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Effect of Natural Zeolite on Cure Characteristics of DGEBA/MDA/GN System

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DGEBA/MDA/GN계의 경화특성에 미치는 천연 제올라이트의 영향

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초 록 고분자 재료의 가격을 낮추거나 물리적, 열적 성질을 향상시키기 위해 고분자 복합재료 분야에서 무기 첨가제의 사용이 크게 증가되고 있다. 본 연구에서는 DBEBA/MDA/GN계의 경화특성에 미치는 천연 Zeolite의 영향을 고찰하였다. DGEBA/MDA/GN계의 경화 메카니즘과 DGEBA/MDA/GN/natural zeolite계의 경화 메카니즘은 매우 유사하였다. Zeolite의 함량이 20 phr까지 증가함에 따라 속도 상수는 증가하였으나 Zeolite의 함량이 증가함에 따라 속도 상수는 감소하였다.

Abstract To reduce the cost of polymer materials or to improve their special physical and thermal properties, many inorganic fillers in the polymer composite industry have been used. In this study, the effect of natural zeolite as a filler on cure characteristics of DGEBA/MDA/GN system was investigated by DSC and FT-IR. The cure mechanism of DGEBA/MDA/GN system with natural zeolite was very similar to that of the system without natural zeolite. As the content of natural zeolite increased up to 20 phr, rate constant of the system increased. However, above 20 phr, rate constant decreased with increasing the zeolite content.

1. Introduction

With the increasing demands for thermosetting or thermoplastic resins in different branches of engineering applications, many researchers have studied the polymer composite filled with inorganic fillers to reduce the cost of polymer materials and at the same time to improve in their physical and thermal properties. Widely applied fillers are metal powder, carbon black, zeolite, silica, mica, oxides, glass, etc. Mica is abundant and has many good characteristics, such as high strength, good thermal stability, excellent dielectric properties, and so on. Silica is used to reinforce elastomeric materials. Zeolites have the characteristics of low density and large porosity, and have been applied in many fields of catalysis, molecular sieve, ion exchange mineral, and so forth[1~5].

It is essential to understand cure kinetics and cure mechanism because the physical and mechanical properties of polymers have a close relation with their structure and extent of their reaction.

A lot of techniques such as DSC, HPLC, FT-IR and NMR have been developed[2,3,6~13] for the cure reaction of thermosetts. DSC analysis has been a well-known technique for studying cure kinetics of thermosetting epoxy resins with the assumption that the heat evolution recorded by DSC is proportional to the extent of monomer conversion[8].

In this study, the cure mechansim of epoxy composite was investigated by FT-IR and the cure kinetics was also studied by using Kissinger equation as a dynamic DSC analysis. Kissinger equation is expressed as follows[8].

$$-\ln(q/T^2_p) = \frac{E_a}{R}\frac{1}{T_p} - \ln(AR/E_a)$$

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

From the relationship between $-\ln(q/T^2_p)$ and $\frac{1}{T_p}$, activation energy and pre-exponential factor can be calculated.

2. Experiment

2.1. Materials

Epoxy resin and curing agent used in this study were diglycidyl ether of bisphenol A(DGEBA) supplied by Shell company and 4,4'-methylene dianiline (MDA), respectively. In order to improve the toughness of the DGEBA/MDA system, glutaronitrile(GN) was employed as a reactive additive. Clinoptilolite type natural zeolite from Kampo area in Korea was used as an inorganic filler and its particle size was under 325 mesh.

2.2. Procedure

To study the cure mechanism, FT-IR analysis was used as follows. Various contents of natural zeolite were filled to DGEBA/MDA(30 phr)/GN(10 phr) system. To prevent the natural zeolite from sinking, the systems were stirred and cured at different temperatures. The partially cured epoxy systems were analyzed by FT-IR. The samples for FT-IR were prepared in the liquid or solid state. Liquid sample was analyzed directly and solid sample was done in the wafer form. In order to investigate the effect of natural zeolite on the cure reaction of epoxy composite, cure kinetics was also studied by DSC (Cahn) analysis. The samples were prepared by mixing DGEBA/MDA(30 phr)/GN(10 phr) system with various zeolite contents. The mixtures were stored at -13℃. The heating rates were 2, 5, 10 and 20 ℃/min in the temperature range of 30℃~350 ℃.

