

# Thermal degradation of epoxy/natural zeolite composites

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The characteristics of thermal degradation of epoxy system filled with natural zeolite were studied by thermogravimetry analysis (TGA). All the epoxy composites were degraded in one stage regardless of the zeolite content. In the Freeman & Carroll equation, the activation energy at 20 phr of zeolite was lower than that at any other content of zeolite and these values decreased with the increment of heating rate. In the Kissinger equation, activation energy decreased until 30 phr of zeolite was added and the value abruptly increased at 40 phr of zeolite content. The activation energy and thermal degradation temperature showed the same tendency according to the change of zeolite content. The activation energy obtained from the Freeman & Carroll equation was larger than that from the Kissinger equation. © 2001 Kluwer Academic Publishers

## 1. Introduction

With increasing demands for polymer materials for the high temperature applications, many researchers have investigated to improve the thermal stability of polymers and many methods have been proposed to evaluate the thermal degradation of polymers or polymer composites [1–8]. Many inorganic materials such as carbon black, calcium carbonate, silica and talc have been used to give them special properties, and zeolite minerals are concerned about in these days [5, 8, 9]. 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. 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 that of another zeolite are important factor. 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 a flame retardant is adsorbed on zeolite filler prior to compositing with polymer matrix, these materials will be desorbed by fire and retard the fire.

In this study, the effect of natural zeolite on the thermal degradation of epoxy composites was investigated by thermogravimetry analysis (TGA). Zeolites are very stable materials to high thermal stress over 500°C without any degradation of the crystal structure. Many thermogravimetry analysis methods such as Freeman & Carroll equation [3, 4], Kissinger equation [1, 2], Horowitz and Metzger's equation [6], Toop's

equation [7] have been proposed with the assumption that the thermal degradation rate is proportional to the weight loss rate of the epoxy/zeolite composite. The former two equations are used in this study.

## 2. Experiment

The materials used in this study were diglycidyl ether of bisphenol A (DGEBA), 4,4'-methylene dianiline (MDA) as a curing agent, malononitrile (MN) as a reactive additive and clinoptilolite type natural zeolite as a filler from Kampo area in Korea [9–13]. The natural zeolite had small part of quartz and feldspar as impurities. The chemical composition and some physical properties are listed in Table I.

The natural zeolite was washed, dried and pulverized into 325–270 mesh (average particle size: 25.84  $\mu\text{m}$ ) and it was dehydrated at 110°C for 2 hrs. The dried filler was stored in desiccator to be filled to epoxy resin. To disperse the zeolite homogeneously into epoxy resin, DGEBA and zeolite (0–40 phr) were agitated and vacuumed for 2 hrs at 80°C. The melted MDA (30 phr) and MN (10 phr) were added to the DGEBA/zeolite mixtures and vacuumed for 20 min at 80°C, which was the best viscosity condition of the epoxy/zeolite mixture to prevent the sedimentation of zeolite filler and to pour them into the mold easily. The epoxy/zeolite mixtures were cured at 150°C for 60 min after curing at 80°C for 70 min.

To study thermal degradation of the cured epoxy composites, thermogravimetry (Cahn-121) was employed at the nitrogen flow rate of 100 ml/min to prevent the oxidation of the composites. The heating rates were

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TABLE I Chemical composition and physical properties of natural zeolite

SiO <sub>2</sub>	61.90
Al <sub>2</sub> O <sub>3</sub>	14.70
Fe <sub>2</sub> O <sub>3</sub>	3.70
CaO	6.09
MgO	0.78
K <sub>2</sub> O	2.13
Na <sub>2</sub> O	2.72
Ig. Loss	8.40
Average particle size, μm	25.84
Surface area, m <sup>2</sup> /g	129.96
Concentration of hydroxyl group on the surface, mol/g	3.22 × 10 <sup>-3</sup>
Specific gravity	2.12
pH	6.2
Degradation temperature of the crystal structure, °C	540

5, 10, 20 and 30°C/min. The data of thermogravimetry analysis are introduced to Freeman & Carroll equation and Kissinger equation. Freeman & Carroll equation is

$$-\frac{\Delta \ln(dw/dt)}{\Delta \ln W_r} = \frac{Ea}{R} \frac{\Delta T^{-1}}{\Delta \ln W_r} - n \quad (1)$$

where,  $dw/dt$ : rate of weight loss,  $W_r$ : total weight loss,  $Ea$ : activation energy,  $R$ : gas constant,  $T^{-1}$ : inversion of temperature and  $n$ : reaction order. The values of  $dw/dt$ ,  $W_r$  and  $T^{-1}$  can be obtained directly from the TGA thermograms and activation energy of thermal degradation can be calculated from the relationship between  $-\frac{\Delta \ln(dw/dt)}{\Delta \ln W_r}$  and  $\frac{\Delta T^{-1}}{\Delta \ln W_r}$ .

