Substitution Effects of Methyl and Trifluoromethyl Groups on the Physicochemical Properties of Epoxy Resins

Jae-Rock Lee, Fan-Long Jin, Soo-Jin Park

Advanced Materials Division, Korea Research Institute of Chemical Technology, Yusong, Daejeon 305-600, Korea

ABSTRACT: We studied the effects of functional groups on the physicochemical properties, such as rheological behavior, thermal stability, glass-transition temperature, and electrical and mechanical properties, of 4,4'-diaminodiphenyl methane (DDM) cured methyl-substituted and trifluoromethyl-substituted difunctional epoxy resins [i.e., 2-diglycidylether of toluene (DGET) and 2-diglycidylether of benzotrifluoride (DGEBTF)]. The DGEBTF/DDM system showed higher thermal stability and lower dielectric constant values than the DGET/DDM system. The impact strength of the DGEBTF/DDM system was significantly higher than that of the DGET/DDM system. The increase in intermolecular interactions because of the increasing polarity of the fluorine in the epoxy backbone was probably the key to these results. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1860–1864, 2005

Key words: curing of polymers; dielectric properties; fluoropolymers; mechanical properties; thermosets

INTRODUCTION

Epoxy resins, which are widely used in matrices, coatings, structural adhesives, and microelectronics, have good heat resistance, a high modulus, and high electrical resistance.[1] Among epoxy resins, fluorine-containing epoxy resins are especially important in optical communication and microelectronics due to the unique characteristics, such as high chemical resistance and water impermeability and a low coefficient of friction, refractive index, and dielectric constant, given to them by the presence of fluorine.[2–4]

Some fluorine-containing epoxy resins have been synthesized, and their physicochemical properties have been studied by several researchers. Griffith[5] and Lee et al.[6] presented the synthesis of trifluoromethyl (CF₃) group containing epoxy resins and a highly fluorinated epoxy resin. Maruno and Nakamura[7] reported the synthesis of fluorinated epoxy acrylate resins and applications for them as adhesives for optical communications devices. Recently, Sangermano et al.[8] used fluorinated epoxides as surface-modifying agents in ultraviolet-curable systems. Dammont and Kwei[9] and Twardowski and Geil[10] studied the dynamic mechanical properties of partially fluorinated epoxy resins and the behaviors of difunctional epoxy resin/highly fluorinated epoxy resin blends.

It is of interest to investigate the physicochemical properties of epoxy resins containing CF₃ groups and to compare them with their hydrocarbon analogues because the bulky substituents in the polymers would affect the properties of the polymers.[11] In this study, the effects of methyl and CF₃ functional groups on the resins' final properties, such as rheological, thermal, electrical, and mechanical properties, were investigated with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), dielectric spectrometer, Izod impact testing, and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The epoxy resins used in this study, 2-diglycidylether of toluene (DGET) and 2-diglycidylether of benzotrifluoride (DGEBTF), were examined and selected by a recent study.[4] 4,4'-diaminodiphenyl methane (DDM), purchased from Aldrich Chemical Co. (St. Louis, MO), was selected as a curing agent. The chemical structures of the materials are shown in Figure 1.

Synthesis of the epoxy resins

DGET and DGEBTF epoxy resins were prepared as follows. To synthesize DGET epoxy resin, we placed a solution of 2-chlorobenzotrifluoride (19 g, 0.15 mol), glycerol diglycidylether (30.6 g, 0.15 mol), hydroquinone (0.12 g), and pyridine (0.28) in a round, four-necked, 500-mL flask equipped with a mechanical stir-

2-Diglycidylether of toluene (DGET)

2-Diglycidylether of benzotrifluoride (DGEBTF)
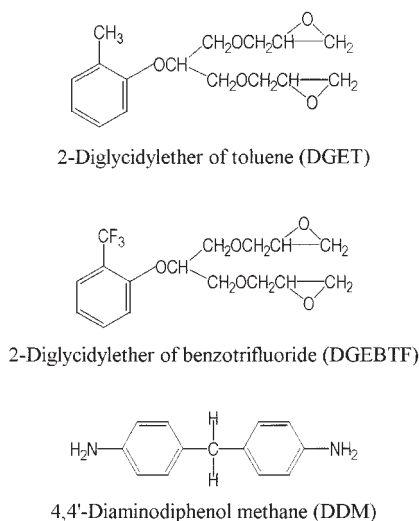
4,4'-Diaminodiphenol methane (DDM)

