

# Synthesis and characterization of epoxy film cured with reactive polyimide

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## Abstract

Reactive polyimide containing hydroxyl functionalities was prepared from the reaction of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 3,3'-diamino-4,4'-dihydroxybiphenyl. Commercial epoxy resin was cured in the presence of different ratios of the reactive polyimide, giving a series of polyimide modified epoxy films. The transparent films had excellent solvent resistance. The tensile measurements of the films showed that, with the increase of the polyimide content, tensile modulus of the film increased but there was almost no change in the elongation at break. Viscoelastic measurements showed that glass transition temperature shifted with the increase of the polyimide content; 127°C for 13.5%, 220°C for 29.4%, 260°C for 45.4% and 290°C for 62.5%. Thermogravimetric analysis showed the increase of the thermal stability with the increase of the polyimide content. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Reactive polyimide; Epoxy resin; Network structure

## 1. Introduction

Epoxy resins are a versatile group of crosslinked polymers that have excellent chemical resistance, good electrical insulating properties, good adhesion to glass and metals, and can be easily fabricated. The variety of properties help the epoxy resins to meet the performance requirements of some demanding applications. These include areas as diverse as construction, electronics, adhesives, and coatings [1]. The usefulness of epoxy resins for many applications is often limited due to their inherent brittleness arising from their crosslinked structure. Development of approaches for toughening the epoxy resins without sacrificing modulus and glass transition temperature ( $T_g$ ) would lead to an increase in their applications [2,3].

The most studied approach to toughen epoxy resin was the use of organic rubbers as toughening additives [4–9]. While rubbers can be extremely effective as toughening agents, epoxy resins suffer from some drawbacks such as a reduction in overall resin modulus and in end use temperatures. A method which has found increasingly widespread use is the incorporation of the thermoplastic toughening

agents for epoxy resins such as poly(ethersulfone) [10–12], poly(phenylenether) [13], poly(etherketone) [14], polyester [15], and poly(etherimide) [16,17].

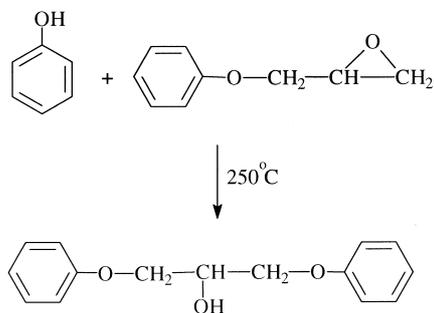
Polyimides are widely used for applications that require high degree of thermal stability, excellent mechanical properties and chemical resistance [18,19]. There are many studies which have used polyimides in epoxy systems intending mainly to improve the thermal stability and toughness. Almost all of the studies are based on physical blending of unreactive linear polyimides. Hay et al. [20] studied the molding of linear unreactive polyimide for toughening of the epoxy-resin–diaminodiphenyl-sulfone system [20]. They achieved increase in the fracture toughness with no loss of modulus but there was a little influence on the thermal capability across the range of modifying polyimides. They also used polyimide end capped with amine with the intention of facilitating the reaction with epoxy and obtained increase in toughness. Another example is the incorporation of polyimide-siloxane in epoxy to form protective coatings with high heat and chemical resistance [21].

Recently, Kakimoto et al. [22,23] developed a novel epoxy system cured with poly(amide acid) followed by thermal imidization. They used the polyimide precursor as a hardener instead of traditional hardeners to improve the thermal stability and adhesion strength. The curing reaction of the novel system, however, is very complicated. In this study, we made another novel approach to prepare

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Scheme 1. Model reaction.

polyimide–epoxy (PI–EP) composites of high thermal stability and good mechanical properties. We used soluble reactive polyimide containing hydroxyl functionalities as a hardener. This novel method of using reactive polyimide has the advantage that the shrinkage during cure encountered with using poly(amide acid) is avoided. The presence of polyimide is capable of exhibiting flexibility characteristics and noticeable thermal stability as well as being curing agents on their own.