3. Results and Discussion

The change of relative peak intensities in DGEBA/MDA/GN/natural zeolite system cured at 100℃ for different time were presented in Table 1. As shown in the Table, the relative peak intensities of hydroxyl, ether linkage and =C=N- groups increased but those of amine, epoxide and nitrile groups decreased with the increment of cure time. These results meant that hydroxyl group was produced by the reaction between epoxide group and amine group of MDA. The generated hydroxyl group also reacted with epoxy group and then formed ether linkage. GN reacted with amine group of MDA and then produced =C=N-[9].

Fig. 1 displayed FT-IR spectra of cured DGEBA/MDA(30 phr)/GN(10 phr) system and DGEBA/MDA (30 phr)/GN(10 phr)/natural zeolite(20 phr) system. There was little difference between two systems. Thus, it could be confirmed that there was no effect of natural zeolite on the cure mechanism of DGEBA/MDA/GN system.

Table 1. Relative Peak Intensity in DGEBA/MDA/GN/Natural Zeolite System Cured at 100℃ for Different Time.

Time(min) / Functional Group	10 min	20 min	30 min
Hydroxyl Group (3500 cm^{-1})	0.17	0.28	0.40
Amine (3300 cm^{-1})	0.52	0.50	0.41
-C≡N (2250 cm^{-1})	0.095	0.086	0.063
=C=N- (1650 cm^{-1})	0.056	0.064	0.11
Ether Linkage (1120 cm^{-1})	0.28	0.35	0.70
Epoxide Group (915 cm^{-1})	0.41	0.36	0.19

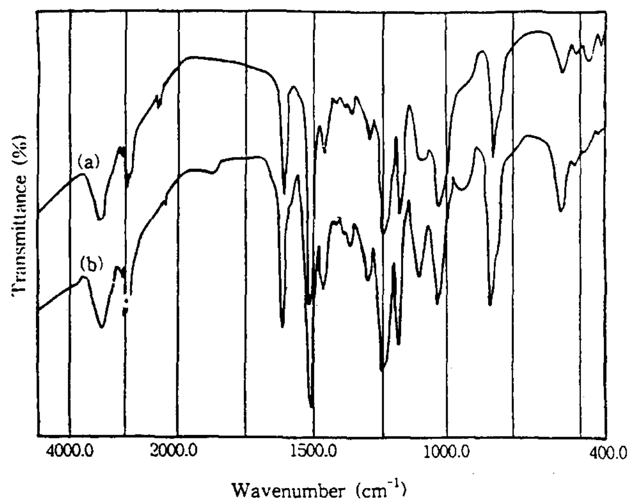

Fig. 1. FT-IR spectra of (a) DGEBA/MDA(30 phr)/GN(10 phr) system and (b) DGEBA/MDA(30 phr)/GN(10 phr)/natural zeolite(20 phr) system.

DSC scans for DGEBA/MDA/GN/natural zeolite(30 phr) system at different heating rates were shown in Fig. 2. There was only one exothermic peak on each thermogram of the system. On the thermogram of 2 ℃/min, cure reaction initiated at 96.9℃ and terminated at 180.6℃. However, on the thermogram of 20 ℃/min, cure reaction started at about 98℃ and stopped at 270 ℃. The exothermic peak temperatures at 2, 5, 10 and 20 ℃/min were 128.1, 151.0, 168.9 and 189.0℃, respectively. As the heating rate increased, the peak temperature appeared at high point. It was explained by the increasing exothermic heat because the quantities of reacted functional groups for identical time increased as heating rates increased[7].