Kissinger equation is

$$-\ln\left(\frac{\beta}{T_m^2}\right) = \frac{Ea}{R} \cdot \frac{1}{T_m} - \ln[A_n(1 - \alpha)_m^{n-1}] \quad (2)$$

where,  $\beta$ : heating rate,  $T_m$ : temperature at the peak value of the DTG curve,  $\alpha$ : fractional weight loss and  $A$ : pre-exponential factor. A plot of  $-\ln(\beta/T_m^2)$  as a function of  $1/T_m$  gives activation energy from the slope of the straight line.

### 3. Results and discussion

Typical curves of TG and derivative thermogravimetry (DTG) for epoxy composites filled with 40 phr of natural zeolite at various heating rates are shown in Fig. 1. The samples were degraded in nitrogen atmosphere of 100 ml/min to prevent the degradation of the epoxy composites at lower temperature by the effect of oxygen in the air. On the TG curve, the weight of the sample is almost stable below a temperature and above the temperature, the weight loss increases rapidly in the short temperature range due to the removing of low molecules produced by the pyrolysis of the composite. This temperature is called as degradation temperature,  $T_d$  and it increases with the increment of heating rate. These values at 5, 10, 20 and 30°C/min were 352.5°C, 366.5°C, 376.2°C and 383.1°C, respectively. The total weight loss at 500°C was about -60% regardless of the heating rate. Further

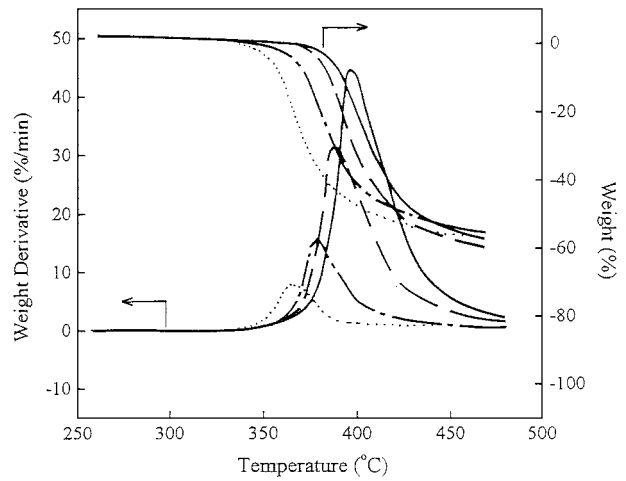


Figure 1 Thermogravimetric curves for epoxy/zeolite (40 phr) system at different heating rates. ....: 5°C/min, - · - ·: 10°C/min, — — —: 20°C/min, and —————: 30°C/min.

increment in the temperature caused only slight decrement of the residual weight. On the DTG curve, the sample degraded in one stage and the peak temperature of the curve increased with the increment of heating rate.

To get degradation activation energy through Freeman & Carroll equation (Equation 1), the values of  $-\frac{\Delta \ln(dw/dt)}{\Delta \ln W_r}$  and  $\frac{\Delta T^{-1}}{\Delta \ln W_r}$  could be calculated from TG and DTG curves in Fig. 1, and the relationship between two terms was plotted in Fig. 2. Activation energies were obtained from the slopes of the straight lines and these values at 5, 10, 20 and 30°C/min were 81.5, 87.5, 107.3 and 99.4 kcal/mol, respectively.

Fig. 3 shows TG and DTG curves for epoxy composites filled with various contents of zeolite at the heating rate of 10°C/min. All these systems were stable below degradation temperatures and degraded in one stage

