4관능성 에폭시 수지/불소를 함유한 에폭시 수지 블렌드 시스템의 경화거동 및 파괴인성에 관한 연구

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Studies on Curing Behavior and Fracture Toughness of Tetrafunctional Epoxy Resin/Fluorine-containing Epoxy Resin Blend System

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Key Words: Tetrafunctional epoxy resin, Fluorine, Activation energy, Fracture toughness.

ABSTRACT

In this studies, curing behavior and mechanical properties of tetrafunctional epoxy resin (4EP)/ fluorine-containing epoxy resin (FEP) blend systems was investigated with 4,4'-diaminodiphenol methane (DDM) as a curing agent. The cure activation energies (E_a) were studied by Flynn-Wall-Ozawa's equation with dynamic DSC method. For the fracture toughness of the casting specimens, the critical stress intensity factor (K_{IC}) and the specific fracture energy (G_{IC}) were determined by fracture toughness test.

1. INTRODUCTION

The tetrafunctional epoxy resins (4EP) are widely used as matrix material in advanced polymer composite.[1] However, 4EP have a major drawback of brittleness, which constrains their many end-use applications. Recently, many attempts have been made to improve the toughness of highly crosslinked 4EP. Various types of thermosetting resins have been explored to modify 4EP. Fluorine-containing resins, which have good thermal stabilities, chemical resistance, and mechanical properties, are largely used in adhesives and coatings.[2]

In this study, curing behavior and mechanical properties of 4EP/FEP (fluorine-containing epoxy resin 4,4-diglycidylether benzotrifluoride) blend systems was investigated.

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2. EXPERIMENTAL

2.1 Materials

Tetrafunctional epoxy resin used was LER 430 (E.E.W.=110~130 g/eq), supplied from LG Chemical Co., Korea. 4,4'-diaminodiphenol methane (DDM) was analytically pure grade and was supplied by Aldrich Chemical Co., USA. Fruorine-containing epoxy resins 4,4-diglycidylether benzotrifluoride was prepared by reaction of 4-chlorobenzotrifluoride with glycerol diglycidyl ether in the presence of pyridine catalyst. The structure of resins was confirmed by FT-IR, ^{13}C NMR, and ^{19}F NMR spectroscopy. FT-IR (KBr): ν = 504, 703, 758, 851, 910, 986, 1103, 1256, 1330, 1435, 1458, 1510, 1612, 2877, 2920, 3001, 3058, 3494 cm^{-1}. ^{13}C NMR spectrum (Acetone-d_6): δ = 29.2, 43.3, 50.5, 70.6, 78.4, 127.7, 205.3 ppm. ^{19}F NMR spectrum (Acetone-d_6): δ = -61.95 ppm.

2.2 Measurement

Curing studies were carried out on a differential scanning calorimeter (Perkin Elmer, DSC-6), under a nitrogen flow of 30 ml/min. The critical stress intensity factor (K_{IC}) and the specific fracture energy (G_{IC}) were characterized by a single-edge-notched beam fracture toughness test in three-point bending flexure according to ASTM E 339.

3. RESULTS AND DISCUSSION

3.1 Curing behavior

Figure 1 shows the dynamic DSC thermograms of 4EP/FEP blend systems. The peak exotherm temperature of the blend systems is decreased with increasing FEP contents. The cure activation energies (E_a) are determined by Flynn-Wall-Ozawa's equation (1) with the heating rate and the peak exotherm temperature.[3]

$$\log g(\alpha) = \log(\frac{AE_a}{R}) - \log q - 2.315 - 0.457\frac{E_a}{RT_m} \quad (1)$$

where q is the heating rate, T_m the peak exotherm temperature, $g(\alpha)$ the factor dependent on conversion, and R the gas constant.

The E_a values of the blend systems indicate that show maximum values in the 20~40 wt% FEP content compared with neat 4EP.

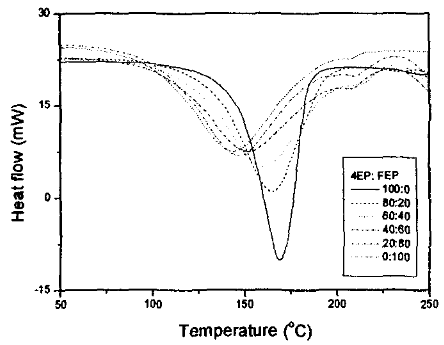

Fig. 1. Dynamic DSC thermograms for 4EP/FEP blend systems

Table 1. Cure activation energies (E_a) for 4EP/FEP blend system

4EP:FEP	100:0	80:20	60:40	40:60	80:20	0:100
E_a	54.7	55.4	56.3	55.5	54.3	53.7

3.2 Mechanical properties

The critical stress intensity factor (K_{IC}) and the specific fracture energy (G_{IC}) were determined using the relationship (2) and (3).[4,5]

$$K_{IC} = \frac{P \cdot L}{b \cdot d^{3/2}} \cdot Y \quad (2)$$

$$G_{IC} = \frac{(1-\nu^2)K_{IC}^2}{E} \quad (3)$$

where P is critical load, L the length of the span, b the specimen width, d the specimen thickness, Y the geometrical factor, E Young's modulus, and ν the Poisson ratio.

Figure 2 shows the results for K_{IC} and G_{IC} of 4EP/FEP blend systems. The K_{IC} and G_{IC} values increases with increasing FEP contents. This is probably due to the introduction of trifluoromethyl (CF_3) group into the side chain of the epoxy resins result in improving fracture toughness of the blend system.[6]

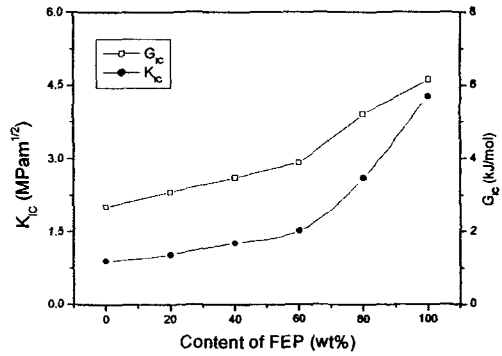

Fig. 2. K_{IC} and G_{IC} of 4EP/FEP blend systems as a function of FEP contents

4. CONCLUSION

The results indicate that the E_a of 4EP/FEP blend systems shows maximum values in the 20~40 wt% FEP content compared with neat 4EP. The K_{IC} and G_{IC} of cured specimen increases with increasing FEP contents.

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