Figure 1 Chemical structures of the materials.

rer, a thermometer, and a reflux condenser. The mixture was reacted at 30°C for 24 h. After the completion of the reaction, the crude product was dissolved in toluene and filtered; then, toluene and the unreacted reactant were distilled off at 100°C with a low pressure of 100 mmHg. Finally, the product was dried in a vacuum oven at 100°C for 8 h. The obtained DGET epoxy resin was a viscous liquid, and the yield was 81%. The characterization data are shown next. The epoxy-equivalent weight of the epoxy resin was 207 g/equiv:

Fourier transform infrared (FTIR) spectroscopy (KBr, cm^{-1}): 1105 (CF$_3$ group); 910, 835 (epoxide group); 3074, 1593, 1178 (aromatic ring). ^{1}H-NMR (300 MHz, chloroform-d, ppm, δ): 129.7–130.2 (aromatic ring), 2.8–3.2 (epoxide group). ^{13}C-NMR (300 MHz, chloroform-d, ppm, δ): 133.9–126.3 (aromatic ring); 70.8, 50.6, 43.8 (epoxide group).

DGEBTF epoxy resin was prepared from 2-chlorobenzotrifluoride (18.1 g, 0.10 mol), glycerol diglycidylether (20.4 g, 0.10 mol), hydroquinone (0.08 g), and pyridine (0.19) in a manner similar to the synthesis of the DGET epoxy resin. The obtained DGEBTF epoxy resin was a viscous liquid, and the yield was 84%. The characterization data are shown next. The epoxy-equivalent weight of the epoxy resin was 197 g/equiv:

FTIR (KBr, cm^{-1}): 1105 (CF$_3$ group); 910, 835 (epoxide group); 3074, 1593, 1178 (aromatic ring). ^{1}H-NMR (300 MHz, chloroform-d, ppm, δ): 129.7–130.2 (aromatic ring), 2.8–3.2 (epoxide group). ^{13}C-NMR (300 MHz, chloroform-d, ppm, δ): 134–127.7 (aromatic ring), 127.5 (CF$_3$ group); 70.6, 50.5, 43.3 (epoxide group). ^{19}F-NMR (300 MHz, chloroform-d, ppm, δ): −61.95 ppm (CF$_3$ group).

Sample preparation

The epoxy resin was heated in an oil bath at 100°C for 30 min, and then, DDM was added to the resin. The

resin and the curing agent were completely mixed with a mechanical stirrer and degassed in a vacuum oven. The bubble-free mixture was poured into a stainless mold, cured at 110°C for 1 h and at 140°C for 2 h, and postcured at 170°C for 1 h in a convection oven.

Characterization and measurements

IR spectra were obtained with a Bio-Rad Co. digilab FTS-165 spectrometer (Hercules, CA) with KBr pellets. ^{1}H-NMR, ^{13}C-NMR, and ^{19}F-NMR spectra were characterized on a Bruker Co. DRX300 spectrometer

(a)

(b)