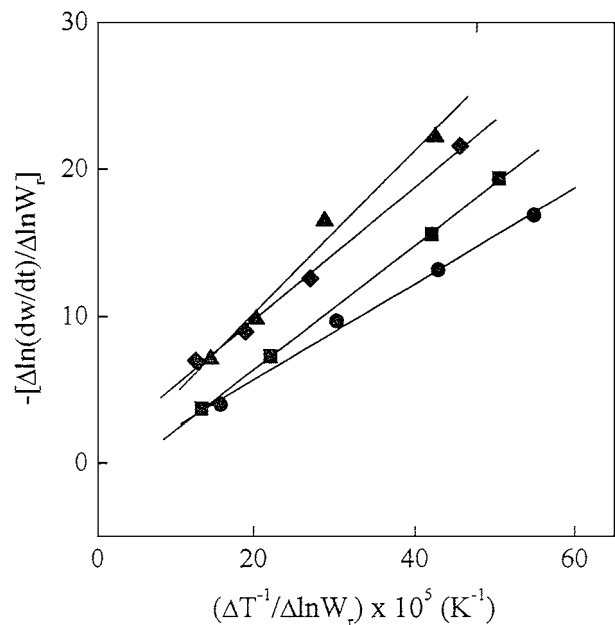


Figure 2 Evaluation of activation energy through Freeman & Carroll equation for epoxy/zeolite (40 phr) system at different heating rates. (●) 5°C/min, (■) 10°C/min, (▲) 20°C/min, and (◆) 30°C/min.

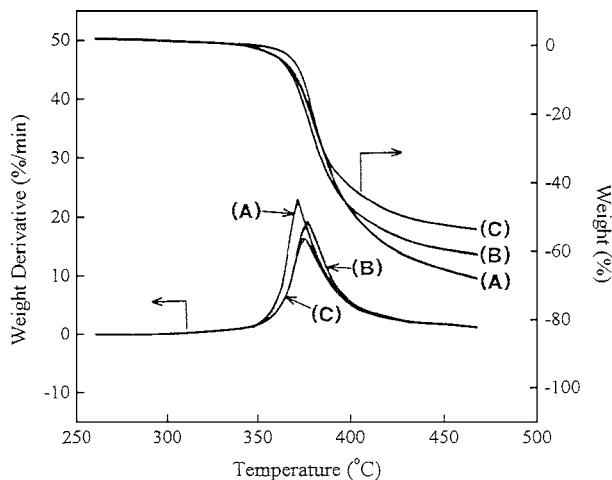


Figure 3 Thermogravimetric curves for epoxy systems with various zeolite contents at the heating rate of 10°C/min. Zeolite content: (A) 0 phr, (B) 20 phr, and (C) 40 phr.

regardless of zeolite content. As zeolite content increased, the degradation temperatures on TG curves and the peak temperatures on DTG curves decreased and the  $T_d$  values of the epoxy composites filled with 0 phr, 20 phr and 40 phr of zeolite were 368.2°C, 366.7°C and 366.5°C, respectively.

From the TG and DTG curves in Fig. 3, Fig. 4 was plotted by Freeman & Carroll equation and activation energy was obtained. These values for the system with 0 phr, 20 phr and 40 phr of zeolite were 103.3, 57.6, and 87.4 kcal/mol. The other activation energies obtained from Freeman & Carroll equation for the systems with different zeolite contents and at various heating rates were listed in Table II. Except 40 phr of zeolite content, those values decreased with the increment of heating rate. This was because with the increment of heating rate, more heat was

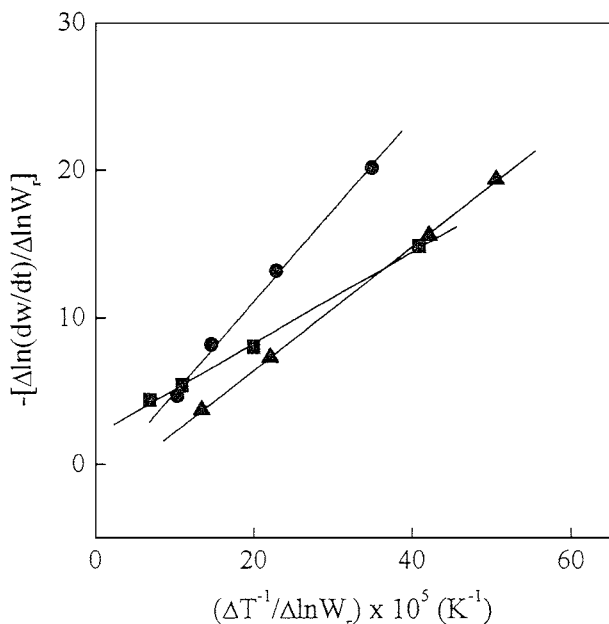


Figure 4 Evaluation of activation energy through Freeman & Carroll equation for epoxy systems with various zeolite contents at the heating rates of 10°C/min. Zeolite content: (●) 0 phr, (■) 20 phr, and (▲) 40 phr.