## 2. Experimental

### 2.1. Reagents

2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was purified first by recrystallization from acetic acid and acetic anhydride (7.5:1), and then by sublimation. 3,3'-Diamino-4,4'-dihydroxybiphenyl (AHBP) (obtained from Tokyo Kasei Organic Chemicals) was used as supplied without further purification. *N*-methyl-2-pyrrolidinone (NMP) was purified by distillation over calcium hydride just before using. Phenol and glycidyl phenyl ether were used as supplied. Epoxy resin D.E.R.331 J (epoxy equivalent weight equals 186–190) based on diglycidyl ether of bisphenol A (DGEBA) was kindly supplied by Dow Chemical Japan Ltd. The molecular weight of the epoxy calculated from the formula is 340.4, and the average molecular weight calculated from the epoxy equivalent weight is 376. We used the latter value for the formulation.

### 2.2. Synthesis of polyimide

Into a 50 ml flask equipped with a nitrogen inlet and a mechanical stirrer, AHBP (3.00 mmol, 0.649 g) and NMP (25 g) were placed. The mixture was stirred for 3 h until a clear solution was obtained. Equimolar amount of solid 6FDA (3.00 mmol, 1.333 g) was added in one batch to the solution of AHBP and the walls of the flask washed with 3 g of NMP. The reaction mixture was stirred for 14 h at room temperature. Then the obtained brown viscous solution was precipitated in water (500 ml), filtered, washed with water, and dried under vacuum at 50°C for 16 h. The overall yield of poly(amide acid) was 1.82 g (91.8%). The reduced

viscosity of the poly(amide acid) was 0.57–0.60 dl g<sup>-1</sup> (0.5 g dl<sup>-1</sup> in NMP at 30°C).

Poly(amide acid) powder was heated in vacuo at 150°C for 1 h and 200°C for 2 h to convert it into polyimide. The polyimide is soluble in common organic solvents such as NMP, dimethylacetamide (DMAc), dimethylsulfoxide (DMSO) and tetrahydrofuran (THF). IR (KBr, cm<sup>-1</sup>): 1780 and 1720 (C=O); 1370 (C–N); 3400 (OH).

### 2.3. Synthesis of 1,3-diphenoxy-2-propanol as a model reaction

Reaction between phenol and glycidyl phenyl ether was carried out, as shown in Scheme 1, as a model reaction between the epoxy group and the phenolic compound. Into a 50 ml flask, phenol (25.00 mmol, 2.353 g) and glycidyl phenyl ether (25.00 mmol, 3.755 g) were charged and the mixture was heated at 250°C. The progress of the reaction was monitored by TLC which showed that the time for the completion of the reaction was almost 2 h at 250°C. The reaction mixture was cooled to give a pale brown solid which was purified by sublimation to give white crystals with m.p. 77–79°C. The overall yield was 5.80 g (24 mmol, 95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 2.6 (d, 1H, OH), 4.2 (d, 4H, CH<sub>2</sub>), 4.4 (m, 1H, CH), and 6.9–7.2 (m, 10H, Ar) (in ppm).

### 2.4. Formulation of epoxy resin with polyimide

The epoxy resin and the polyimide were mixed together in various weight ratios into NMP. The mixture was stirred at room temperature for 2–5 h until a clear homogeneous 10 wt.% solution was obtained. The solution was cast on a glass substrate followed by drying at 50°C for 16 h. The cast film was then thermally cured, as fixed on a glass plate, at 100°C for 1 h, 200°C for 1 h and then at 250°C for 3 h. The films were peeled off from the glass substrate by immersing in boiling water.

### 2.5. Measurements

Viscosity of poly(amide acid) was measured by using an Ubbelohde viscometer. IR spectra were obtained with a JASCO spectrophotometer model FT/IR-420. <sup>1</sup>H NMR spectra were obtained using a JEOL spectrophotometer model JNM-5X270. Differential scanning calorimetry was recorded using Rigaku Thermo Plus 2 DSC8230 at a heating rate of 10°C min<sup>-1</sup> under nitrogen. Thermogravimetric analysis (TGA) was determined with Rigaku Thermo Plus 2 TG-DTA TG8120 at a heating rate of 10°C min<sup>-1</sup> under argon. Dynamic viscoelastic measurements were conducted on a ORIENTEC Automatic Dynamic Viscoelastomer Rheovibron model DDV-01FP at 35 Hz at a heating rate of 4°C min<sup>-1</sup>. Tensile properties were recorded with an Imada Seisaku-sho Model SV-3 at a crosshead speed of 1 mm min<sup>-1</sup> using films that were 2 cm long. The tensile