DSC scans for DGEBA/MDA/GN system with different contents of natural zeolite at the heating rate of

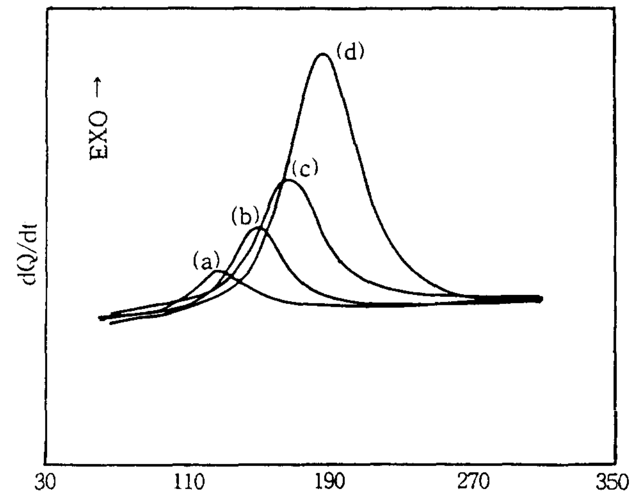

Fig. 2. DSC scans for DGEBA/MDA/GN/natural zeolite(30) system at different heating rates. (a) 2 ℃/min, (b) 5 ℃/min, (c) 10 ℃/min, (d) 20 ℃/min.

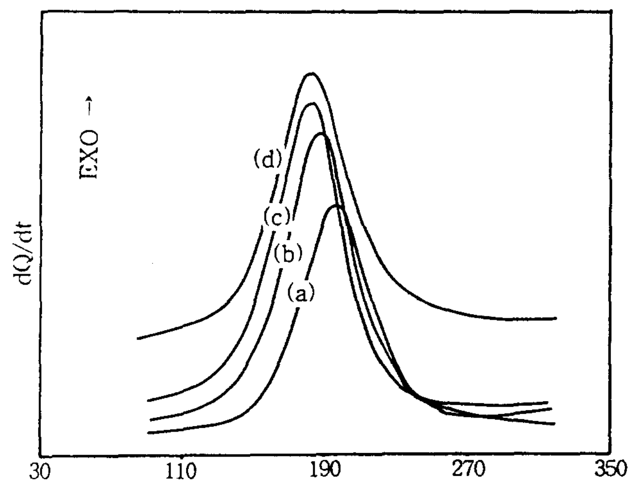

Fig. 3. DSC scans for DGEBA/MDA/GN system with different natural zeolite contents at the heating rate of 20 ℃/min. (a) 0 phr, (b) 10 phr, (c) 20 phr, (d) 30 phr.

20 ℃/min were shown in Fig. 3. In the zeolite contents of 0, 10, 20 and 30 phr systems, the temperatures at the peak were 198.3, 189.0, 186.2 and 187.6℃, respectively. As the contents of natural zeolite increased from 0 to 20 phr, the temperature at the peak decreased. When zeolite content was over 30 phr, temperature at the peak increased no more. These results implied that natural zeolite made positive effect on the cure rate of epoxy system until 20 phr. But, after that phr, natural zeolite did negative effect on the cure rate.

Fig. 4 exhibited the relation between $-\ln(q/T^2_p)$ and$1/T_p \times 10^3$ for different zeolite contents through Kissinger equation. The slopes at 0, 10, 20 and 30 phr

Table 2. Energies of Activation and Pre-exponential Factors of DGEBA/MDA/GN/Natural Zeolite System.

Zeolite Content (phr)	Activation Energy (kcal/mol)	Pre-exponential Factor($\times 10^{-3}$ sec^{-1})
0	12.34	4.85
10	12.18	5.35
20	12.67	11.60
30	12.58	9.39
40	13.17	20.31
50	12.68	10.41

of zeolite content were 6.21, 6.13, 6.38 and 6.33, respectively and the y-intercepts were 3.85, 3.96, 4.69 and 4.49. The activation energies and pre-exponential factors were obtained from the slopes and y-intercepts, and the values were listed on Table 2. The activation energies had the values of the range of 12.2 ~ 13.2 kcal/mol and pre-exponential factors were from 4.85×10^3 to 20.31×10^3 sec^{-1}.

