Studies on Curing Process of Epoxy Resins by High-Resolution Pyrolysis-Gas Chromatography

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ABSTRACT: The curing processes of epoxy resins cured with a dicarboxylic acid anhydride or in the presence of an imidazole catalyst were studied by high-resolution pyrolysis-gas chromatography. The yields of the pyrolyzates with epoxide groups decreased with increase in the degree of curing, while those of various phenols characteristic of prepolymer skeleton increased. Additionally, the yields of low boiling pyrolyzates such as ethylene oxide, propylene, acrolein and acetone also specifically changed with the degree of curing. The obtained results are discussed in comparison with the results from other techniques such as glass transition temperature measurements and FT-IR.
       KEY WORDS   Pyrolysis-Gas Chromatography / Epoxy Resin / Curing
           Process /

The curing process of epoxy resins has been most often studied by IR from the changes in the spectra due to the change in the chemical structures through the curing process. Klaban et al.[1] studied curing reactions between an epoxy prepolymer and hexahydrophthalic acid anhydride. It was found that cure reactions were accelerated by alkali halides such as NaCl and LiCl. Stevens[2,3] assigned the molecular vibrational peaks ranging from 400 to 4000 cm^{-1} and discussed the cure kinetics of a bisphenol A epoxy resin/dicarboxylic acid anhydride system on the basis of the changes in optical density through the cure reactions. Strecker[4] studied the curing reaction between an epoxy resin and carboxyl-terminated polybutadiene after the gel point, using IR transmittance and reflection spectrophotometric techniques. Curing processes of epoxy resin

systems catalyzed by tertiary amine and imidazole were studied by Saunders et al.[5] and Farkas et al.,[6] respectively by IR and NMR. More recently, Smith et al.[7,8] studied the curing process of epoxy resins catalyzed by boron trifluoride monoethylamine (BF$_3$-MEA) by FT-IR and ^{19}F NMR. They concluded that fluoroboric acid formed from BF$_3$-MEA acted effectively as a catalyst.

Differential scanning calorimetry (DSC) also has been extensively used to study the cure reactions of epoxy resin systems.[9-11] Crane et al.[9] has evaluated the heat of cure reactions, the kinetic order and the activation energy for an epoxy-phenolic adhesive by DSC, while Barton[10] has monitored cross-linking reactions of epoxy resins through glass transition temperature (T_g) measurements by DSC. Horie et al.[11] also investigated the cure re-

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actions of epoxy resins with aliphatic diamines by DSC. The heat of the reactions and the rate constants based on the third order kinetics were determined and discussed for the model reactions. The final conversion was also calculated based on the theory of T_g of the cross-linked polymer systems.

On the other hand, pyrolysis-gas chromatography (PyGC) is another technique applied to intractable materials with network structures which are substantially insoluble and often contain many additives. Previously, the thermal degradation behaviour of epoxy resins cured with various curing agents was studied by high-resolution PyGC.[12] Various phenols characteristic of prepolymer skeletons and pyrolyzates characteristic of curing agents including intact dicarboxylic acid anhydride were observed. Additionally, pyrolyzates with epoxide groups were also observed on the pyrograms of incompletely cured resins, which suggested potential ability of this technique to study the curing process of epoxy resins.

In the present work, the curing processes of epoxy resin samples cured with a dicarboxylic acid anhydride or an imidazole catalyst to various degrees of cure were studied by high-resolution PyGC. In both cases, the yields of the pyrolyzates with epoxide groups decreased with increase in the degree of cure, while those of various phenols characteristic of prepolymer skeleton increased. Additionally, the yields of low boiling pyrolyzates such as ethylene oxide, propylene, acrolein, and acetone proved to change with the degree of cure. These results observed by PyGC corresponded well to those deduced from T_g measurements by DSC. The PyGC results are also discussed in comparison with the results obtained by FT-IR.