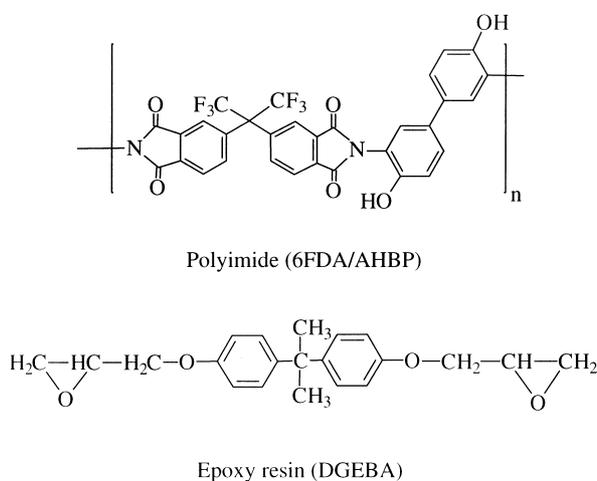


Fig. 1. Structure of polyimide and epoxy resin.

properties of each sample were determined from an average of at least five tests.

### 3. Results and discussion

#### 3.1. Preparation of polyimide–epoxy films

To prepare a series of PI–EP composites, we attempted a novel method which is based on a reaction between an epoxy resin and a soluble polyimide containing hydroxyl functionalities. As an epoxy resin can react for curing with hydroxyl compounds, the epoxide groups are considered to react with hydroxyl functionality on the polyimide. Thus, we prepared a soluble polyimide that contains phenolic hydroxyl functionalities from 6FDA and AHBP (Fig. 1). Standard epoxy resin (DGEBA) was blended with the soluble polyimide in various ratios using NMP as shown in Table 1. All the blend solutions were clear and transparent in any weight ratio. The cast films were still transparent after drying at 50°C for 16 h with pale yellow color.

According to the model reaction using phenol and phenyl glycidyl ether, the reaction between the phenolic OH and oxirane groups was almost completed after 2 h at 250°C. Thus, the PI–EP films were heat treated for curing at 100°C, 150°C, and 200°C for 1 h each and then at 250°C for 3 h. The films became reddish brown but were still transparent. Fig. 2 shows the IR spectra of PI and PI–EP

(45/55) films which were obtained after each stage of the cure cycle employed for the preparation of the film. The absorption at 915  $\text{cm}^{-1}$  is attributable to the stretching absorption of C–O in the epoxide ring. This absorption clearly decreased at each stage of cure and almost disappeared by the 200°C cure. Presence of an absorption of PI in the same region made it difficult to assume if the absorption of epoxy completely disappeared or not. However, the IR spectra suggest the formation of network structure through the reaction of epoxy with polyimide. The reaction between phenolic hydroxyl groups on the polyimide and epoxide group results in the formation of secondary hydroxyl group which further reacts with epoxide groups, as shown in Scheme 2 [24,25].

#### 3.2. Curing of polyimide–epoxy system studied by differential scanning calorimetry

Differential scanning calorimetry (DSC) was measured to monitor the curing of the PI–EP composite. Fig. 3 represents the thermogram of the PI–EP (63/37) film. In case of the film cured at 100°C for 1 h, a broad exotherm appeared starting at 105°C and reaching a maximum at 166°C. This exotherm representing the curing of epoxy almost disappeared for the film cured at 200°C for 1 h. These DSC behaviors confirmed that curing of epoxy and formation of network structure between epoxy and polyimide occurred by the 200°C cure.

All the other PI–EP films showed similar exothermic behavior and the results are summarized in Table 2. The onset of the curing was in the range 105–119°C. The onset of curing exotherm started at lower temperature with higher polyimide content owing to the increase of the hydroxyl groups for reaction with epoxy. The exotherm maximum, however, appeared at a similar temperature range. The amount of exotherm was in the range of 19.1–4.5  $\text{cal g}^{-1}$ . As can be seen in Table 2, the amount of exotherm depended almost solely on the amount of OH functionality in the polyimide and did not depend on the amount of epoxy functionality.