TABLE II Activation energy for thermal degradation of DGEBA/MDA/MN (10 phr), systems with various contents of natural zeolite through Freeman & Carroll equation

Zeolite content (phr)	Heating rate (°C/min)	Activation energy (kcal/mol)
0	5	117.2
	10	103.3
	20	99.3
	30	91.4
10	5	115.2
	10	117.2
	20	103.3
	30	81.5
20	5	59.6
	10	57.6
	20	41.7
	30	47.7
30	5	73.5
	10	61.6
	20	57.6
	30	53.6
40	5	81.5
	10	87.5
	20	107.3
	30	99.4

exposed to the sample in shorter time, so the sample decomposed easily. However, for the system with 40 phr of zeolite content, activation energy increased with the increment of heating rate below 20°C/min. The degradation activation energy of the composites effected by the zeolite content was decreased until 20 phr of zeolite was added and the value became increased after the zeolite content. This was different from the thermal degradation properties of the system filled with metal powder. Generally, when metal powder was filled to polymer matrix, the degradation activation energy became higher due to the increased thermal conductivity and the reduced hot spots [14–16]. However, when inorganic fillers such as zeolite, silica, etc. were added, the inorganic fillers were not able to act as effective heat sinks. Until 20 phr of zeolite content, thermal stress concentrated on the surface of zeolite filler and thermal degradation took place easily on the interface between the zeolite and epoxy matrix. However, above this content, activation energy increased, and it was due to the increasing effect of thermal conductivity of zeolite particle which was somewhat higher than that of neat epoxy matrix.

Kissinger equation (Equation 2) is relatively simple and activation energy can be obtained easily from the relationship between heating rate,  $\beta$  and temperature at the peak value of the DTG curve,  $T_m$ . To calculate activation energy of epoxy/zeolite (40 phr) system,  $\beta$  and  $T_m$  were obtained from Fig. 1 and  $-\ln(\beta/T_m^2)$  as a function of  $1/T_m$  was displayed in Fig. 5. The slope of the straight line was  $21.31 \times 10^3$  and the activation energy was 42.3 kcal/mol.

Fig. 6 shows derivative thermogravimetry curves for epoxy system without zeolite at different heating rates.

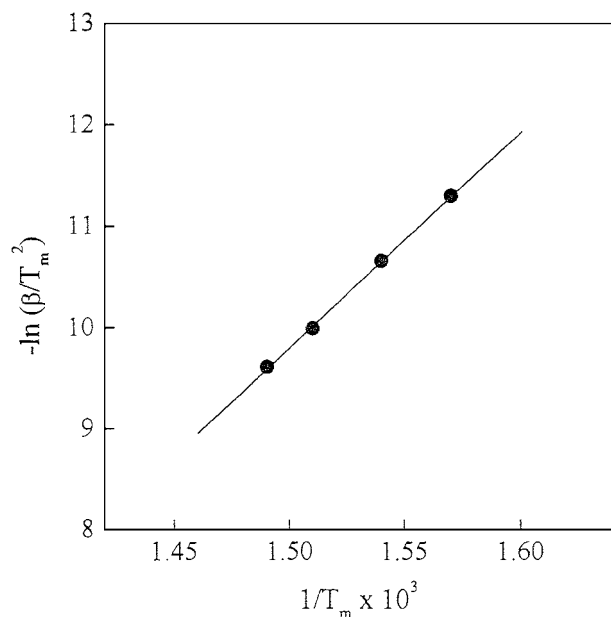


Figure 5 Kissinger plot of epoxy/zeolite (40 phr) system.

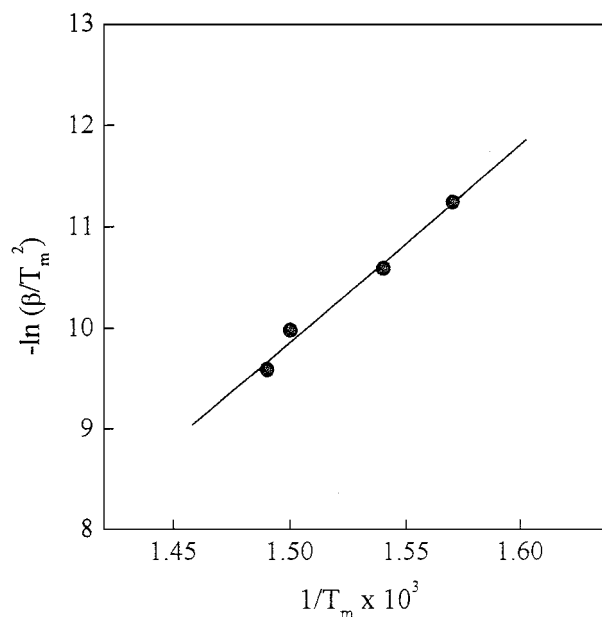


Figure 7 Kissinger plot of epoxy system without zeolite.

