

Epoxidized soybean oil (ESO)의 합성 및 4 관능성 에폭시 수지 /ESO 블렌드 시스템의 물성

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Synthesis of Epoxidized Soybean Oil (ESO) and its Blends with Tetrafunctional Epoxy Resins

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Key Words : soybean oil, TGDDM, epoxidation, critical stress intensity factor, flexural strengths

ABSTRACT

In this work, a potential inexpensive epoxy resin, epoxidized soybean oil (ESO) was synthesized and applied as a toughening agent for 4,4'-tetradiglycidyl diaminodiphenyl methane (TGDDM). The chemical structure of ESO was characterized by FT-IR, ¹H NMR, and ¹³C NMR spectroscopy. The curing behaviors, thermal stabilities, fracture toughness, and flexural strength of TGDDM/ESO blend systems were investigated by using the dynamic DSC, thermogravimetric analysis (TGA), and flexural tests. The thermal stabilities of TGDDM/ESO blend systems were decreased with increasing ESO contents, whereas the critical stress intensity factor (K_{IC}) and flexural strength (σ_f) were increased with ESO contents up to 10 wt% ESO.

1. INTRODUCTION

Soybean oil is readily regenerated via photosynthesis. Although soybean oil is primarily used as an edible oil, there is a continuing demand for its use of industrial application, such as epoxidized soybean oil, soybean oil modified polyesters. Soybean oil can be functionalized via epoxidation with organic peracids or H₂O₂. Epoxidized soybean oil (ESO) is mainly used as plasticizer, stabilizer, reactive modifier, and diluents (1).

The tetrafunctional epoxy resins, 4,4'-tetradiglycidyl diaminodiphenyl methane (TGDDM) with their high performances, including good thermal and mechanical properties are widely used as matrix materials in advanced polymer composites (2). However, TGDDM

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 TGDDM. To modify TGDDM, various types of thermosetting resins have been explored, such as sulfone-containing epoxy, phosphorus-containing epoxy, polyester-containing epoxy (3).

The objective of this work is the synthesis of epoxidized soybean oil (ESO) and characterization. The chemical structure of ESO is characterized by FT-IR, ¹H NMR, and ¹³C NMR spectra. The effect of ESO content on the curing behavior, thermal, and mechanical properties of TGDDM/ESO blend systems has been studied by using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), universal test machine (UTM).

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2. EXPERIMENTAL

2.1 Materials

Soybean oil used in this study was supplied from Wako Chem. of Japan and the fatty acid composition of soybean oil was included in Table 1. Used epoxy resins were 4,4'-tetradiglycidyl diaminodiphenyl methane (TGDDM) supplied by LG Chem. of Korea (LER 430), which had an epoxide equivalent weight of 110-130 g.eq⁻¹. Acetic acid, H₂O₂, Amberlite, toluene, and anhydrous sodium sulfate were purchased by Wako Chem. Curing agent was diaminodiphenyl methane (DDM), was purchased by Aldrich Chem.

Table 1. Fatty acid composition of soybean oil

Fatty acid composition	Weight (%)
Palmitic acid	10-12
Stearic acid	2-5
Oleic acid	20-25
Linoleic acid	50-57
Linolenic acid	5-9

2.2 Synthesis of epoxidized soybean oil

Soybean oil (100 g, 0.49 mol), glacial acetic acid (30 g, 0.5 mol), Amberlite (25 g), and toluene (40 g) were placed in a 500 ml four-neck round flask equipped with mechanical stirrer, thermometer sensor, and reflux condenser. The mixtures were heated and the temperature was maintained at 55 °C. Then 30% H₂O₂ (111.3 g, 1.0 mol) were added slowly through a separatory funnel and reacted at 55 °C for 7 h. After the reaction was completed, the crude product was filtered and washed with distilled water repeatedly until PH was 7.0. The oil phase was dried with anhydrous sodium sulfate and then filtered. Finally, the toluene was removed in a vacuum oven at 80 °C. The yield of the obtained ESO was 90%.