Fig. 5 showed the rate constants of DGEBA/MDA/GN system with different zeolite content. Cure rate constants were calculated by Arrhenius equation. As zeolite contents increased from 0 phr to 20 phr, rate constant increased and had the highest value of 4.36×10^{-4} sec^{-1} at 20 phr. However, rate constant decreased slightly from 20 phr to 40 phr of zeolite content and sharply downed above 40 phr. These results were explained as follows. Zeolite has hydroxyl groups on surface and water molecules in the pore of the zeolite. When 0~20 phr of zeolite were filled, cure kinetics was accelerated by hydroxyl groups of the surface and water molecules[9~10]. But above 20 phr of zeolite content, cure rate was retarded because zeolite particles disturbed the diffusion of functional groups, such as epoxide group and amine groups.

The relative peak intensities of DGEBA/MDA/GN/zeolite(10 phr) system which cured at different temperatures for 30 min were shown in Fig. 6. As cure temperature increased, hydroxyl group and ether linkage increased. Therefore, cure rate was accelerated at high temperature. Thus, the extent of cure improved with the increment of cure temperature.

4. Conclusions

The effect of natural zeolite on the cure characteristics of DGEBA/MDA/GN/natural zeolite system was investigated. The obtained conclusions were summerized as follows.

1) The cure mechanism of DGEBA/MDA/GN/natural zeolite system was similar with that of DGEBA/