EXPERIMENTAL

Conditions for PyGC

A vertical microfurnace-type pyrolyzer (Yanagimoto GP-1018) was directly attached to a gas chromatograph (Yanagimoto G3800) with a high-resolution fused silica capillary column (0.2 mm i.d. × 25 m long) coated with immobilized methylphenylsilicone (5% phenyl) supplied from Hewlett Packard. Details of this pyrolyzer were described in a previous report, where the advantages of the microfurnace-type pyrolyzer in handling thermally changeable materials such as epoxy resins were empirically discussed.[12] The capillary column was used in a temperature programming mode from 50 to 330°C at a rate of 4°C min⁻¹. The nitrogen carrier gas flow (30 ml min⁻¹) at the pyrolyzer was reduced to 0.4 ml min⁻¹ at the capillary column through a splitter. Additionally, another PyGC system (Shimadzu GC-7A with the pyrolyzer) which could be temperature programmed from 0°C (4°C min⁻¹) was also used to separate the lower boiling pyrolyzates. In this case, a fused silica capillary column (0.25 mm i.d. × 50 m long) coated with immobilized OV-1701 (14% cyanophenylmethyl-silicone) was used, and the nitrogen carrier gas flow (40 ml min⁻¹) at the pyrolyzer was reduced to 0.5 ml min⁻¹ through a splitter. In both cases, weighed samples of about 150 µg were pyrolyzed at 600°C.

Conditions for DSC

The T_g measurements for epoxy resin samples were carried out by DSC using Du Pont Thermal Analyzer 910. Samples of about 1 mg were measured under a nitrogen atmosphere from ambient temperature to about 200°C at a rate of 20°C min⁻¹.

Conditions for FT-IR

FT-IR spectra were obtained using Degilab FTS-15C at 4 cm⁻¹ resolution and 500 scans. Samples of about 1 mg were cast into KBr pellets and measured at ambient temperature under a nitrogen atmosphere. The absorbance of the residual epoxide groups at 910 cm⁻¹ was calculated from the peak height measurement of difference spectra from that of the completely cured sample using benzene C–H and

Table I. Epoxy resin samples with various degrees of cure

Samples	Curing-agent [composition[a]]	Accelerator [composition[b]]	Curing-condition
DGEBA/1B2MZ			
A	—	—	—
B	—	1-Benzyl-2-methyl-imidazole (1B2MZ) [0.25]	180°C, 3 h
C	—	1B2MZ [0.50]	180°C, 3 h
D	—	1B2MZ [1.5]	180°C, 3 h
E	—	1B2MZ [2.0]	180°C, 3 h
F	—	1B2MZ [4.0]	180°C, 3 h
G	—	1B2MZ [6.0]	180°C, 3 h
H	—	1B2MZ [1.5]	180°C, 6 h
DGEBA/HHPA			
I	Hexahydrophthalic acid anhydride (HHPA) [80]	Benzyldimethyl-amine (BDMA) [0.50]	—
J	HHPA [80]	BDMA [0.50]	100°C, 20 min
K	HHPA [80]	BDMA [0.50]	100°C, 40 min
L	HHPA [80]	BDMA [0.50]	100°C, 1 h
M	HHPA [80]	BDMA [0.50]	100°C, 2 h
N	HHPA [80]	BDMA [0.50]	100°C, 3 h
O	HHPA [80]	BDMA [0.50]	100°C, 7 h

[a] Weight percent per prepolymer.
[b] μl per 100 mg prepolymer.

C–C band as an internal standard. Similarly, absorbance for the ether band at $1040 \, \mathrm{cm}^{-1}$ was calculated from the peak height measurement of the difference spectra from that of the uncured sample.

Materials

Two types of epoxy resin samples with various degrees of cure utilized are listed in Table I together with their curing-conditions and compositions. Diglycidyl ether of bisphenol A (DGEBA, $\bar{M}_n \fallingdotseq 340$) prepolymer cured at 180°C for 3 h with various amounts of an imidazole catalyst (1-benzyl-2-methylimidazole, 1B2MZ) (samples A to H), and DGEBA cured with hexahydrophthalic acid anhydride (HHPA) at 100°C for various cure-times (samples I to O) were utilized.

