value. But the activation energy value of initiation is different from the reported value. This might due to the effect of the length of the pendant side chain of ASA on the initiation of curing reaction with epoxy.

As reported in Table 4, T$_g$ of the ASA itself increased with increase in the pendant side chain length of ASA, while T$_g$ of the cured epoxy materials decreased. Higher value of the activation energy of the initial stage is probably due to the higher value of pendant side chain length of ASA itself.

The value of 130.4 kJ/mol of the activation energy of epoxy curing with HSA as a anhydride at DABCO as a catalyst is similar value of 140 kJ/mol of the activation energy for the initiation in the curing reaction of the epoxy/amine with tertiary amine, which is the activation energy for the formation of anion due to the interaction of tertiary amine with epoxy. As the length of the pendant side chain of ASA increases, the activation energy as a function of conversion shows an autocatalytic behavior like a curing of epoxy/amine with tertiary amine as a catalyst, which mentioned in the works of Vyazovkin et al..[8]

Above results indicated that as the length of the pendant side chain of ASA increases, the reaction species in the initiation stage change from the reaction of anhydride and tertiary amine which is the activation energy for the initiation is about 20

kJ/mol to the reaction of epoxy and tertiary amine which is the activation energy for the initiation is about 140 kJ/mol.

The densities of the cured products are shown in Table 4. The system for HSA shows lower value than other systems. We continue to study the relationship between high value of the activation energy for the initiation and low value of density.

IV. Conclusion

The curing kinetics of epoxy resins with 3 different kinds of alkenylsuccinic anhydride having C-8 (OSA), C-12 (DSA), and C-16 (HSA) pendant side chain length with diazobicyclo[2,2,2]octane (DABCO) or 2,4,6-tris(dimethylaminomethyl)phenol (TDMAMP) as catalyst was studied by using differential scanning calorimetry (DSC).

From the characterization of activation energy for the overall process by applying the methods of Barrett and Kissinger, we can not figure out the significant difference in the effect of the pendant side chain length of ASA in the reaction of epoxy.

Isoconversional analysis shows that the value of the activation energy for the propagation reaction of alkenylsuccinic anhydride (ASA) is about 57.3~65 kJ/mol which is similar to the reported value. But the values of activation energy for the initiation reaction of OSA, DSA, and HSA were 61.7~57.7 kJ/mol, 63.0~57.3 kJ/mol, and 130.4~94.2 kJ/mol, respectively.

The values of activation energy for the initiation is different as reported value of 20 kJ/mol that is the activation energy for the formation of anion due to the interaction of tertiary amine with anhydride. For the system of HSA, the value of activation energy for the initiation is similar for the curing reaction of the epoxy/amine with tertiary amine that is the formation of anion due to the interaction of tertiary amine with epoxy.

Above results indicated that as the length of the pendant side chain of ASA increases, the reaction species in the initiation stage change from the

reaction of anhydride and tertiary amine which is the activation energy for the initiation is about 20 kJ/mol to the reaction of epoxy and tertiary amine which is the activation energy for the initiation is about 140 kJ/mol.

We found that the system for HSA shows lower value of density of cured materials than that for other ASA. We continue to study the relationship between high value of the activation energy for the initiation and low value of density.

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