

Effect of Substituted Trifluoromethyl Groups on Thermal and Mechanical Properties of Fluorine-containing Epoxy Resin

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Abstract: In this study, 2-diglycidylether of benzotrifluoride (2-DGEBTF) and 4-diglycidylether of benzotrifluoride (4-DGEBTF) epoxy resins, which contained fluorine groups in the main chain, were synthesized. The resins were characterized by FTIR, ^1H NMR, ^{13}C NMR and ^{19}F NMR spectroscopy. The 2-DGEBTF and 4-DGEBTF epoxy resins were cured with triethylene tetramine (TETA), and the effect of the fluorine group on the synthesized epoxy resin on the cure behavior, thermal, and mechanical properties was investigated. The 2-DGEBTF/TETA system was more reactive than the 4-DGEBTF/TETA system, whereas the thermal stability factor i.e., the decomposition activation energy (E_d), of 4-DGEBTF/TETA was higher than that of 2-DGEBTF/TETA. These results can be explained by the decrease in cross-linking density and decomposition of the short side chains, resulting in the CF_3 group at the para position. However, the K_{TC} value of 4-DGEBTF/TETA was higher than that of 2-DGEBTF/TETA. This was attributed to the increase in flexibility in the epoxy backbone, resulting in a difference in steric hindrance and polarizability.

Keywords: epoxy resins, contained fluorine groups, short side chains, para position, steric hindrance, polarizability.

Introduction

For the past few decades, epoxy resins as typical thermosetting resins have been widely used as adhesives, high performance coatings, packaging, and lamination materials because these resins have excellent electrical properties, low shrinkage, good adhesion to many metals, and resistance to moisture, thermal and mechanical shock.¹⁻³ However, with the rapid development of advanced electronic material technology, these epoxy resins should have improved their physical, mechanical, thermal, and electronic properties, including 1) good thermal properties, 2) high mechanical properties, 3) low water absorption, and 4) a low dielectric constant. Therefore, much effort, such as the development of a new type of epoxy resins, have been made to satisfy such requirements.^{4,5}

Meanwhile, it is well known that the introduction of fluorinated substituents into a polymer backbone can effectively improve the electrical properties, such as the dielectric constant.⁵ The dielectric constant of polymers can be decreased with the introduction of fluorinated substituents because of the small dipole and the low polarizability of the C-F bond.^{6,7} Also, the positive effect of polymers, which have the fluorinated substituents could reduce the moisture absorption the non-polar character of the fluorocarbon

group.⁸ Therefore, recently, many authors have focused on the investigation of fluorinated epoxy resins because of these effects.^{9,10}

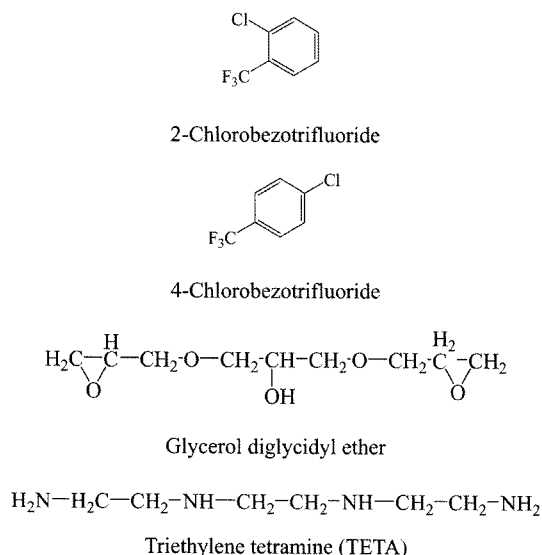
Sasaki *et al.*⁹ reported the properties of cured epoxy containing the perfluorobutenyloxy group. Also, the cure and transition behaviors of partially fluorinated epoxy resins were investigated by Twardowski and Geil.¹⁰ In another report, Zhiqiang *et al.*¹¹ described the thermal and mechanical properties of a novel fluorinated epoxy resin based on bis(4-glycidylesterphenyl)-trifluoromethylphenyl trifluoroethane, which was synthesized in a four-step procedure.