2.3 Sample preparation

The TGDDM and ESO were mixed in an oil bath at 100 °C for 1 h and then the stoichiometric amount of DDM was added to the resins. The mixtures were full stirred by a mechanical stirrer and degassed in a vacuum oven to eliminate air bubbles before measuring. The preparation of the specimens for the mechanical tests was as follows: bubble-free mixtures were poured into the mold and cured at 110 °C for 1 h, at 140 °C for 2 h, and at 170 °C for 1 h in a convection oven.

2.4 Characterization and measurements

IR spectra were recorded with a Bio-Rad Co. digilab FTS-165 spectrometer by using KBr pellets. ¹H NMR and ¹³C NMR spectra were performed on a BRUKER Co.

DRX300 spectrometer operation at 300 MHz in chloroform-d. The molecular weights were obtained by Waters 2690 gel permeation chromatography (GPC) using a column of 2Mixed-B with porosity of 500 Å.

The cure behaviors of the TGDDM/ESO blend systems were studied with a dynamic differential scanning calorimeter (Perkin Elmer, DSC6) under the nitrogen flow of 30 ml/min.

Thermogravimetric analyses were performed with a du Pont TGA-2950 analyzer to investigate the thermal stabilities of the cured TGDDM/ESO blend systems from 30 to 850 °C at a heating rate of 10 °C/min in the nitrogen atmosphere.

The critical stress intensity factor (*K_{IC}*) of the TGDDM/ESO blend systems was characterized by single-edge-notched (SEN) tested in a three-point flexural test, which was conducted by the universal test machine (Instron Model 1125 mechanical tester) according to the ASTM E-399. The flexural properties of the systems were measured by the Instron Model 1125 mechanical tester according to ASTM D-790.

3. RESULTS AND DISCUSSION

3.1 Synthesis of epoxidized soybean oil

The epoxidized soybean oil (ESO) is synthesized by reaction of soybean oil (SO) with glacial acetic acid and hydrogen peroxide using Amberite IR-120 as a catalyst. The obtained ESO is a low viscous liquid. The structure of the synthesized ESO is characterized by FT-IR, ¹H NMR, and ¹³C NMR spectra.

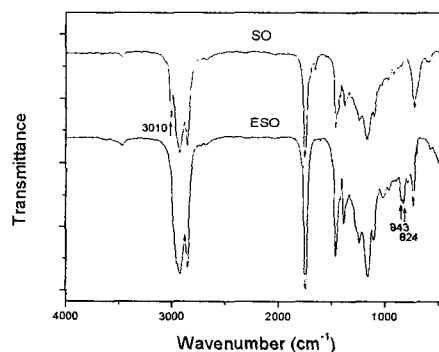


Figure 1. FT-IR spectra of ESO and SO.

Figure 1 shows FT-IR spectra of the SO and ESO, which exhibit the characteristic absorption peaks at 3009 cm⁻¹ due to the double bonds. In the spectrum of ESO, disappearance of the double bonds and formation of characteristic absorption peaks at 822 and 833 cm⁻¹ are

attributed to the epoxy groups (4).

For ^1H NMR spectra (chloroform-d), the chemical shift at 5.3 ppm belongs to the double bonds and the chemical shift at 2.9-3.1 ppm corresponds to the epoxide groups. For ^{13}C NMR spectra (chloroform-d), the chemical shift of the double bonds exhibit at 129.7-130.2 ppm and chemical shift of the epoxide groups appears at 54.0, 54.3 ppm (4). Through the structural characterization of FT-IR, ^1H NMR, and ^{13}C NMR spectra, the chemical structure of ESO is confirmed.

The average molecular weights of ESO are measured by GPC and the M_n , M_w , and M_w/M_n values of ESO are 1469, 1527, and 1.04, respectively.

3.2 Dynamic DSC

TGDDM/ESO blend systems are subjected to dynamic DSC evaluation to investigate their curing behaviors. Figure 2 shows the dynamic DSC curves for TGDDM/ESO blend systems at a heating rate of $10^\circ\text{C}/\text{min}$. The peak maximum temperature of TGDDM/ESO blend systems is shifted to higher temperature with increasing ESO contents. These indicate that the introduction of ESO into the epoxy resins and effect the curing reactions, lead to an increasing of cure temperature.