#### 3.3. Tensile properties of polyimide–epoxy films

Tensile properties of the films were examined and the results are summarized in Table 3. The tensile modulus of typical amine-cured epoxy systems is ca. 1 GPa [26–28]. As

Table 1  
Formulations of polyimide and epoxy resin

Code <sup>a</sup>	Polyimide (g (mmol)) <sup>b</sup>	Epoxy (g (mmol))	Polyimide (wt.%)
PI–EP (63/37)	0.6000 (0.9608)	0.3606 (0.9590)	62.5
PI–EP (45/55)	0.3000 (0.4804)	0.3606 (0.9590)	45.4
PI–EP (29/71)	0.3000 (0.4804)	0.7212 (1.9181)	29.4
PI–EP (13/87)	0.1500 (0.2402)	1.0000 (2.6596)	13.0

<sup>a</sup> PI–EP: polyimide–epoxy.

<sup>b</sup> In mmol for the repeat unit.

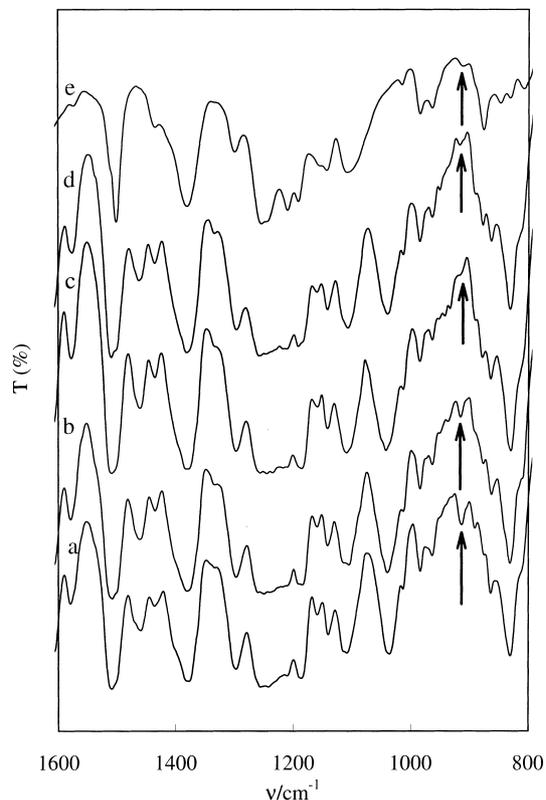


Fig. 2. IR-spectra of the curing profile of polyimide-epoxy (PI-EP (45/55)): (a) cured at 100°C, (b) at 150°C, (c) at 200°C, (d) at 250°C, and (e) polyimide as a reference.

we can see from Fig. 4, the tensile modulus of epoxy increases with increase of the imide content. The increase is owing to the higher modulus of polyimide (3.89 GPa) than that of the epoxy. Incorporation of only 13% of polyimide increased the value of the modulus to 2.41 GPa which is more than twice that of the typical amine-cured systems. As shown in Table 3, the tensile strength and elongation at break were not changed significantly which reflects their independence on the PI-EP ratio on the film within the ratios used in this study.

### 3.4. Viscoelastic analysis of polyimide-epoxy films

The dynamic mechanical properties of the PI-EP films were examined as a function of temperature. Fig. 5 represents the viscoelastic properties of PI-EP (63/37) after each

