

Cure Kinetics of Natural Zeolite/Epoxy Composites

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천연 제올라이트/에폭시 복합재료의 경화반응 속도론

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Abstract: Natural zeolite/epoxy resin composites were prepared and the cure kinetics was studied by dynamic DSC analysis. With the increment of natural zeolite content, the reaction starting temperature and the exothermic peak temperature were decreased. When diglycidyl ether of bisphenol A(DGEBA)/4,4'-methylene dianiline(MDA)/malononitrile(MN, 10phr) was filled with 20phr of zeolite, DSC thermogram had one peak and when it was filled with 30phr of zeolite, a shoulder appeared on the DSC thermogram. With the filling of 40phr of zeolite, DSC thermogram was separated into two peaks and the activation energy of the first peak, E_{a1} was 12.30 kJ/mol and that of the second peak, E_{a2} was 12.70 kJ/mol.

요약: 천연 제올라이트/에폭시 수지 복합재료의 경화반응 속도론을 연구하기 위해 DSC 분석법 중 승온적 방법을 이용하였다. 천연 제올라이트의 함량이 증가함에 따라 반응 시작온도와 발열피크의 온도가 낮아졌다. Diglycidyl ether of bisphenol A(DGEBA)/4,4'-methylene dianiline(MDA)/malononitrile(MN, 10phr)에 제올라이트를 20phr 충전한 경우에는 하나의 발열피크가 나타나며, 30phr인 경우에는 shoulder가 나타났다. 40phr의 제올라이트가 충전된 경우에는 발열피크가 두 개로 분리되며, 첫번째 발열피크의 활성화에너지, E_{a1} 은 12.30 kJ/mol이고, 두번째 발열피크의 활성화에너지, E_{a2} 는 12.70 kJ/mol이었다.

1. Introduction

With the increasing demand for polymer composites, many inorganic materials such as carbon black, calcium carbonate, silica and talc have been used to reduce the cost and at the same time to improve the physical, mechanical, thermal and electrical properties of the composites[1-5]. Because these properties are significantly changed by the

slight change of species and contents of inorganic fillers, many researchers have been interested in this sensitive effect and reported many modified polymer composites. Fu and Wang[1, 2] reported that polyethylene was successfully toughened by rigid calcium carbonate particles, Al-ghamdi and Mark[3] showed that zeolite was an effective reinforcing filler for elastomer, and Kim[4] and Nakatsuka[5] studied the interfacial phenomena between

polymer matrix and inorganic filler.

Zeolites are crystalline aluminosilicate minerals and have high internal surface area due to the channels and pores available for the adsorption of low weight molecules[6-8]. So zeolites have been used in many industrial fields as catalysts, molecular sieves, sorptive agents, ion exchange materials, etc. and the structures of them are well defined. To apply zeolite as a filler to polymer materials, the internal surface area and the pore size, which of one zeolite are different from those of another zeolite are important factors. If the side chains or end chains are smaller than the pore size of the zeolite, these chains can go into the pore and the wettability may be improved. And, if flame retardants are adsorbed on zeolite filler prior to compositing with polymer matrix, these materials will be desorbed by fire and retard the fire.

In this study, to get some information on the zeolite/epoxy composites, natural zeolite was used as a filler and epoxy resin was a matrix. The effects of the natural zeolite and malononitrile contents on cure kinetics were investigated by DSC analysis.

2. Experiment

DGEBA(diglycidyl ether of bisphenol A)/MDA (4,4'-methylene dianiline)/MN(malononitrile) systems were used as matrixes and natural zeolite from Kampo area in Korea was used as a filler[8-11].

Natural zeolite was washed, dried at 110 °C for 24 hrs, pulverized and sieved at 325~270 mesh. To remove the water molecule in the pore of natural zeolite, it was placed at 110 °C for 1 hr and stored in desiccator. The particle size distribution was analyzed by particle size analyzer and the shape of the particle was observed by SEM.

DGEBA and MN(10, 20phr) were well mixed with the dried natural zeolite(0, 10, 20, 30, 40phr) at 60 °C, and MDA was added to the mixtures at 80 °C. These samples were quenched and stored at -13 °C. To study cure kinetics by dynamic DSC

analysis, 2~3mg of the samples were placed in DSC container and DSC analysis was performed at the heating rates of 5, 10, 15, 20 °C/min. From these DSC data, activation energy and pre-exponential factor were obtained by Kissinger equation[12, 13], which is as follows.

$$-\ln(q/T_p^2) = E_a/RT_p - \ln(AR/E_a)$$

where, q : heating rate, T_p : temperature at peak, E_a : activation energy, A : pre-exponential factor, R : gas constant.