RESULTS AND DISCUSSION

Typical pyrograms of DGEBA cured with various amounts of 1B2MZ under the same curing conditions (180°C for 3 h) are shown in Figure 1 (samples C, D, and G). Low boiling pyrolyzates and various phenols including bisphenol A characteristic of the prepolymer skeleton were commonly observed on the pyrograms. Among these, intact prepolymer molecules (DGEBA) and monoglycidyl ether of bisphenol A (MGEBA) were markedly observed on the pyrograms of the samples with the lower contents of the catalyst. The DGEBA peak is exclusively due to the thermal volatilization of the original prepolymer remaining in the sample. The MGEBA is formed from the thermal degradation of the intermediate terminals with one unreacted epoxide group as well as from that of the remaining prepolymer. On the other hand, the completely reacted prepolymer moiety mostly yields various phenols characteristic of the prepolymer skeleton although both the remaining prepolymer and the intermediate
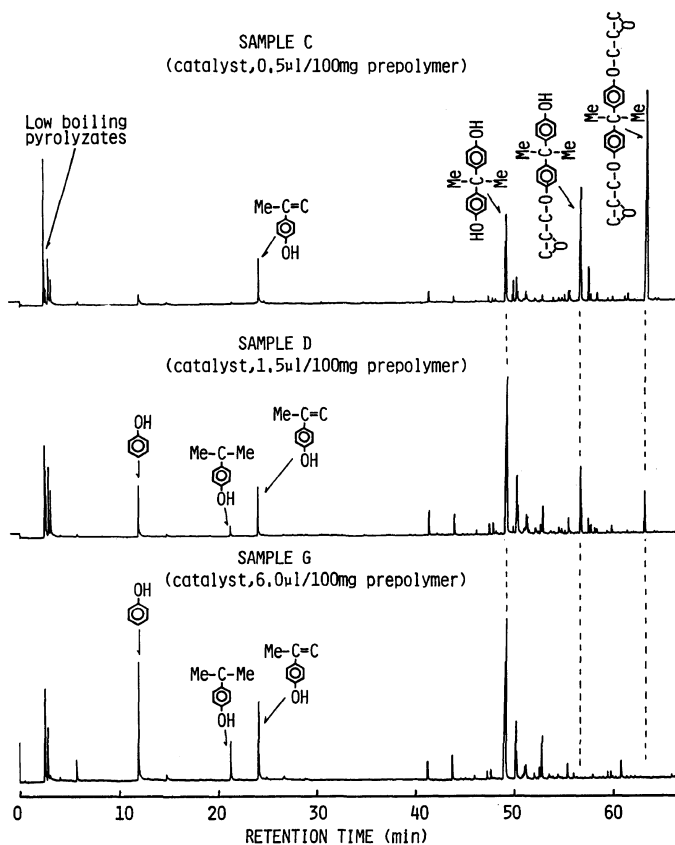
Figure 1. High-resolution pyrograms of epoxy resins cured with various amounts of imidazole catalyst at 180°C for 3 h.

terminals also yield the various phenols through pyrolysis to some extent.

Relationships between the observed peak intensities of the characteristic products and the amounts of the catalyst added to a given amount (100 mg) of prepolymer are shown in Figure 2. In this case, peak intensity is defined as the observed peak area normalized by the sample amount (μg). The peak intensities of DGEBA and MGEBA decrease with increase in the amount of catalyst which corresponds to the degree of cure. As might be expected, the diepoxide compound (DGEBA) decreased more rapidly than the monoepoxide one (MGEBA) with increase of the catalyst content. On the other hand, peak intensity of bisphenol A increases with the degree of cure

and becomes almost constant after the amount of catalyst exceeds 2 μl per 100 mg prepolymer. Under the given cure-conditions, the curing reactions are completed when the amount of the catalyst per 100 mg prepolymer exceeds 4 μl, where the products with epoxide groups completely disappear on the pyrogram.

Typical pyrograms of DGEBA cured with HHPA at 100°C for various cure-times (samples I, K, and O) are shown in Figure 3. In addition to the low boiling pyrolyzates, bisphenol A, and the pyrolyzates with one or two epoxide groups, the peak of intact HHPA molecule was commonly observed on the pyrograms. Also in this case, the peak intensities of the characteristic pyrolyzates change as a function of cure-time.
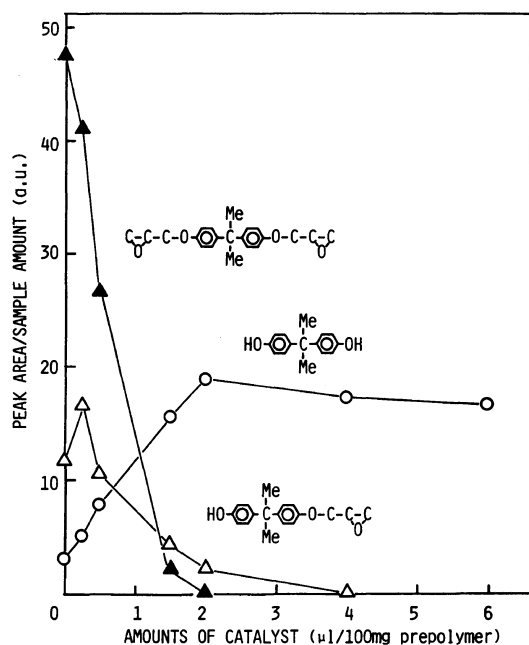
Epoxy-resin: DGEBA + catalyst(⬡-CH₂-N⟋N⟍)
                                        Me
Cure condition: 180°C, 3h
Pyrolysis temp.: 600°C