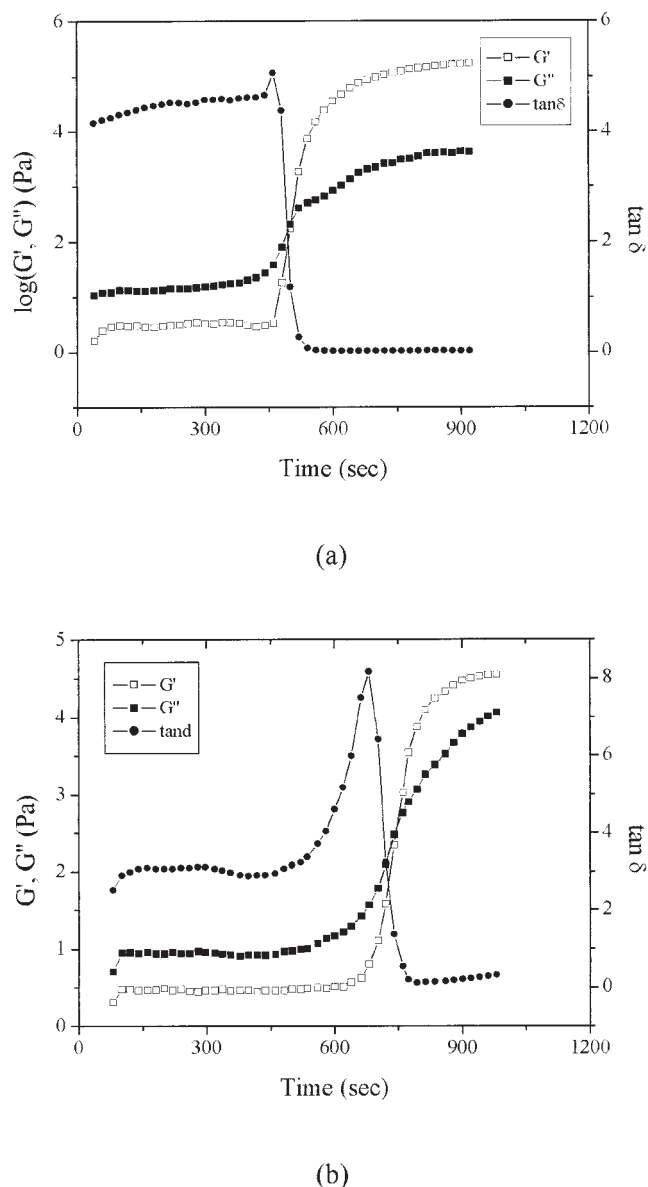**Figure 2** Plots of G′, G″, and tan δ vs. time of the DGET/DDM and DGEBTF/DDM systems (heating rate = 10=°C/min).

TABLE I
t_c and E_c Values of the Epoxy Resin–Amine Mixtures
Obtained from the Rheometer

System	Reaction temperature (°C)	t_c (s)	E_c (kJ/mol)
DGET/DDM	100	1032	39
	110	699	
	120	504	
	130	394	
DGEBTF/DDM	100	1546	42
	110	826	
	120	749	
	130	529	

TABLE II
Thermal Stability Factors of the DGET/DDM
and DGEBTF/DDM Systems Obtained
from TGA Thermograms

System	IDT (°C)	T_{max} (°C)	Char at 800 °C (wt %)
DGET/DDM	105	407	11.6
DGEBTF/DDM	296	424	15.5

RESULTS AND DISCUSSION

Rheological properties

The storage modulus (G'), loss modulus (G''), and tan δ can provide information concerning gelations. G'

(Rheinstetten, Germany) operating at 300 MHz with chloroform-d as the solvent.

The cure behaviors were measured with a differential scanning calorimeter (PerkinElmer DSC6, Boston, MA) under a nitrogen flow of 30 mL/min.

The temperature dependence of the loss factor (tan δ) for the systems was surveyed with a dynamic mechanical analyzer (RDS-II, Rheometries Co., Leatherhead, UK) at a frequency of 1 Hz in the temperature range 35–200°C at a heating rate of 5°C/min.

The dielectric constants of the systems were measured over a frequency range of 1–10 GHz at room temperature with a dielectric spectrometer (Novo Control GmbH, model CONCEPT 40, Hundsangen, Germany).