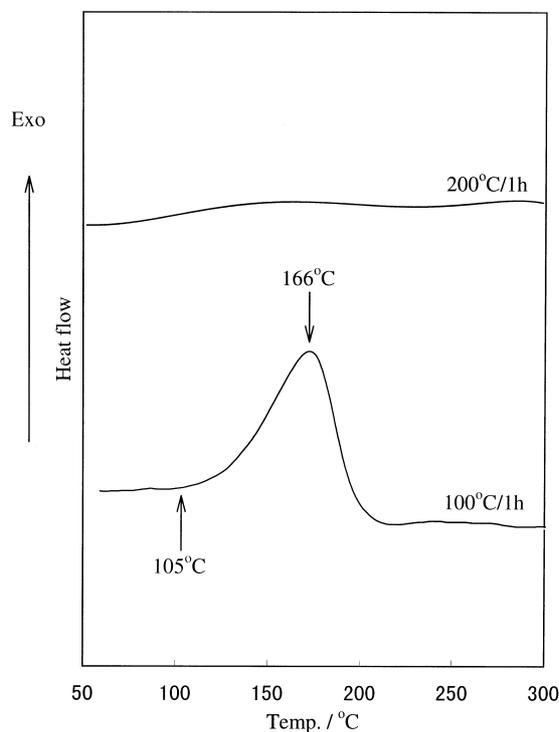
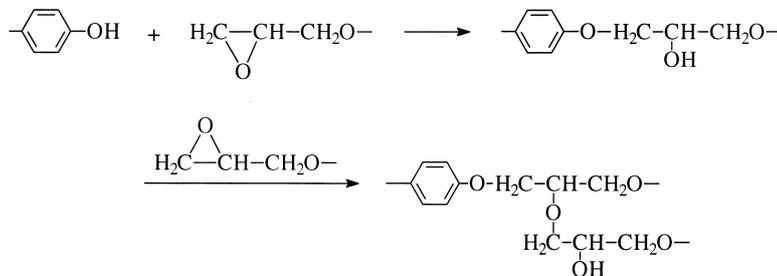


Fig. 3. DSC of polyimide-epoxy (PI-EP (63/37)) cured at 100°C or at 200°C for 1 h each.

cure stage. For the film cured at 100°C, a drop in the storage modulus accompanied a maximum in the loss modulus at ca. 60°C. Storage modulus started to increase again at ca. 120°C owing to the initiation of the curing of the epoxy to form crosslinked structure as suggested by the DSC. In case of film cured at 200°C, glass transition temperature ( $T_g$ ) estimated from the maximum of  $E''$  was at 255°C. Postcuring of the sample at 250°C led to an increase of the  $T_g$  due to increase of the crosslinking density.

Viscoelastic properties of PI-EP films with various PI-EP ratios treated at 250°C are shown in Fig. 6. The  $T_g$  of polyimide film treated at 250°C was above 400°C. The  $T_g$ 's of the PI-EP films were found to be shifted to high temperature as the content of polyimide increase; 127°C for PI-EP (13/87), 220°C for PI-EP (29/71), 260°C for PI-EP (45/55), and 290°C for PI-EP (63/37). It can be seen that the transition temperatures increase progressively with increasing polyimide content, indicative of a miscible character.



Scheme 2. Reaction profile of epoxy resin with the reactive polyimide.

Table 2  
DSC of polyimide–epoxy

Code	Exotherm			Functionality <sup>a</sup>	
	Onset (°C)	Max (°C)	Amount (cal g <sup>-1</sup> )	OH (mmol g <sup>-1</sup> )	Epoxy (mmol g <sup>-1</sup> )
PI–EP (63/37)	105	166	19.1	2.0008	1.9960
PI–EP (45/55)	111	165	11.8	1.4540	2.9036
PI–EP (29/71)	115	158	9.7	0.9404	3.7570
PI–EP (13/87)	119	163	4.5	0.4174	4.6254

<sup>a</sup> Functionality of OH and epoxy in a gram of each polyimide–epoxy composite.

Table 3  
Tensile properties of polyimide–epoxy films<sup>a</sup>

Code	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PI	3.89	91.7	4.11
PI–EP (63/37)	3.29	63.4	2.09
PI–EP (45/55)	2.89	57.9	2.27
PI–EP (29/71)	2.85	58.5	2.02
PI–EP (13/87)	2.41	50.9	2.07

<sup>a</sup> The cure condition is 100°C, 150°C and 200°C for 1 h each and 250°C for 3 h.

### 3.5. Solvent resistance of polyimide–epoxy films

Solvent resistance of the PI–EP films after curing at 250°C was investigated. The films were immersed in various solvents (0.03 g/10 ml) such as NMP, DMAc dimethylformamide, THF, and dichloromethane for one week. As shown in Table 4, the polyimide used in this study is soluble in these solvents. All the PI–EP films, however, did not change in the solvents in which polyimide film dissolved. This reflects the formation of network structure between the soluble polyimide and epoxy resins. This allowed the films to have excellent solvent resistance.