3. Results and Discussion

It was found that the natural zeolite used in this study was mainly composed with clinoptilolite type zeolite and was coexisted with some quartz and feldspar[8]. Fig. 1 shows the particle size distribution of natural zeolite as an inorganic filler. The

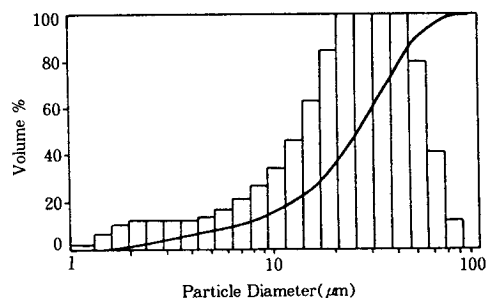


Fig. 1. Particle size distribution of the natural zeolite.

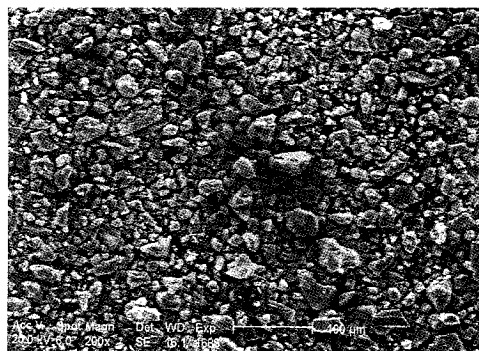


Fig. 2. SEM of the natural zeolite.

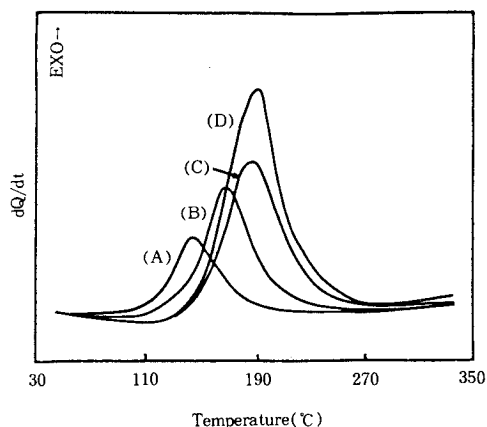


Fig. 3. DSC scans for DGEBA/MDA/MN(10phr) system at different heating rates.

(A) 5°C/min, (B) 10°C/min, (C) 15°C/min and (D) 20°C/min.

particle size ranged from 0.5 μm to 83.3 μm and the average particle size was 25.84 μm . And, Fig. 2 shows the shape of the natural zeolite and the filler came in variety of irregular particle shapes and sizes. It is well known that the size of the filler required for composite was under 40 μm and this value was higher than the average size of the natural zeolite and the shape of an individual particle had a great influence on the physical, mechanical, thermal and electrical properties of a composite [16].

DSC thermograms from 30°C to 350°C at different heating rates of 5, 10, 15 and 20°C/min for DGEBA/MDA/MN(10phr) system without natural zeolite are shown in Fig. 3. As heating rate increased, the cure reaction of epoxy resin took place rapidly in a short time, so the exothermic peak temperatures appeared at higher point. As shown in Fig. 3, each thermogram showed only one exothermic peak and, it has been well known that the exothermic peak is due to amine-epoxide reaction, epoxy-hydroxyl reaction, amine-nitrile reaction and hydroxyl-nitrile reaction[13-15].

Fig. 4 shows the DSC thermograms for DGEBA/MDA/MN(10phr) system with natural zeolite(20phr)

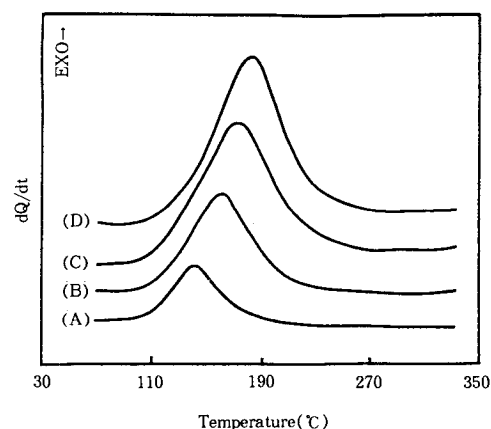


Fig. 4. DSC scans for DGEBA/MDA/MN(10phr)/Zeolite(20phr) system at different heating rates. (A) 5°C/min, (B) 10°C/min, (C) 15°C/min and (D) 20°C/min.