The impact strengths of the systems were tested with an Izod impact tester (Tinius Olsen, Horsham, PA). The specimen size was $5 \times 12.7 \times 63.5$ mm^3. We calculated the mechanical property values by averaging the five experimental values. The fractured surfaces were examined by SEM.
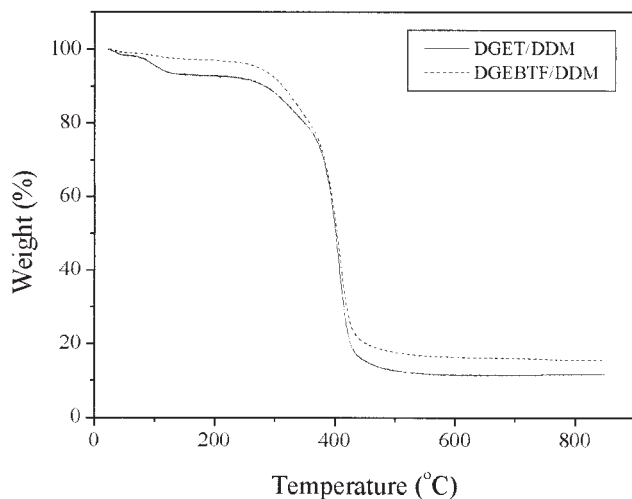

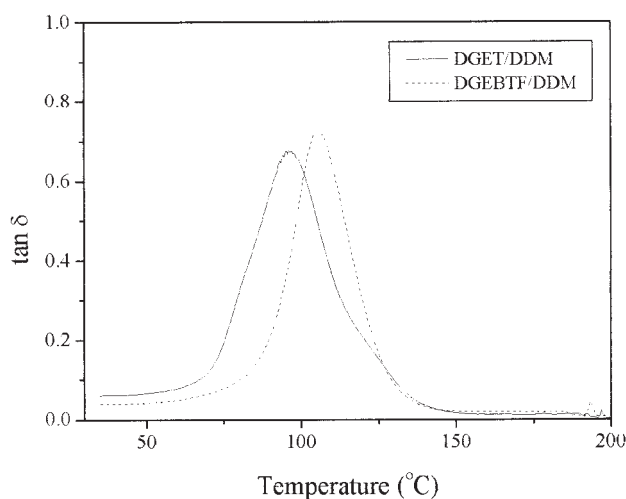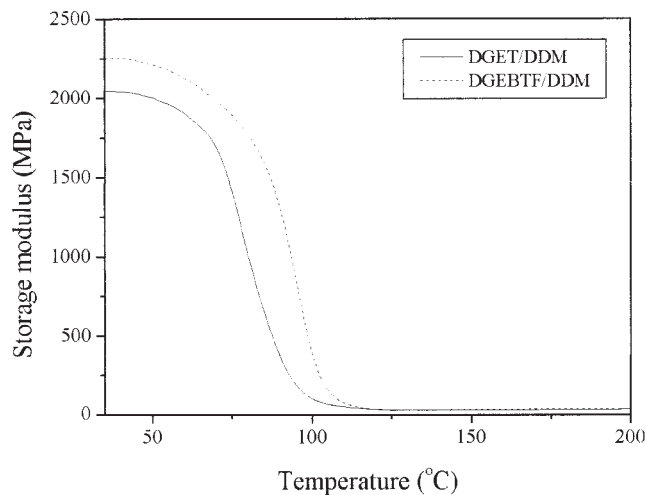**Figure 3** TGA thermograms of the DGET/DDM and DGEBTF/DDM systems.

(a)

(b)

Figure 4 (a) Tan δ and (b) G' of the DGET/DDM and DGEBTF/DDM systems as a function of temperature.

TABLE III
DMA of the Cured DGET/DDM and DGEBTF/DDM Systems

System	T_g (°C)	G' (MPa) Glassy region[a]	G' (MPa) Rubbery region[b]
DGET/DDM	96	2045	28.8
DGEBTF/DDM	105	2249	29.3

[a] G' at 35°C.
[b] G' at $T_g + 30$°C.

indicates the elastic character of the materials, and G'' is related to the viscous response of the materials. A crosslinking polymer, such as epoxy at its gel point, is in a transition state between a liquid and a solid.[12] The gel time (t_c) was determined according to the time at the intersection of G' and G'', that is, tan $\delta = 1$.