In this work, the novel epoxy resins containing the trifluoromethyl groups were synthesized in a one-step procedure. In addition, the effect of the substituted groups on the curing behavior and the thermal and mechanical properties is discussed as determined by differential scanning calorimetry (DSC) and thermal stability factors of cured specimens are investigated by thermogravimetric analysis (TGA). Also the critical stress intensity factor (K_{IC}) is measured by a universal test machine.

Experimental

Materials. All organic materials used for the synthesis of epoxy resins were purchased from the Aldrich Chem. Co. 2-Chlorobenzotrifluoride, 4-chlorobenzotrifluoride and glycerol diglycidyl ether were used as starting materials. Hydro-

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Figure 1. Chemical structures of the materials.

quinone and pyridine were used as an inhibitor and a catalyst, respectively. Other solvents were used as received and all reagents were used without further purification. Triethylene tetramine (TETA) was used as a curing agent in this study. The chemical structure of materials used for the synthesis was shown in Figure 1.

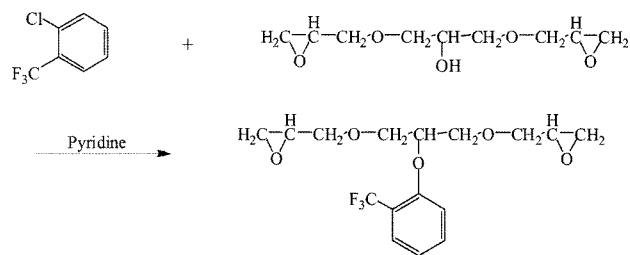
Synthesis and Characterization of Fluorinated Epoxy Resins.

2-Diglycidylether of Benzotrifluoride (2-DGEBTF): The solution of 2-chlorobenzotrifluoride (72.2 g, 0.4 mol), glycerol diglycidyl ether (81.7 g, 0.4 mol), hydroquinone (0.3 g) and pyridine (0.5 g) were placed in a four-neck flask equipped with a mechanical stirrer, thermometer, and reflux condenser. Then the mixture was reacted at room temperature for 24 h. After the reaction was completed, the synthesized resin was dissolved in toluene and collected by filtration. Finally, the 2-DGEBTF was obtained by distillation to remove the unreacted reactant and the toluene. The obtained 2-DGEBTF epoxy resin was a viscous liquid. The chemical structure and reaction mechanism are shown in Scheme I.

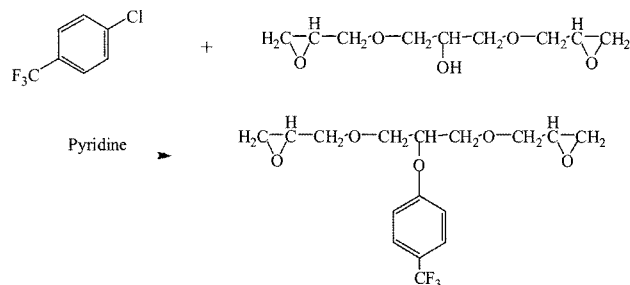
FTIR (KBr, cm^{-1}): $\nu=3074, 1593, 1178, 1105, 910, 835$ cm^{-1} . ^1H NMR (CDCl_3 , δ , ppm): 129.7~130.2, 2.8~3.2. ^{13}C NMR (CDCl_3 , δ , ppm): 134~127.7, 127.5, 70.6, 50.5, 43.3. ^{19}F NMR (CDCl_3 , δ , ppm): -61.95.

4-Diglycidylether of Benzotrifluoride (4-DGEBTF): 4-DGEBTF was prepared from 4-chlorobenzotrifluoride (72.2 g, 0.4 mol), glycerol diglycidyl ether (81.7 g, 0.4 mol), hydroquinone (0.3 g) and pyridine (0.5 g) in a manner similar to the synthesis of the 4-DGEBTF epoxy resin. The obtained 4-DGEBTF epoxy resin was a viscous liquid. The chemical structure and reaction mechanism are shown in Scheme I.