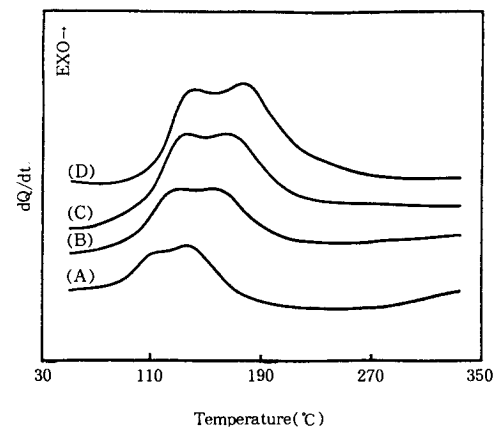


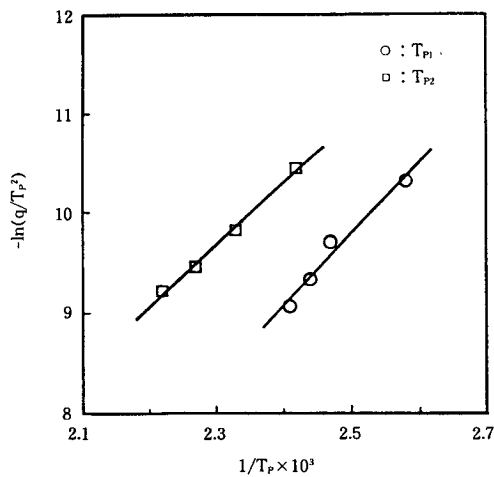
Fig. 5. DSC scans for DGEBA/MDA/MN(10phr)/Zeolite(40phr) system at different heating rates. (A) 5°C/min, (B) 10°C/min, (C) 15°C/min and (D) 20°C/min.

at different heating rates. This system also increased with the increment of heating rates and one exothermic peak appeared for every thermogram, but the exothermic peak temperatures were lowered about 2~3°C than those of the system without zeolite.

When 40phr of natural zeolite was filled to DGEBA/MDA/MN(10phr) system, the thermograms of Fig. 5 show two exothermic peaks and these

Table 1. Activation Energy and Pre-exponential Factors of DGEBA/MDA/MN/Zeolite System.

MN Content(phr)	Zeolite Content(phr)	Activation Energy(kJ/mol)		Pre-exponential factor($\times 10^3 \text{ sec}^{-1}$)	
10	10	12.68		3.27	
	20	11.98		6.70	
	30	Ea ₁	10.03	A ₁	18.80
		Ea ₂	12.30	A ₂	0.12
	40	Ea ₁	12.30	A ₁	4.89
		Ea ₂	12.22	A ₂	4.18
20	10	12.20		5.86	
	20	11.98		6.90	
	30	12.74		2.98	
	40	Ea ₁	12.24	A ₁	1.51
		Ea ₂	12.70	A ₂	2.91

**Fig. 6.** Plots of $-\ln(q/T_p^2)$ vs. $1/T_p \times 10^3$ by Kissinger equation for DGEBA/MDA/MN(10phr)/Zeolite(40phr) system.

peaks also increased with the increment of heating rates. The first peak temperatures, T_{p1} appeared at lower points about $35 \sim 45^\circ\text{C}$ than those of DGEBA/MDA/MN(10phr) system without zeolite and the second peak temperatures, T_{p2} did at lower points about 10°C . These meant that the cure rate of DGEBA/MDA/MN(10phr) system increased with the addition of zeolite and the cure mechanism changed. Generally, the reaction rate of polymer composites decreased with the addition of inorganic filler, but that of the system filled with zeolite increased. It may be because the hydroxyl group of

zeolite surface or the water molecules desorbed from the zeolite acted as a catalyst like the general autocatalytic reaction of epoxy resin[13, 15].

To get activation energy and pre-exponential factor from the relationship between the heating rates and exothermic peak temperatures, Kissinger equation was used and, even if the exothermic peaks are two or more, Kissinger equation can be used easily. Through the Kissinger equation, the straight lines in Fig. 6 were plotted from Fig. 5 and, activation energies and pre-exponential factors could be obtained from the slopes and the y-intersections, respectively, and these parameters were listed on Table 1. The activation energy of the first peak was 12.30 kJ/mol and that of the second peak was 12.22 kJ/mol. The kinetic parameters for DGEBA/MDA system with different MN and zeolite contents are also listed on Table 1.