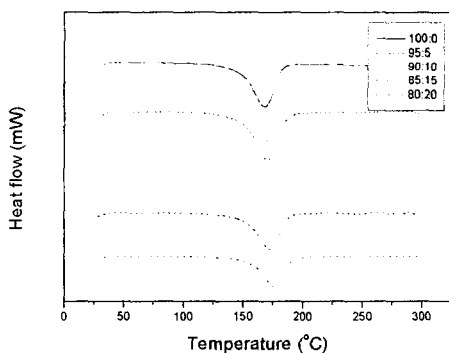


Figure 2. Dynamic DSC thermograms of TGDDM/ESO blend systems.

3.3 Thermal stabilities

The thermal degradation behavior of TGDDM/ESO blend systems is studied with TGA at the heating rate of $10^\circ\text{C}/\text{min}$ in the nitrogen atmosphere and the TGA thermograms are shown in Figure 3. Thermal stability parameters, including initial decomposed temperature (IDT) and temperatures of maximum rate of degradation (T_{max}) of TGDDM/ESO blend systems can be determined from TGA thermograms (5).

The results of the IDT and T_{max} of TGDDM/ESO blend systems are listed in Table 2. As a result, the T_{max}

of TGDDM/ESO blend systems are not varied and IDT of blend systems are decreases with increasing ESO contents. This may be caused by the introduction of linear structure of ESO into the epoxy resins and thus the stable aromatic ring of epoxy resins is decreased, resulting in decreasing the thermal properties of the cured TGDDM/ESO blend systems (6).

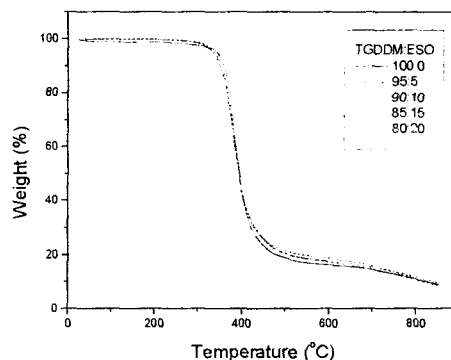


Figure 3. TGA thermograms of TGDDM/ESO blend systems.

Table 2. Thermal Stabilities of Cured TGDDM/ESO Blend Systems

TGDDM: ESO	IDT (°C)	T_{max} (°C)
100:0	343.2	383.5
95:5	337.6	382.4
90:10	336.8	381.6
85:15	333.3	382.4
80:20	333.9	382.2

3.4 Mechanical properties

The mechanical properties of TGDDM/ESO blend systems are determined in terms of the fracture toughness, flexural strength (σ_f), and elastic modulus in flexure (E_b). Fracture toughness of the DDM cured TGDDM/ESO specimens have been measured by three-point bending test for the critical stress intensity factor (K_{IC}) and the values of K_{IC} is calculated by eq [1], as follows (7):

$$K_{\text{IC}} = \frac{P \cdot L}{b \cdot d^{3/2}} \cdot Y \quad [1]$$

where P is the rupture force, L the span between the supports, a the depth of notch, b the specimen width, d the specimen thickness, and Y the geometrical factor.

The result of K_{IC} of blend systems is shown in Figure 4, and the values of K_{IC} of blend systems are increased with increasing of ESO contents and is achieved a maximum value at 10 wt% ESO content. It can be due to the introduction of ESO into the epoxy resins and increase the flexible skeleton of epoxy resins, leads to an

increasing of toughness of blend systems (6).

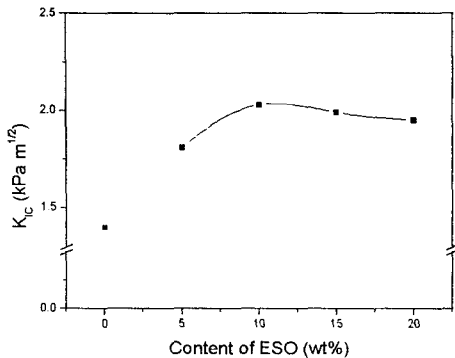


Figure 4. K_{IC} values of TGDDM/ESO blend systems as a function of ESO content.