FTIR (KBr, cm^{-1}): $\nu=3057, 1638, 1178, 1105, 910, 831$



Reaction mechanism of 2-DGEBTF epoxy resin



Reaction mechanism of 4-DGEBTF epoxy resin

Scheme I. Reaction mechanism of 2-DGEBTF and 4-DGEBTF epoxy resins.

cm^{-1} . ^1H NMR (CDCl_3 , δ , ppm): 129.7~130.2, 2.8~3.2. ^{13}C NMR (CDCl_3 , δ , ppm): 135~130, 128, 72~70, 51.2, 44. ^{19}F NMR (CDCl_3 , δ , ppm): -62.

Sample Preparation. Triethylene tetramine was added to the synthesized epoxy resin (2-DGEBTF or 4-DGEBTF), and then the mixture was stirred and poured into a silicon rubber spacer mold. The curing steps were 60 °C for 30 min, 90 °C for 2 h, and 120 °C for 2 h in a convection oven.

Thermal Analyses. The curing process was monitored by a differential scanning calorimeter (Perkin-Elmer DSC, model DSC 6) between room temperature and 150 °C using a heating rate of 10 °C/min under a nitrogen atmosphere. The cure behavior properties of the synthesized epoxy resins were evaluated by the measurement of the conversion as a function of the curing temperature with the dynamic DSC method. Thermogravimetric analysis was performed with a thermal analyzer (du Pont TGA 2590) at a heating rate of 10 °C/min from 30 to 850 °C under a nitrogen atmosphere to investigate the thermal stability of the cured specimens.

Fracture Properties. The critical stress intensity factor (K_{IC}) test was carried out using a single-edge notch (SEN) specimen according to the ASTM D5045-95 at room temperature. The specimens were $3 \times 6 \times 30$ mm³ rectangular bars, each of which had a notch of 1.5 mm in depth in the middle, made with a band saw machine. The measurement was conducted on a UTM (Universal Test Machine, Lloyd). The support span was 24 mm and the crosshead speed was fixed to 2 mm/min.

Results and Discussion

Thermal Analyses. Figure 2 shows the DSC thermograms of the 2-DGEBTF and 4-DGEBTF systems cured by TETA. As shown in Figure 2, the DSC thermograms of the 2-DGEBTF/TETA and 4-DGEBTF/TETA systems are very similar and the main exotherm peaks of 2-DGEBTF/TETA and 4-DGEBTF/TETA systems showed maximum exotherm peaks at 81 °C and 84 °C, respectively. The cure properties of the 2-DGEBTF/TETA and 4-DGEBTF/TETA systems are characterized with the measurement of the conversion as a function of the temperature. The conversion is determined on the basis of the DSC thermograms (Figure 2) and the following eq. (1):¹²

$$\text{Conversion}(\alpha_t) = \frac{\Delta H_t}{\Delta H_{Total}} \times 100 \quad (1)$$

where α_t is the conversion at time (t), ΔH_t is the accumulated heat released before time t , ΔH_{Total} and is the total heat released at the end of the reaction.

Figure 3 shows the conversion as a function of the curing temperature for the 2-DGEBTF/TETA and 4-DGEBTF/TETA systems obtained from the DSC thermograms. As shown Figure 3, it is clear that the 2-DGEBTF/TETA system is more reactive than the 4-DGEBTF/TETA system. This result explains why the CF_3 group of para position into the epoxy backbone increases the steric hindrance, resulting in a decrease in the reactivity of oxirane and TETA in the 4-DGEBTF/TETA system.^{10,13}

In this study, TGA thermograms are used for thermal information regarding the thermal stability and thermal degradation behavior of the 2-DGEBTF/TETA and 4-DGEBTF/TETA systems. Figure 4 shows the thermal degradation (under a nitrogen atmosphere) curves of the 2-DGEBTF/TETA and 4-DGEBTF/TETA systems and the thermal stability factors, i.e., initial decomposition temperature (IDT, weight loss 5%) and temperature of the maximum rate of weight loss (T_{max})