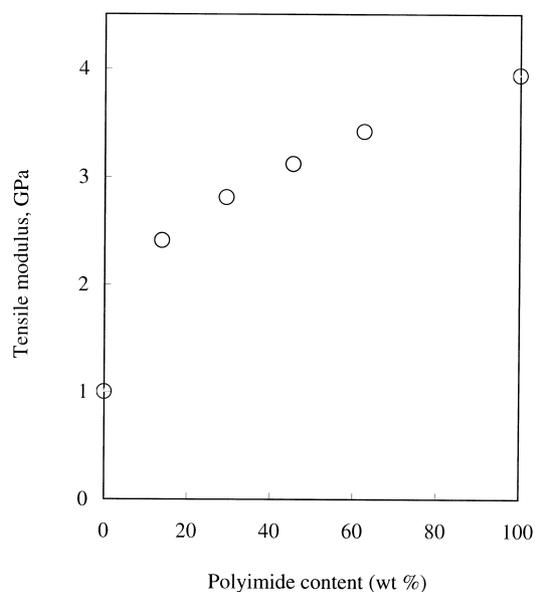


Fig. 4. Effect of polyimide content on the modulus in the polyimide–epoxy films.

### 3.6. Thermal stability of polyimide–epoxy films

Thermal stability of the PI–EP films along with polyimide film was investigated by TGA. As shown in Fig. 7, polyimide degrades in two steps owing to the initial degradation of the hydroxyl functionalities at 394–452°C. The 5% weight loss of polyimide was at 421°C (Table 5). The

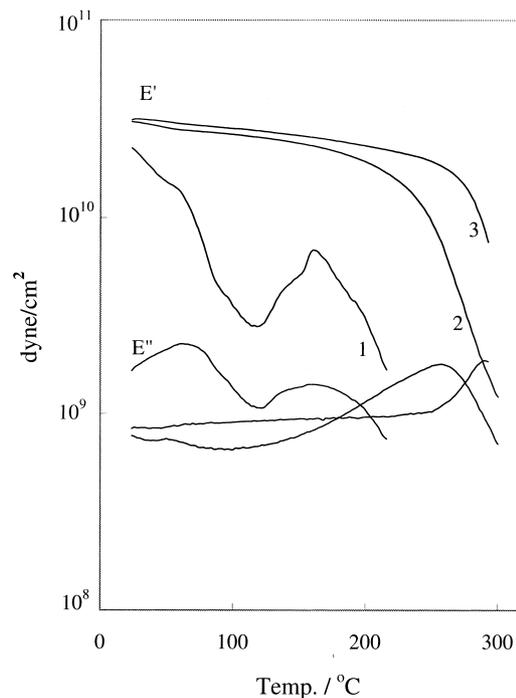


Fig. 5. Viscoelastic analysis of polyimide–epoxy film (PI–EP (63/37)) cured at different temperatures: (1) at 100°C, (2) at 200°C for 1 h each, and (3) at 250°C for 3 h.

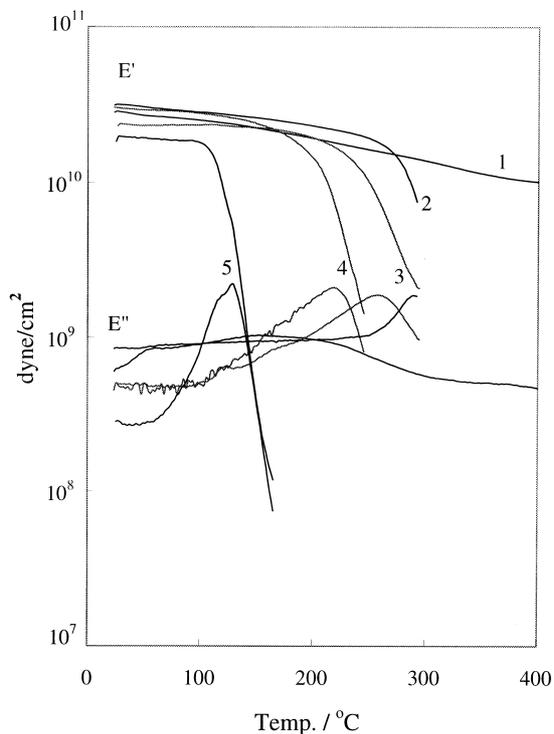


Fig. 6. Viscoelastic analyses of polyimide and various polyimide-epoxy films treated at 250°C for 3 h: (1) PI, (2) PI-EP (63/37), (3) PI-EP (45/55), (4) PI-EP (29/71), and (5) PI-EP (13/87).