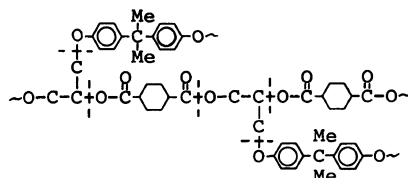**Figure 2.** Changes of characteristic products from epoxy resins as a function of catalyst-amount.

Relationships between the peak intensities of the characteristic pyrolyzates and cure-time are shown in Figure 4. Similar to the samples cured with the imidazole catalyst, the peak intensities of the pyrolyzates with epoxide groups decrease with increase in cure-time, while those of bisphenol A increase. However, the fact that MGEBA is still observed on the pyrogram of the sample over-cured up to 7 h suggests that a small amount of epoxide groups remains unreacted in this system even after the cure is completed. On the other hand, the peak intensity of HHPA slightly decreases in the first stage of cure but remains constant at extended cure-time. This suggests that volatilization of HHPA occurs to some extent competitively in the early stage of the curing process while the reacted HHPA monomer is not completely recovered as the original molecule on the pyrogram through pyrolysis. The fact that the peak intensities of the characteris-

tic products become almost constant after 3 h of cure-time indicates that the cure reactions are completed by about 3 h at the cure-temperature of 100°C, which agrees well with the cure-conditions recommended by the supplier.

Typical pyrograms in the low boiling-point region are shown in Figure 5 for the two resin systems. The characteristic pyrolyzates of ethylene oxide, propylene, acrolein, acetone, and allyl alcohol are commonly observed on the pyrograms. Furthermore, toluene characteristic of the imidazole catalyst (1B2MZ) is observed on the pyrograms of the resin samples cured with 1B2MZ, which increases with rise in the amounts of 1B2MZ contained in the samples. On the other hand, cyclohexene characteristic of HHPA and benzene characteristic of benzyldimethylamine used as a catalyst are observed on the pyrograms of the resin samples cured with HHPA.

Changes of the low boiling products are shown as a function of the degree of cure in Figures 6 and 7 for the samples cured with 1B2MZ and HHPA, respectively. In both resin systems, the peak intensity of ethylene oxide decreases as the degree of cure increases, while those of propylene and acetone increase. These phenomena suggest that propylene and acetone are likely formed from the reacted epoxide groups, while ethylene oxide from the unreacted epoxide groups.

On the other hand, it is interesting to note that the peak intensity of acrolein increases with rise in the degree of cure for the HHPA-cured samples, while the opposite tendency is observed for the 1B2MZ-cured samples. This phenomenon suggests that acrolein is likely formed from the reacted epoxide groups with acid anhydride through ester linkages as shown below,
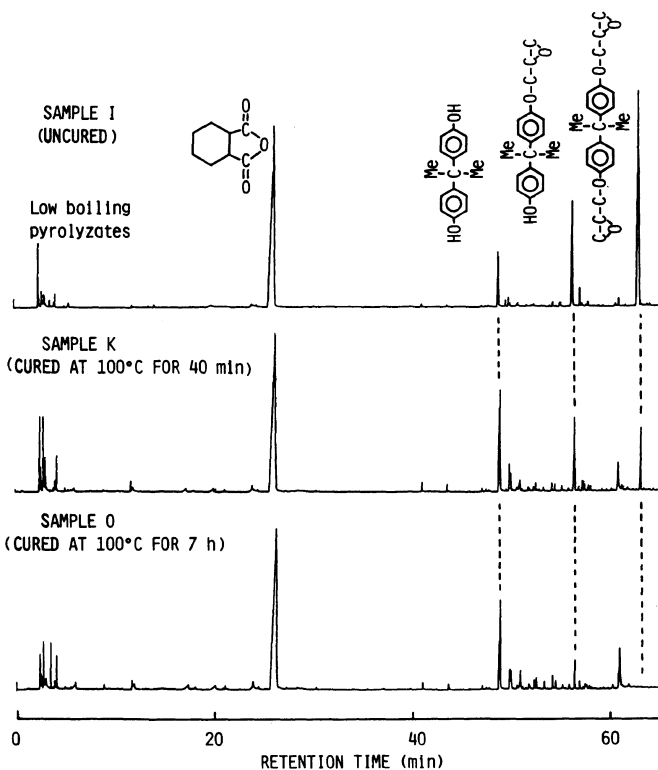
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Figure 3. High-resolution pyrograms of epoxy resins cured with HHPA at 100°C for various cure-time.