Figure 2 shows G', G'', and tan δ of the DGET/DDM and DGEBTF/DDM systems as a function of the reaction time at 120°C. The two moduli increased sharply at t_c and then gradually level off as the cure approached completion. Table I shows t_c as function of the reaction temperature. t_c decreased with increasing curing temperature, which due to the high temperature led to increasing molecular mobility. t_c of the DGEBTF/DDM system was higher than that of the DGET/DDM system under the same conditions. This may have been caused by the high nucleophilic ability of the CF$_3$ group, which was introduced into the chain of the epoxy resin and may have resulted in an increase in t_c.[11]

The crosslinking activation energy (E_c) of the DGET/DDM and DGEBTF/DDM systems was determined by t_c and the reaction temperature according to eq. (1):[13]

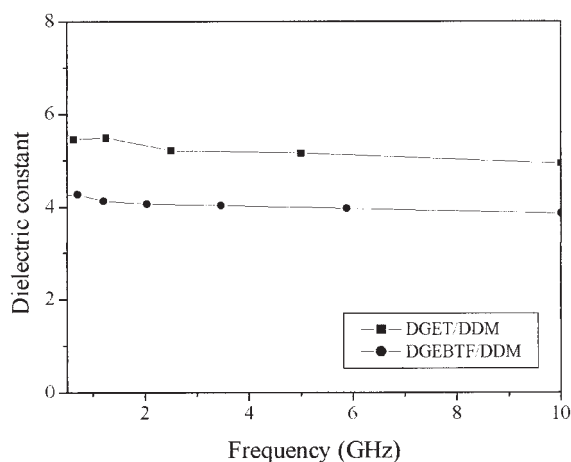$$\ln t_c = \frac{E_c}{RT} + C \tag{1}$$

Figure 5 Dielectric constant of the DGET/DDM and DGEBTF/DDM systems as a function of frequency.

TABLE IV
Impact Strengths of the Cured DGET/DDM and DGEBTF/DDM Systems

	System DGET/DDM	System DGEBTF/DDM
Impact strength (kgf cm/cm)	3.42 ± 0.12	5.31 ± 0.21

where R is the gas constant and C is a constant. E_c was calculated from the slope of a plot of ln t_c against $(1/T)$, and the obtained E_c values are listed in Table I. As an experimental result, the DGEBTF/DDM system showed a higher E_c than that of the DGET/DDM system. This was due to the high nucleophilic ability of the CF$_3$ group introduced into the chain of the epoxy resin, which resulted in a delay in the crosslinking reaction, as mentioned previously.[4]

Thermal properties

The thermal stability and the glass-transition temperature (T_g) of the epoxy resins were examined with TGA and DMA. Thermal stability factors, including initial decomposition temperature (*IDT*) and temperature of the maximum rate of degradation (T_{max}), of the DGET/DDM and DGEBTF/DDM systems were determined from TGA thermograms, as shown in Figure 3.[14,15]

As shown in Table II, the obtained *IDT* and T_{max} values of the DGEBTF/DDM system were higher than those of the DGET/DDM system. This was probably due to the fact that the bulky fluorine substituents caused a decrease in the flexibility of the epoxy chain, and the fluorine increased the possibility of the intermolecular reconstruction during the high-temperature application, which prevented the collapse of three-dimensional networks.[16] The weight percentage of char residue in the DGEBTF/DDM system at 800°C was higher than that of the DGET/DDM system.

Figure 4 shows the temperature dependence of tan δ and G' for the cured DGET/DDM and DGEBTF/DDM specimens. The obtained T_g and G' values of the specimens are summarized in Table III. The results indicate that T_g and G' in the glassy region of the DGEBTF/DDM specimens were higher than those of the DGET/DDM specimens. The presence of bulky CF$_3$ groups in the epoxy resins hindered the motion of the segments of the macromolecules, which resulted in an increase in T_g and G'.[17]

