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A Comparative Study on Electron-Beam and Thermal Curing Properties of Epoxy Resins

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:
· , benzylquinoxalinium hexafluoroantimonate(BQH)가
· (TGA) , Coats - Redfern
가
가
· ,
· ,
가가 (NIRS)

ABSTRACT : A comparative study using electron - beam(EB) and thermal curing techniques was carried out to determine the effect of cure behavior and thermal stability of epoxy resins. In this work, benzylquinoxalinium hexafluoroantimonate(BQH) was used as a latent cationic catalyst for an epoxy resin. According to the thermogravimetric analysis(TGA), the decomposed activation energy based on Coats - Redfern method was higher in the case of thermal curing technique. This could be interpreted in terms of slow thermal diffusion rate resulted from high crosslink density of the thermally cured epoxy resin. However, the increase of hydroxyl group in the epoxy resin cured by EB technique was observed in near - infrared spectroscopy(NIRS) measurements, resulting in improving the stable short aromatic chain structure, integral procedural decomposition temperature, and finally ductile properties for high impact strengths.

Keywords : electron-beam, thermal curing, latent cationic catalyst, near-infrared spectroscopy, thermal stability.

가

·
· 1

· 2

diglycidylether of bisphenol A (DGEBA) 가 가 , 가 ,

3 , 3 가 , 10,11 Sundell 12 aromatic onium 가 가

(T_g) 3

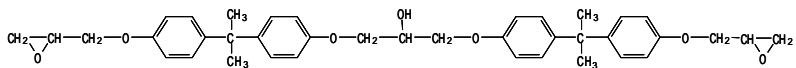
(thermal curing) 4 UV benzylquinoxalinium hexafluoroanti- monate (BQH) 2

(ultra - violet curing),⁵ (microwave curing),⁶ 가 가 , UV Rockwell hardness (electron - beam curing) 7 가 , tester M scale ,

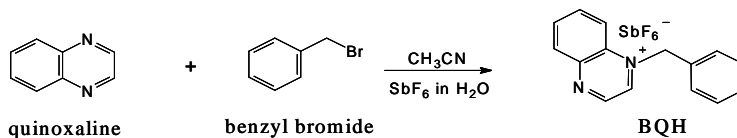
가 4-7 가 , 2 diglycidyl - ether of bisphenol A (DGEBA, () : YD - 128, 12000 cps, 1.16 g/cm³ E.E.W=185 190 g/eq) benzyl bromide quinoxaline BQH

가 , Crivello 9 Endo 10 BF_4^- , PF_6^- , BQH

AsF_6^- , SbF_6^- aromatic onium BQH BQH



Structure of DGEBA



Synthesis of BQH

Figure 1. Structure of DGEBA(YD - 128) and synthesis of BQH.

Quinoxalium (10 g, 0.0768 mol)
 acetonitrile 40 mL benzylbromide
 (25 g, 0.1462 mol) 4 5
 1 1
 acetonitrile
 acetonitrile
 ether
 NaSbF₆ (sodium hexa-
 fluoroantimonate) 가
 methanol
 : 67%, 18.8 g, mp : 147.8 151.2
 FT - IR (KBr) =3096, 1514, 1359, 1073, 765,
 662 cm⁻¹
¹H NMR (acetone d₆)
 9.832 9.823 : 2H (pyrazine), 9.618 9.608 :
 2H (pyrazine)
 8.839 8.348 : 4H (phenyl), 7.651 7.475 : 5H
 (phenyl), 6.627 : 2H (benzyl)
 Elemental analysis
 C₁₅H₁₃N₂SbF₆ Calc'd C : 33.39% H : 2.84% N : 6.13%
 Found C : 35.42% H : 2.76% N : 6.15%

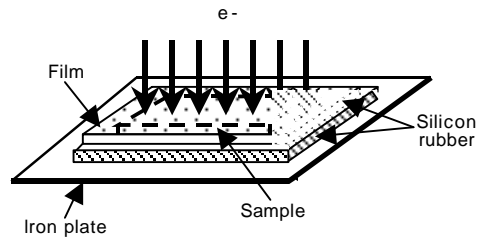


Figure 2. The mold used in electron - beam curing.

BQH
 BQH
 1 wt% 가
 80
 , Airtec
 Release #19 80 30 x
 30 x 3 mm³ spacer
 80
 (30), 150 (2), 200 (1)
 Figure 2
 30 x 30 x 3 mm³ spacer

가
 (electron - beam accelerator: Samsung ELV - 4)
 1 MeV dose energy, 39.8 mA
 current, 40 kW beam power, 3
 Mrad/min dose
 200 kGy 50 kGy 4
 (thermo -
 gravimetric analysis, TGA: Du Pont, TGA - 2590)
 10 /min
 30 850
 ,¹³
 13,14
 가 (400 14000 cm⁻¹)
 (near -infrared spectroscopy,
 NIRS) ¹⁴
 , Perstorp Analytical NIR
 system 6500 NIR
 Rockwell hardness
 tester , 1/4 inch steel ball 100
 kgf 가 Mscale
 30 x 30 x 3 mm³