Fig. 7 shows the DSC scans for DGEBA/MDA/MN(10phr) with various zeolite contents at $10^\circ\text{C}/\text{min}$ of heating rate. Until 20phr of zeolite was filled, only one exothermic peak was shown and these temperatures decreased with the increment of zeolite content. When 30phr of zeolite was added, a shoulder appeared at 132.3°C and one peak was shown at 163.2°C . When 40phr of zeolite was added, the peak separated into two, whose temperatures were 131.0°C and 156.0°C . As explained above, the exothermic peak temperatures were lowered with the increment of zeolite content and this meant that

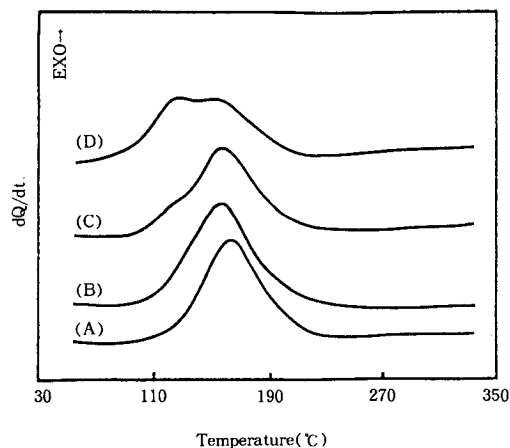


Fig. 7. DSC scans for DGEBA/MDA/MN(10phr) at different zeolite content at 10°C/min of heating rate. Zeolite content : (A) 10phr, (B) 20phr, (C) 30phr and (D) 40phr.

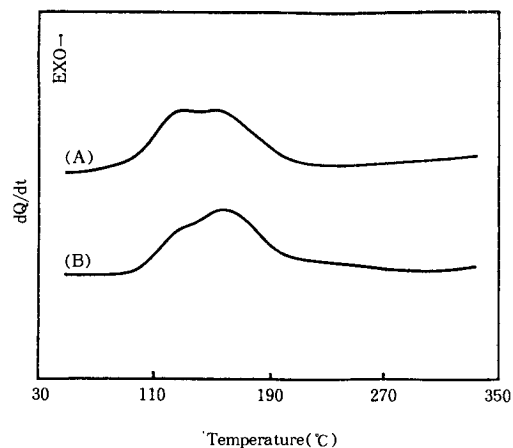


Fig. 8. DSC scans for DGEBA/MDA/Zeolite(40phr) at different MN content at 10°C/min. MN content : (A) 10phr, (B) 20phr.

the hydroxyl group of the surface of zeolite or of the water molecules in the zeolite pore may act as a catalyst.

Fig. 8 shows the effect of MN content on the DSC thermogram. DGEBA/MDA/Zeolite system with 10phr of MN had two exothermic peaks and the system with 20phr of MN also had two peaks but the first peak was weak. From the thermograms, the reaction starting temperature and the exothermic

peak temperature of the system with 10phr of MN were lower than those of the system with 20phr of MN. And from Table 1, activation energy of the system with 10phr of MN was lower but pre-exponential factor was higher than those of the system with 20phr of MN. These meant that the nitrile group disturbed the cure reaction of epoxy-amine group reaction[15, 17, 18].

4. Conclusion

From these results, the following conclusions can be obtained.

1. At the DSC thermograms for DGEBA/MDA/MN(10phr)/Zeolite system, when 20phr of zeolite was filled, only one exothermic peak was shown, when 30phr of zeolite was added, shoulder appeared at 132.3°C and one peak was shown at 163.2°C and when 40phr of zeolite was added, the peak separated into two, whose temperatures were 131.0°C and 156.0°C.

2. The exothermic peak temperatures were shown in lower points with the increment of zeolite content. This meant that the cure rate increased with the increment of zeolite content. It was because of the hydroxyl group of the zeolite surface or the water molecule in the zeolite pore.

3. With the increment of MN content, the exothermic peak temperature and activation energy decreased but pre-exponential factor increased.

4. It was difficult to compare the kinetic parameters of the system with various zeolite content, because the exothermic peak divided into two when 30phr of zeolite was filled.

Acknowledgement

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