The σ_f and E_b values of TGDDM/ESO blend systems are determined with the three-point bending test and are calculated as follows (7).

$$\sigma_f = \frac{3PL}{2bd^2} \quad [2]$$

$$E_b = \frac{L^3}{4bd^3} \cdot \frac{\Delta P}{\Delta m} \quad [3]$$

where P is the applied load, L the span length, b the width of specimen, d the thickness of the specimen, ΔP the change in force in the linear portion of the load-deflection curve, and Δm the change in deflection corresponding to ΔP .

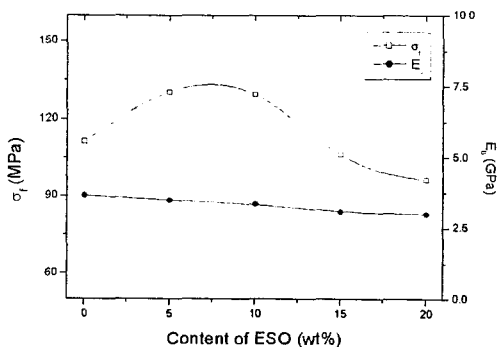


Figure 5. σ_f and E_b values of TGDDM/ESO blend systems as a function of ESO content.

Figure 5 shows the σ_f and E_b as a function of ESO content. The σ_f values of blend systems are increased with ESO up to 10 wt% ESO content. These results probably due to the fact that the introduction of ESO into the epoxy resins and increase the flexibility of epoxy resins, leads to an increasing of flexural strength of blend

systems. Whereas, the E_b values are decreased with increasing ESO contents. These phenomena explain that the introduction of ESO into the epoxy resins leads to a decrease of the rigidity of epoxy resins, resulting in decreasing elastic modulus of blend systems (6).

4. CONCLUSIONS

In this work, the epoxidized soybean oil (ESO) was synthesized and the effect of ESO content on the curing behavior, thermal, and mechanical properties of TGDDM/ESO blend systems has been studied in terms of cure behavior, thermal stability parameters, fracture toughness, flexural strength, and elastic modulus.

As a result, the chemical structure of ESO was confirmed by FT-IR, ^1H NMR, and ^{13}C NMR spectra. From the result of thermal properties, thermal stability of blend systems was decreased with increasing ESO content. The mechanical result exhibit that the K_{IC} and σ_f values were increased with ESO content up to 10 wt% ESO, whereas E_b values were decreased with increasing ESO content.

REFERENCES

- (1) D. L. Kaplan, *Biopolymers from Renewable Resources*, Springer, Berlin Heidelberg, 1998.
- (2) H. Lee and K. Neville, *Handbook of Epoxy Resin*, McGraw-Hill, New York, 1967.
- (3) S. Podzimek, V. Sykora, J. Horalck, and S. Svestka, "Epoxy Resins Based on Bisphenol S. II. HPLC Analysis," *Journal of Applied Polymer Science*, Vol. 58, 1995, pp. 1491-1494.
- (4) S. N. Khot, J. J. Lascala, and E. Can, "Development and Application of Triglyceride-Based Polymers and Composites," *Journal of Applied Polymer Science*, Vol. 82, 2001, pp. 703-723.
- (5) C. D. Doyle, "Estimating Thermal Stability of Experimental Polymers by Empirical Thermogravimetric Analysis," *Analytical Chemistry*, Vol. 33, 1961, pp. 77-79.
- (6) S. J. Park, T. J. Kim, and H. Y. Kim, "Thermal and Mechanical Properties of Diglycidylether of Bisphenol A/trimethylolpropane Triglycidylether Epoxy Blends Cured with Benzylpyrazinium Salts," *Polymer International*, Vol. 51, 2002, pp. 386-392.
- (7) S. J. Park, M. K. Seo, J. R. Lee, and D. R. Lee, "Studies on Epoxy Resins Cured by Cationic Latent Thermal Catalysts: The Effect of the Catalysts on the Thermal, Rheological, and Mechanical Properties," *Journal of Polymer Science Part A: Polymer Chemistry*, Vol. 39, 2001, pp. 187-195.