(scanning electron microscopy, SEM, JEOL JXA 840A) 3000

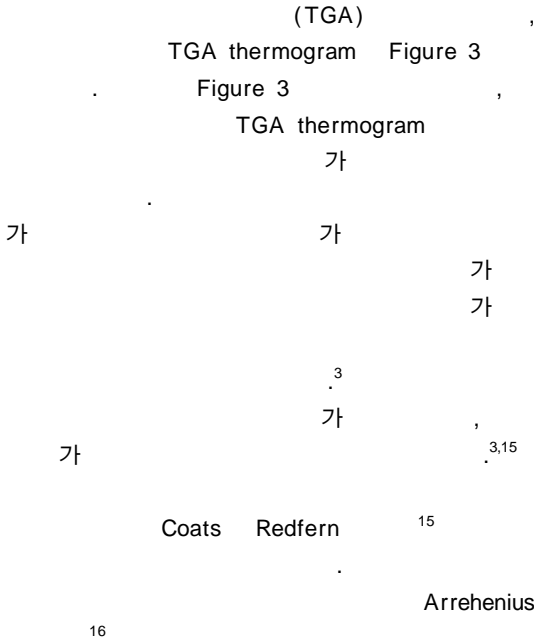


Figure 3. TGA thermograms of thermal curing and electron - beam curing.

$$\frac{da}{dt} = f(a) A \exp\left(-\frac{E_t}{RT}\right) \quad (3)$$

$$f(a) = (1-a)^n \quad (4)$$

$$\frac{da}{dt} = (1-a)^n A \exp\left(-\frac{E_t}{RT}\right) \quad (5)$$

$$\frac{da}{dt} = (1-a)^n A \exp\left(-\frac{E_t}{RT}\right) \quad (6)$$

$$\frac{da}{dt} = (1-a)^n A \exp\left(-\frac{E_t}{RT}\right) \quad (7)$$

$$\frac{da}{(1-a)^n} = \frac{A}{b} \exp\left(-\frac{E_t}{RT}\right) dT \quad (8)$$

$$\int_{T_0}^T \exp\left(-\frac{E_t}{RT}\right) dT \quad (9)$$

$$-\ln(1-a) = \frac{A}{b} \int_{T_0}^T \exp\left(-\frac{E_t}{RT}\right) dT \quad (10)$$

$$\int_{T_0}^T \exp\left(-\frac{E_t}{RT}\right) dT \quad (11)$$

$$\int_{T_0}^T \exp\left(-\frac{E_t}{RT}\right) dT = \frac{ART^2}{bE_t} \left(1 - \frac{2RT}{E_t}\right) \exp\left(-\frac{E_t}{RT}\right) \quad (12)$$

$$\int_{T_0}^T \exp\left(-\frac{E_t}{RT}\right) dT \quad (13)$$

$$\ln\left[\frac{-\ln(1-a)}{T^2}\right] = \ln\left[\frac{AR}{bE_t} \left(1 - \frac{2RT}{E_t}\right) \exp\left(-\frac{E_t}{RT}\right)\right] \quad (14)$$

$$\ln\left[\frac{-\ln(1-a)}{T^2}\right] = \ln\left[\frac{AR}{bE_t} \left(1 - \frac{2RT}{E_t}\right) - \frac{E_t}{RT}\right] \quad (15)$$

$$\ln\left[\frac{-\ln(1-a)}{T^2}\right] = \ln\left[\frac{AR}{bE_t} \left(1 - \frac{2RT}{E_t}\right) - \frac{E_t}{RT}\right] \quad (16)$$

Table 1. Decomposition Activation Energy (E_t) of Thermal and Electron-Beam Curing Systems by Coats-Redfern Method

curing methods	E_t (kJ/mol)
thermal curing	272.68
electron - beam curing	241.19

Table 2. Thermal Stabilities of Thermal and Electron-Beam Curing Systems

	IDT (°C)	T_{max} (°C)	$A \cdot K$	IPDT (°C)
thermal curing	363	440	0.612	531
electron - beam curing	352	439	0.616	534

(9) $\ln[-\ln(1 - \frac{W_t}{W_0})/T^2]$ vs $1/T$, R

(9) E_t

Table 1 Table 1
가 30
kJ/mol 가
bulk 가

Doyle¹⁸
(integral procedural decomposition temperature, IPDT)

¹⁹ IPDT
 $IPDT(°C) = A \cdot K(T_f - T_i)$ (10)

$A \cdot K$ TGA
 $[(A_1 + A_2)/(A_1 + A_2 + A_3)] \cdot K \cdot A_1$
 $[(A_1 + A_2)/A_1] \cdot T_i$

T_f
TGA thermogram
(initial decomposition temperature, IDT),
(temperature of maximum rate of

weight loss, T_{max}),
IPDT Table 2
A · K
IPDT

TGA thermogram

가 가

가

17

(NIRS)

4000 4900 cm^{-1} finger print

가 5000 6000 cm^{-1}

7000 cm^{-1}

13,14,20

Figure 4

Table 3

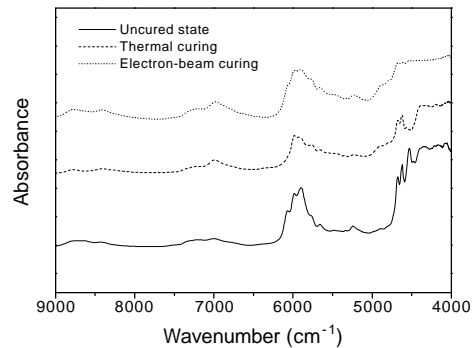


Figure 4. Near - IR spectrum of thermal curing and electron - beam curing.