TGA degradation profiles of PI-EP samples also show two distinct thermal stages. The first stage of weight loss is due to the degradation of epoxy at 300–440°C, and the second due to the polyimide at 500–550°C. The 5% weight loss temperatures are 343–366°C for the PI-EP films. As seen from these degradation temperatures, the increase of the polyimide content slightly increases the degradation temperature. The thermal stability of the PI-EP composites prepared by this method was almost the same as the PI-EP prepared using poly(amide acid) from PMDA and ODA [22], and superior to that of the epoxy cured with the standard diamines such as diaminodiphenylsulfone which decomposes below 300°C [22].

Table 4  
Solubility behavior of polyimide and polyimide-epoxy films

Code	Solvents <sup>a</sup>				
	NMP	DMF	DMAc	DCM <sup>b</sup>	THF
PI	○	○	○	△	△
PI-EP (63/37)	×	×	×	×	×
PI-EP (45/55)	×	×	×	×	×
PI-EP (29/71)	×	×	×	×	×
PI-EP (13/87)	×	×	×	×	×

<sup>a</sup> The symbols indicate: ○, soluble at room temperature; △, soluble by heating; ×, insoluble.

<sup>b</sup> DCM: dichloromethane.

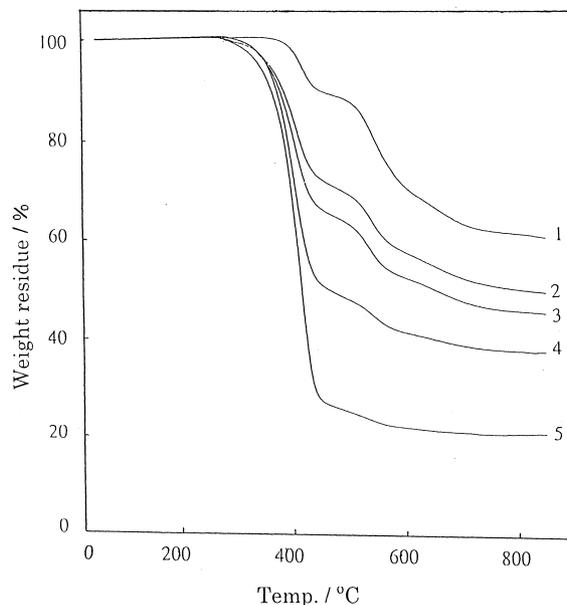


Fig. 7. TGA of polyimide and polyimide-epoxy treated at 250°C for 3 h: (1) PI, (2) PI-EP (63/37), (3) PI-EP (45/55), (4) PI-EP (29/71), and (5) PI-EP (13/87).

#### 4. Conclusion

A series of PI-EP films were prepared by a reaction of epoxy resin with a functionalized soluble polyimide without using external hardener. The reaction between epoxy and polyimide occurs via ring opening of the epoxide ring by the hydroxyl functionalities present on the polyimide and this results in the formation of a network structure. The curing of epoxy with the reactive polyimide was found to start at 105–119°C as confirmed by DSC. Viscoelastic analyses showed that the glass transition temperature shifted to higher temperature with the increase of polyimide content which reflects the miscibility between polyimide and epoxy. Tensile measurements showed that incorporation of polyimide enhanced tensile modulus. The films had excellent solvent resistance which also proved the formation of the network structure between the epoxy matrix and polyimide. TGA showed that the PI-EP films are thermally more stable than the epoxy cured with the traditional diamines. The increase of the polyimide content led to increase of the thermal stability of the films. A detailed study on the

Table 5  
Thermal stability of polyimide-epoxy

Code	Temp. of 5% decomposition (°C)	Temp. of 10% decomposition (°C)
PI	421	452
PI-EP (63/37)	366	388
PI-EP (45/55)	360	375
PI-EP (29/71)	350	368
PI-EP (13/87)	343	363

fracture toughness by using molded sample is one of our on-going research programs.

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