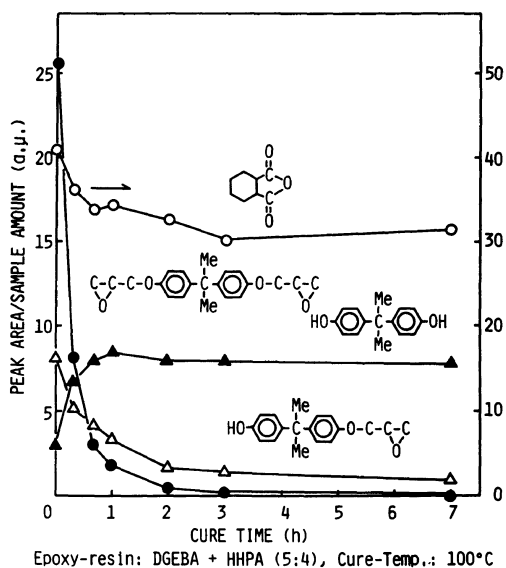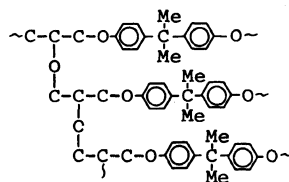Epoxy-resin: DGEBA + HHPA (5:4), Cure-Temp.: 100°C

Figure 4. Changes of characteristic products from epoxy resin as a function of cure-time.

while it is scarcely formed from the homo-polymerized epoxide groups through the ether linkage as shown below.

The fact that HHPA is almost quantitatively recovered on the pyrogram suggests that the preferential scission at the C–O bonds in the ester linkages to yield HHPA, in turn, might be responsible for the acrolein formation from the cured epoxy resin with ester linkages. Furthermore, the peak intensities of these low boiling pyrolyzates become almost constant at the region where the peak intensities shown in Figures 2 and 4 for the corresponding resin
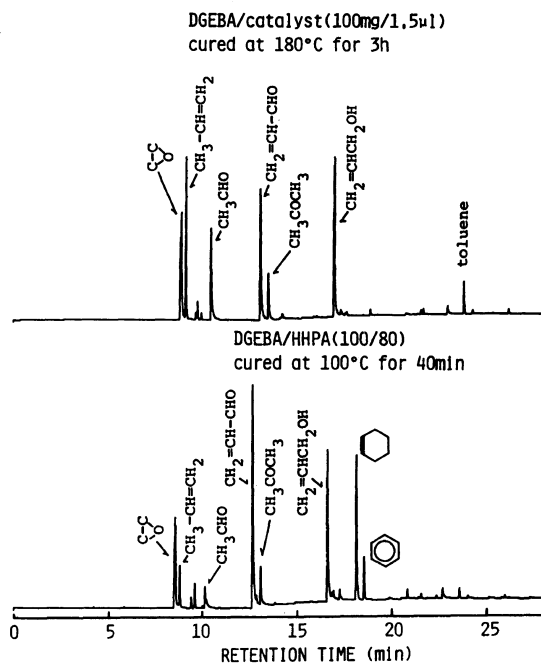
DGEBA/catalyst(100mg/1.5μl)
cured at 180°C for 3h

DGEBA/HHPA(100/80)
cured at 100°C for 40min

RETENTION TIME (min)

Figure 5. Pyrograms in the low boiling-point region for epoxy resin samples.
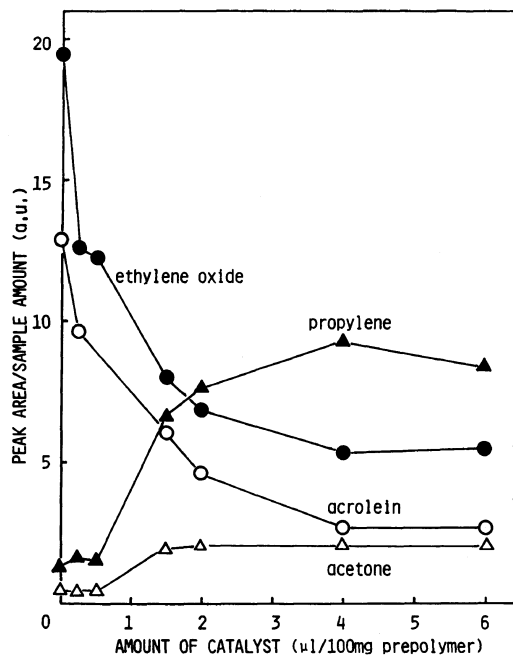