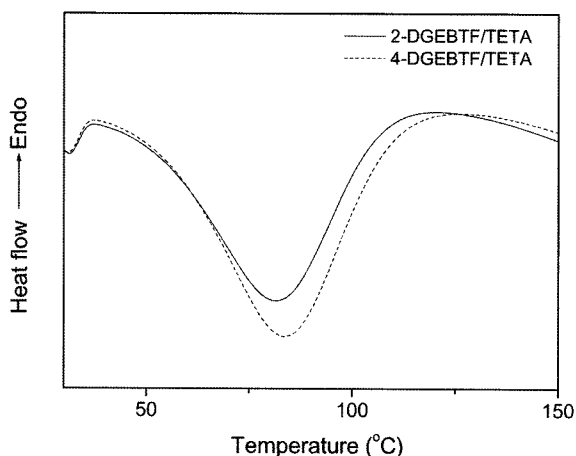


Figure 2. Dynamic DSC thermograms of the 2-DGEBTF/TETA and 4-DGEBTF/TETA systems.

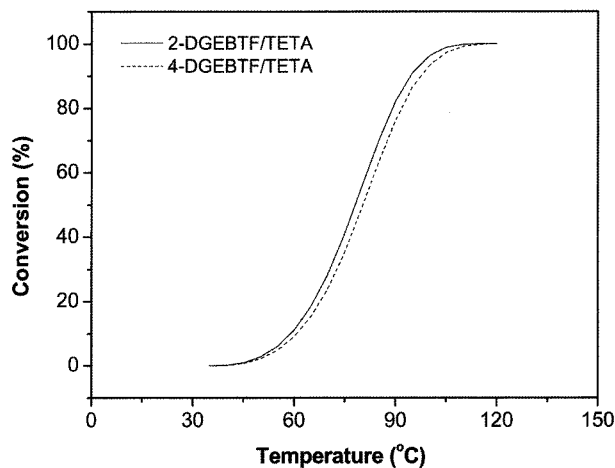


Figure 3. Conversion curves of the 2-DGEBTF/TETA and 4-DGEBTF/TETA systems.

of the 2-DGEBTF/TETA and 4-DGEBTF/TETA systems are summarized in Table I.¹⁴ As shown in the TGA curves, it is confirmed that the IDT of the 4-DGEBTF/TETA systems are lower than that of the 2-DGEBTF/TETA systems.

As a thermal stability factor, the decomposition activation energy (E_d) is used for detailed information of thermal stability. Therefore, in this study, the Coats-Redfern equation derived from the integral method is used to determine the decomposition activation energy (E_d) as follows:^{15,16}

$$\ln[\ln(1-\alpha)^{-1}] = \frac{E_d \theta}{RT_s^2} \quad (2)$$

where $\theta = T - T_s$, and T_s is defined as both a parameter and a characteristic temperature, respectively. T_s is the temperature at which $(1-\alpha)$.

The decomposition activation energies (E_d) are determined from the slope of the $\ln[\ln(1-\alpha)^{-1}]$ vs. θ plots and are indicated in Table I. As shown Table I, the E_d of the 4-DGEBTF/TETA systems is higher than that of the 2-DGEBTF/TETA