Table 3. Band Assignment for Chemical Groups from NIR Absorption Spectra of Cure System

wavenumber (cm ⁻¹)	chemical group
7000	-OH overtone and combination bands
6067	first overtone of terminal (methylene) -CH fundamental stretching vibration
5990	phenyl C - H stretching overtone band
5890	aromatic -CH band
5240	CH ₂ , -CH combination band
4682-4619	combination band of the conjugated C=C stretching with the aromatic -CH fundamental stretching
4530	conjugated epoxy CH ₂ deformation band
4530	amine group NH ₂

Figure 4
3
4530 cm⁻¹
가
가
20
가

$$\text{Conversion (a)} = 1 - \frac{A_{\text{cure}}}{A_{\text{uncure}}} \quad (11)$$

Conversion (a) = 1 - $\frac{A_{\text{cure}}}{A_{\text{uncure}}}$
A_{cure}
A_{uncure}
95.5%, 92.2%
가 3% 가

N - benzylquinoxalinium

가
가
21,22

Figure 4 7000 cm⁻¹

가 가
22,23 Figure 4
가
가
가
가
가
Rockwell hardness tester M
scale
104, 97 HRB

가
가
가
가
가
가
SEM
Figure 5
Figure 5 (a)
(b)

24 (c)
(d) 가 가

NIR
가
short chain network가

2. D. Ratna and G. P. Simon, *Polymer*, 42, 7739 (2001).
3. S. J. Park, T. J. Kim, and J. R. Lee, *J. Polym. Sci., Polym. Phys.*, 38, 2114 (2000).
4. S. J. Park, M. K. Seo, J. R. Lee, and D. R. Lee, *J. Polym. Sci., Polym. Chem.*, 39, 187 (2001).
5. H. Wei, Y. Lu., W. Shi, H. Yuan, and Y. Chen, *J. Appl. Polym. Sci.*, 80, 51 (2001).
6. F. Y. C Boey, B. H. Yap, and L. Chia, *Polym. Testing*, 18, 93 (1998).
7. T. Glauser, M. Johansson, and A. Hult, *Macromol. Mater. Eng.*, 274, 20 (2000).
8. J. V. Crivello, T. C. Walton, and R. Malik, *Chem. Mater.*, 9, 1273 (1997).
9. J. V. Crivello, *J. Polym. Sci., Polym. Chem.*, 37, 4241 (1999).
10. T. Toneri, F. Sanda, and T. Endo, *Macromolecules*, 34, 1518 (2001).
11. S. J. Park and H. C. Kim, *J. Polym. Sci., Polym. Phys.*, 39, 121 (2001).
12. P. E. Sundell, "Cationic Polymerization of Vinyl Ethers using Iodonium and Sulfonium Salts", Ph. D. Thesis, p. 1, Royal Institute of Technology, Stockholm, 1990.
13. M. C. Finzel, J. DeLong, and M. C. Hawley, *J. Polym. Sci., Polym. Chem.*, 33, 673 (1995).
14. S. J. Park, G. H. Kwak, S. Masao, and J. R. Lee, *Polym. Eng. Sci.*, 40, 2569 (2000).
15. A. W. Coats and J. W. Redfern, *Polym. Lett.*, 3, 917 (1965).
16. F. Fraga and E. R. Nunez, *J. Appl. Polym. Sci.*, 80, 776 (2001).
17. T. Glauser, M. Johansson, and A. Hult, *Macromol. Mater. Eng.*, 274, 25 (2000).
18. C. D. Doyle, *J. Appl. Polym. Sci.*, 5, 285 (1961).
19. S. J. Park and M. S. Cho, *J. Mater. Sci.*, 35, 3525 (2000).
20. L. Xu and J. R. Schlup, *J. Appl. Polym. Sci.*, 67, 895 (1998).
21. G. H. Kwak, S. J. Park, and J. R. Lee, *J. Polym. Appl. Polym. Sci.*, 78, 290, (2000).
22. G. A. George, P. C. Clarke, N. John, and G. Friend, *J. Appl. Polym. Sci.*, 42, 643 (1991).
23. J. M. Olinger and P. R. Griffiths, *Anal. Chem.*, 60, 2427 (1988).
24. S. Zheng, J. Wang, Q. Guo, J. Wei, and J. Li, *Polymer*, 37, 4667 (1996).
25. R. E. Peterson, "Stress Concentration Factors", Wiley Interscience, New York, 1974.