Epoxy resin: DGEBA + HHPA (5:4), Cure-Temp.: 100°C

Figure 7. Change of low boiling products as a function of cure-time.

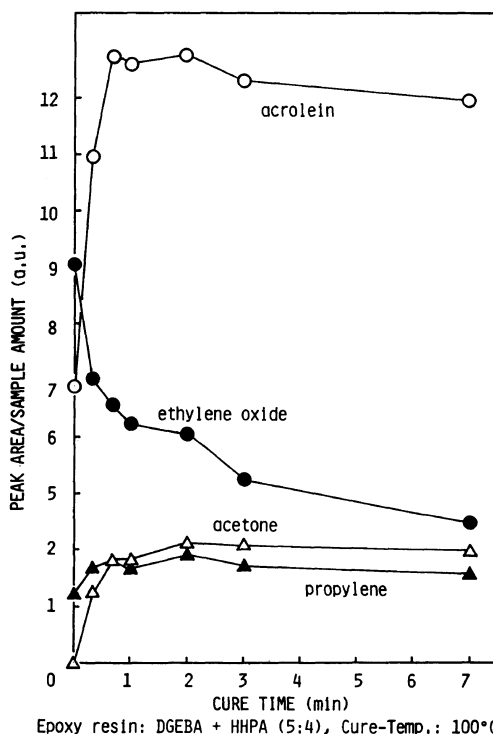Epoxy resin: DGEBA + imidazole catalyst
Cure condition: 180 C, 3h

**Figure 6.** Change of low boiling products as a function of catalyst amount.

systems become constant.

Comparative results of PyGC, T_g measurements by DSC and FT-IR obtained for representative samples are shown in Table II. The unreacted amounts of epoxide groups (%) observed by PyGC are defined by adding the peak intensity of DGEBA and 1/2 of the peak intensity of MGEBA when the values for the uncured samples (samples A and I) are regarded as 100%. In both resin systems, the residual amounts of epoxide groups observed by PyGC correspond well to T_g values by DSC which are conventionally used to evaluate the degrees of cure.[1,11]

Also in the case of the resin samples cured with imidazole catalyst, the relative amounts of epoxide groups measured by PyGC decrease monotonously with decrease in the corresponding amounts obtained by FT-IR, while those of ether group formed through homopo-

Table II. Comparative results of PyGC, DSC, and FT-IR for epoxy resin samples

Samples	Relative amount of $\underset{O}{C-C}$ (%) by PyGC[a]	$T_g(°C)$ by DSC	FT-IR absorbance[b]	
			$\underset{O}{C-C}$ (910 cm^{-1})	C–O–C (1040 cm^{-1})
DGEBA/1B2MZ				
A	100	—	100	0
D	8.1	33.1	55.1	50.0
E	2.1	58.1	25.8	96.0
G	0	99.2	0	100
H	3.7	51.7	29.2	84.0
DGEBA/HHPA				
I	100	—	—	—
K	16.6	47.4	—	—
L	11.6	59.2	—	—
M	3.7	89.4	—	—
O	1.6	104	—	—

[a] The values for samples A and I is regarded as 100% for both the DGEBA/1B2MZ and DGEBA/HHPA systems.
[b] Absorbance for samples A and G is regarded as 100% for both the epoxide and ether bands.

lymerization of the epoxide groups increase. However, the fact that decrements in epoxide groups measured by PyGC are much greater than those observed by FT-IR suggests that the recovery rate of residual epoxide groups as MGEBA from the intermediate terminals with one unreacted epoxide group might be fairly lower than that from DGEBA under given pyrolysis conditions.

In conclusion, the PyGC technique has proved to be a rapid and convenient method for characterizing the cure process of epoxy resins. This technique is also expected to offer a method to analyze the distributions of cure in various practical bulk samples, since a very small amount of sample is enough for PyGC measurements.

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