Electrical properties

The electrical properties of the DGET/DDM and DGEBTF/DDM systems were determined by the measurement of the dielectric constant. The dielectric constant for the systems was measured at different fre-
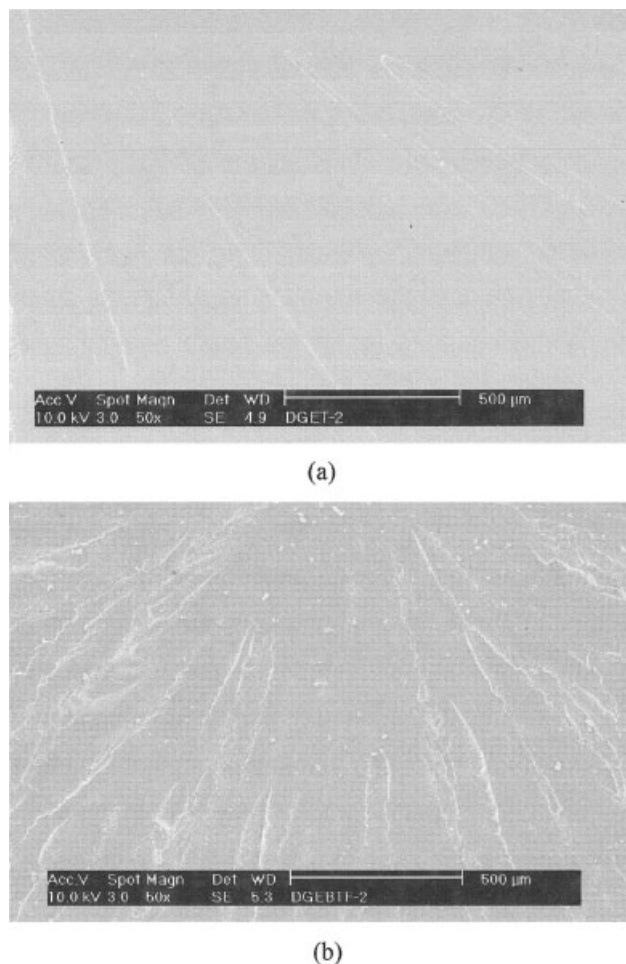
(a)

(b)

Figure 6 SEM results of fracture surface after impact testing: (a) DGET/DDM and (b) DGEBTF/DDM (magnification = 50×).

quencies (1–10 GHz), as shown in Figure 5. The dielectric constant of the DGET/DDM and DGEBTF/DDM systems were 4.9–5.5 and 3.8–4.2, respectively. The lower dielectric constants of the DGEBTF/DDM system were probably due to the small dipole, the low polarizability of the CF bond, and the increase in the free volume that accompanied the replacement of methyl groups by CF_3 groups.[18,19]

Mechanical properties

The mechanical properties of the DGET/DDM and DGEBTF/DDM systems were determined in terms of the impact strength. The impact strength results are presented in Table IV. As shown, the impact strength of the DGEBTF/DDM system was significantly higher than that of the DGET/DDM system. This was caused by an increase in intermolecular interactions due to the increasing polarity of the epoxy backbone in the cured DGEBTF/DDM system.[20]

Figure 6 shows the SEM results of the fractured surfaces after impact testing. The cured DGET/DDM spec-

imen showed a typical brittle fracture surface, whereas the DGEBTF/DDM specimen demonstrated a tough and ductile fracture surface; these results could be correlated to the results of the mechanical values. This signifies that the adoption of fluorine enhanced the stronger three networks due to its strong polarity.

CONCLUSIONS

In this study, the rheological properties, thermal stabilities, and electric and mechanical properties of methyl-substituted and trifluoromethyl-substituted epoxy resins were studied and compared. The cured DGEBTF/DDM specimens showed higher T_g and thermal stability values than the diglycidylether of bisphenol A (DGEBA)/DDM specimens. This could have been due to the motion of the segments of the macromolecules by presence of bulky CF_3 groups in the epoxy backbone. The DGEBTF/DDM system also showed a lower dielectric constant and higher mechanical properties than the DGET/DDM system. This was due to the increase in intermolecular interactions due to the increasing polarity of the epoxy backbone in the cured DGEBTF/DDM system. These results have given us some ideas for the design of new epoxy resin systems for future electronic applications.

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