As explained above, the sample degraded in one stage and the temperature at the peak value of the DTG curve increased with the increment of heating rate. The samples with other content of zeolite also showed the same tendency in thermal degradation. From Fig. 6, of  $-\ln(\beta/T_m^2)$  and  $1/T_m$  were calculated and plotted in Fig. 7. The slope of the straight line was  $19.94 \times 10^3$  and the activation energy was 39.62 kcal/mol. Those values for other samples with various zeolite contents were also calculated by Kissinger equation and were displayed in Fig. 8. The values for 0, 10, 20, 30 and 40 phr of zeolite were 39.62, 40.65, 38.58, 31.93 and 42.30 kcal/mol, respectively. The thermal degradation temperatures were also shown in Fig. 8 and as shown in this figure, activation energy and thermal degradation temperature showed the same tendency according to the change of zeolite content. When zeolite content

was 30 phr, these values were smallest at 30 phr. Zeolite has channels and pores available for the adsorption of low weight molecules and the pores are adsorbed with water molecules in the open air. The water molecules not evacuated at the prior treatment were desorbed by the increasing temperature and the molecules weakened the interface strength between epoxy matrix and the zeolite filler. So, below 30 phr of zeolite, these values decreased with the increment of zeolite content, however at 40 phr, the values increased due to the increasing effect of zeolite particle whose conductivity was somewhat higher than that of neat epoxy matrix. Freeman & Carroll equation had almost the same tendency but the activation energy was smallest at 20 phr of zeolite content. The activation energies obtained from Freeman & Carroll equation were far higher than those obtained from Kissinger equation.

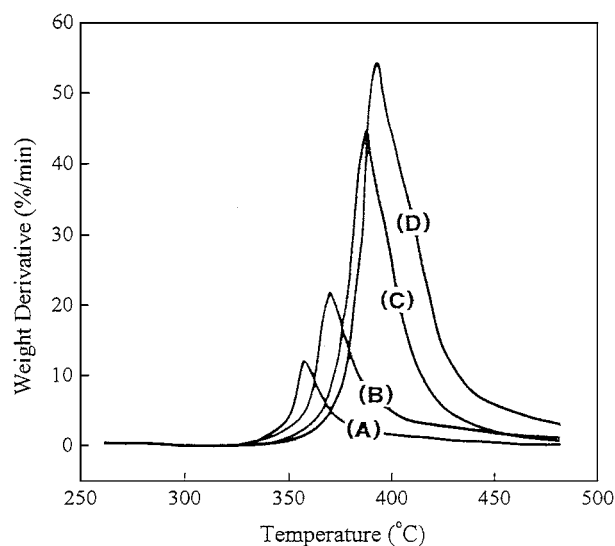


Figure 6 Derivative thermogravimetry curves for epoxy system without zeolite at different heating rates. (A) 5°C/min, (B) 10°C/min, (C) 20°C/min, and (D) 30°C/min.

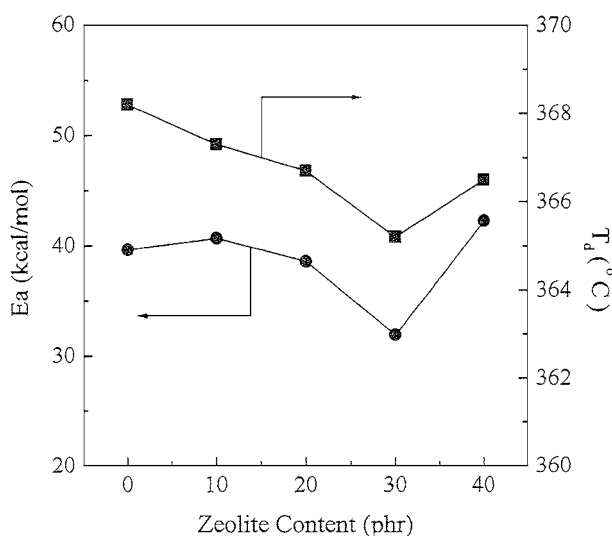


Figure 8 Activation energy (●) through Kissinger equation and degradation temperature (■) at 10°C/min for the systems with various zeolite content.

#### 4. Conclusions

The samples were degraded in one stage regardless of the zeolite content, and the degradation temperature on TG curve and the peak temperature on DTG curve were in increment of heating rate. In Freeman & Carroll equation, activation energy at 20 phr of zeolite was lower than any other content and that decreased with the increment of heating rate. In Kissinger equation, activation energy was smallest at 30 phr of zeolite content, and the activation energy and thermal degradation temperature showed the same tendency according to the change of zeolite content. The activation energy obtained from the Freeman & Carroll equation was larger than that from Kissinger equation.

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