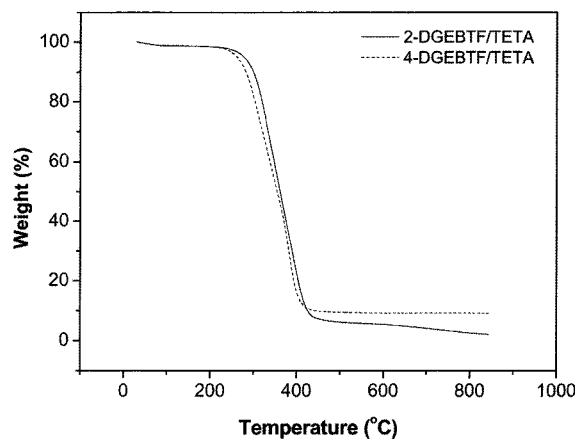
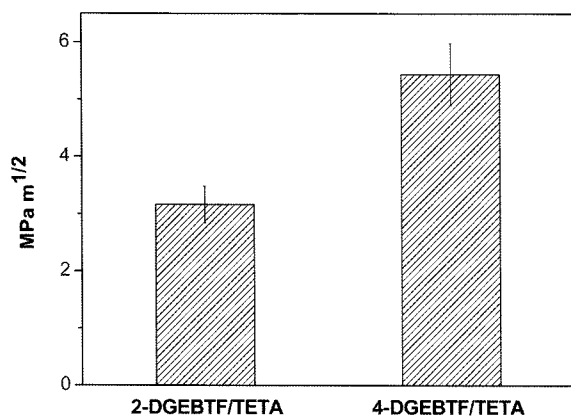


Figure 4. TGA thermograms of the 2-DGEBTF/TETA and 4-DGEBTF/TETA systems.

Table I. Thermal Stability Factors of 2-DGEBTF/TETA and 4-DGEBTF/TETA Systems

System	IDT (°C)	T_{max} (°C)	E_a (kJ/mol)
2-DGEBTF/TETA	277	381	58.8
4-DGEBTF/TETA	265	382	60.0

**Figure 5.** K_{IC} values of the 2-DGEBTF/TETA and 4-DGEBTF/TETA systems.

systems. This is probably due to the fact that the cross-linking density is decreased by the steric hindrance of the CF_3 group of para position.^{13,17} Therefore, during the TGA at high temperature, the short side chains are easily decomposed. However, after the short side chains are decomposed, the decomposition behavior of the 4-DGEBTF/TETA systems is very similar to that of 2-DGEBTF/TETA systems while the residue of 4-DGEBTF/TETA is higher than that of 2-DGEBTF/TETA. These results can be confirmed by the similar value of T_{max} from TGA thermograms.

Mechanical Interfacial Properties. The critical stress intensity factor (K_{IC}) is used to evaluate the fracture toughness of the 2-DGEBTF/TETA and 4-DGEBTF/TETA. The K_{IC} value is calculated as follows:^{18,19}

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

where P is the rupture force, L is the span between the supports, b and d are the specimen width and thickness, respectively, and Y is the geometric factor.

The K_{IC} results are shown in Figure 5. As shown Figure 5, the fracture toughness of the 4-DGEBTF/TETA is significantly higher than that of the 2-DGEBTF/TETA. The higher fracture toughness of 4-DGEBTF/TETA is probably due to the fact that the CF_3 group of para position compared with that of ortho position into the epoxy backbone increases the flexibility of intermolecular interaction.^{13,17,20}

Conclusions

In this study, the 2-DGEBTF/TETA and 4-DGEBTF/TETA

were synthesized and cured with TETA. The effect of the substituted groups on the curing behavior and thermal and mechanical properties was investigated and compared.

The characterization of synthesized 2-DGEBTF/TETA and 4-DGEBTF/TETA was confirmed by FTIR, 1H NMR, ^{13}C NMR, and ^{19}F NMR. The 2-DGEBTF/TETA was more reactive than the 4-DGEBTF/TETA system, and the thermal stability of the 2-DGEBTF/TETA system was higher than that of the 4-DGEBTF/TETA systems. This was probably due to the fact that the cross-linking density is decreased by the steric hindrance of the CF_3 group of para position. However, the K_{IC} value of the 4-DGEBTF/TETA was higher than that of the 2-DGEBTF/TETA. This was due to the increase of flexibility in the epoxy backbone, resulting in the difference of the steric hindrance and polarizability. The CF_3 group of para position compared with that of ortho position made the thermal stability rather poor while the CF_3 group of para position caused an increase in the mechanical properties.

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