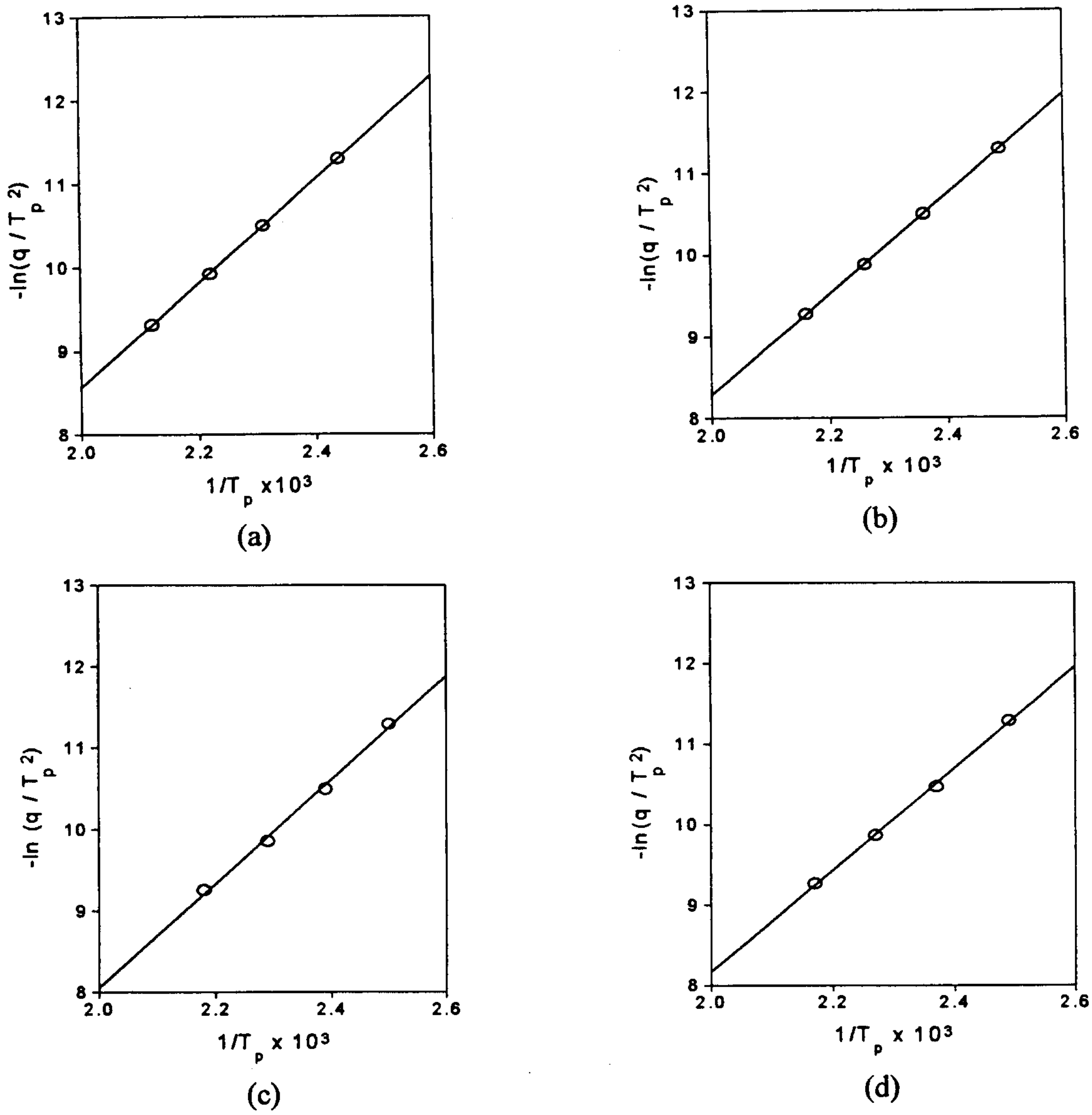

Fig. 4. Plots of $-\ln(q/T^2_p)$ vs. $1/T^2_p \times 10^3$ by Kissinger equation for DGEBA/MDA/GN system with different zeolite contents. (a) 0 phr, (b) 10 phr, (c) 20 phr, (d) 30 phr.

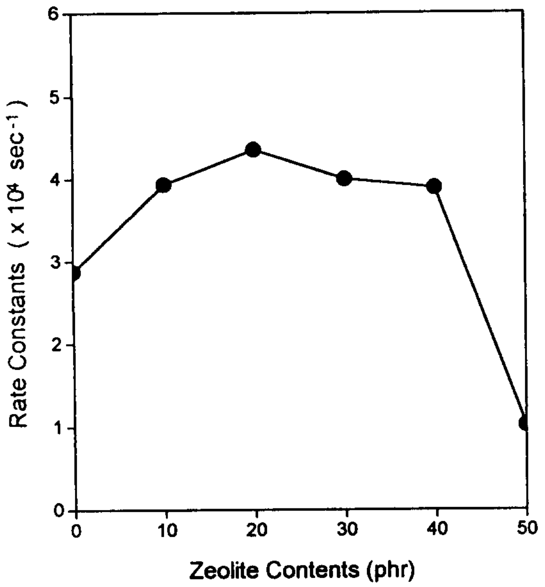

Fig. 5. Rate constant of DGEBA/MDA/GN system with different zeolite contents.

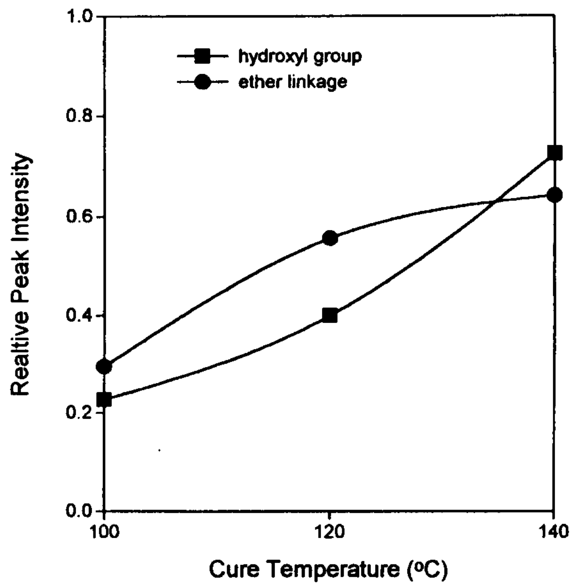

Fig. 6. Relative peak intensities of DGEBA/MDA/GN/natural zeolite system cured at different temperature.

MDA/GN system.

2) As heating rate increased, the temperature at the peak and exothermic heat of DGEBA/MDA/GN/natural zeolite system increased.

3) As the content of natural zeolite increased from 0 to 30 phr, the temperature at the peak decreased.

4) The rate constant increased up to 20 phr of zeolite contents due to the hydroxyl group of zeolite surface but decreased above 20 phr because of the interruption of zeolite particles on the diffusion of functional groups. In particular, rate constant decreased abruptly above zeolite content of 40 phr.

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