Siloxane- and Imide-modified Epoxy Resin Cured with Siloxane-containing Dianhydride

Hsun-Tien Li, Mu-Shih Lin*, Hsun-Ren Chuang and Ming-Wei Wang
Department of Applied Chemistry, National Chiao-Tung University, Hsinchu, Taiwan 30050
(*Author for correspondence; E-mail: mlin43@seed.net.tw)

Abstract

Hydrosilylation of nadic anhydride by tetramethyldisiloxane yielded 5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disiloxanediayl)-bis-norborane-2,3-dicarboxylic anhydride (I), which further reacted with 4-aminophenol to form N,N'-bis(4-hydroxyphenyl)-5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disiloxanediallyl)-binorborane-2,3-dicarboximide (II) reacted with epichlorohydrin to form siloxane- and imide-modified epoxy (i.e. N,N'-diglycidylether-bis-(4-phenyl)-5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disloxanediallyl)-bis-norborane-2,3-dicarboximide (III) (Scheme 1). Various equivalent ratios of III/I for 1/1, 1/0.8 and Bisphenol F epoxy (830LVP DIC Co.)/I for 1/1, 1/0.8 were prepared and cured to produce four crosslinked materials. Thermal and dynamic mechanical properties were measured with TMA and DMA. Kinetic analysis was studied with dynamic DSC, which revealed a relatively lower curing activation energy of III/I systems, because the tertiary amine on the imide group catalyzed the curing reaction. III/I system also indicated moderate Tg, storage modulus but higher loss modulus as compared with Bisphenol F epoxy/I systems. These phenomena were interpreted by the fact that the siloxane group in III toughened the crosslinked materials. In addition, photos of SEM, carbon-mapping-SEM, oxygen-mapping SEM and siloxane-mapping-SEM indicated all homogeneity of these materials.

Introduction

Epoxy resin has excellent mechanical, electrical and adhesion properties and is widely utilized as a high performance thermosetting material in many industrial fields [1–5]. Epoxy resins are generally easy to process, but are also relatively hard and brittle because of its highly crosslinked networks. Blending epoxy resin with liquid elastomers such as carbonyl-terminated butadiene-acrylonitrile copolymer (CTBN) and silicone rubber has been considered a successful method to improve the toughness of epoxy resin after many efforts [6–13]. However, there are inevitable drawbacks in mechanical properties and thermal stability for these rubber-modified epoxy resins. For example, if epoxy is directly blended with elastomer, phase-separation occurs due to imcompatibility of the two components, which leads to a reduction of mechanical properties [14–21]. M. Alagar, and his coworkers in their study of thermal and morphological behavior of siliconized epoxy bismaleimide matrices, prepared an intercrosslinked polymer network, where two components, γ-aminopropyl triethoxysilane modified epoxy and N,N'-bismaleimido-4,4'-diphenyl methane, were blended and crosslinked simultaneously to form a rigid inter-crosslinked matrix [22]. Whereas, we are interested in developing a novel homopolymer containing siloxane, norborane-2,3-dicarboximide and epoxide groups for easy processing to enhance the flexibility and toughness of this modified epoxy with sustaining the thermal and mechanical properties. In this work, siloxane was incorporated in the epoxy resin to improve the toughness and chemical resistance of the material. The rigid norborane-2,3-dicarboximide segment was incorporated into this silicone-modified epoxy in order to prevent from loss of mechanical properties. The resultant polymer, siloxane- and imide-modified epoxy (III), was easy to cure by the siloxane-modified norborane-2,3-dicarboxylic anhydride (I) to form a homogenous matrix, which was found to possess the expected properties. In this article, we would like to report such studies.

Experimental

Materials

5-Norbornene-2,3-dicarboxylic anhydride (nadic Anhydride), and tetramethyldisiloxane were purchased from Merck Co. Platinum divinyl tetramethyl disiloxane complex was purchased from UCT Co. Epichlorohydrin was purchased from TCI. All chemicals were purified before uses. Electronic grade of diglycigyl ether of bisphenol-F (830LVP, DIC Co.) was obtained from DIC Co. 2-ethyl-4-methyl-1-ethylcyanoimidazole (trade name: 2E4MZCN) was purchased from Shikoku Chemicals Co. which was used as the catalyst for the curing reaction of epoxy and anhydride.
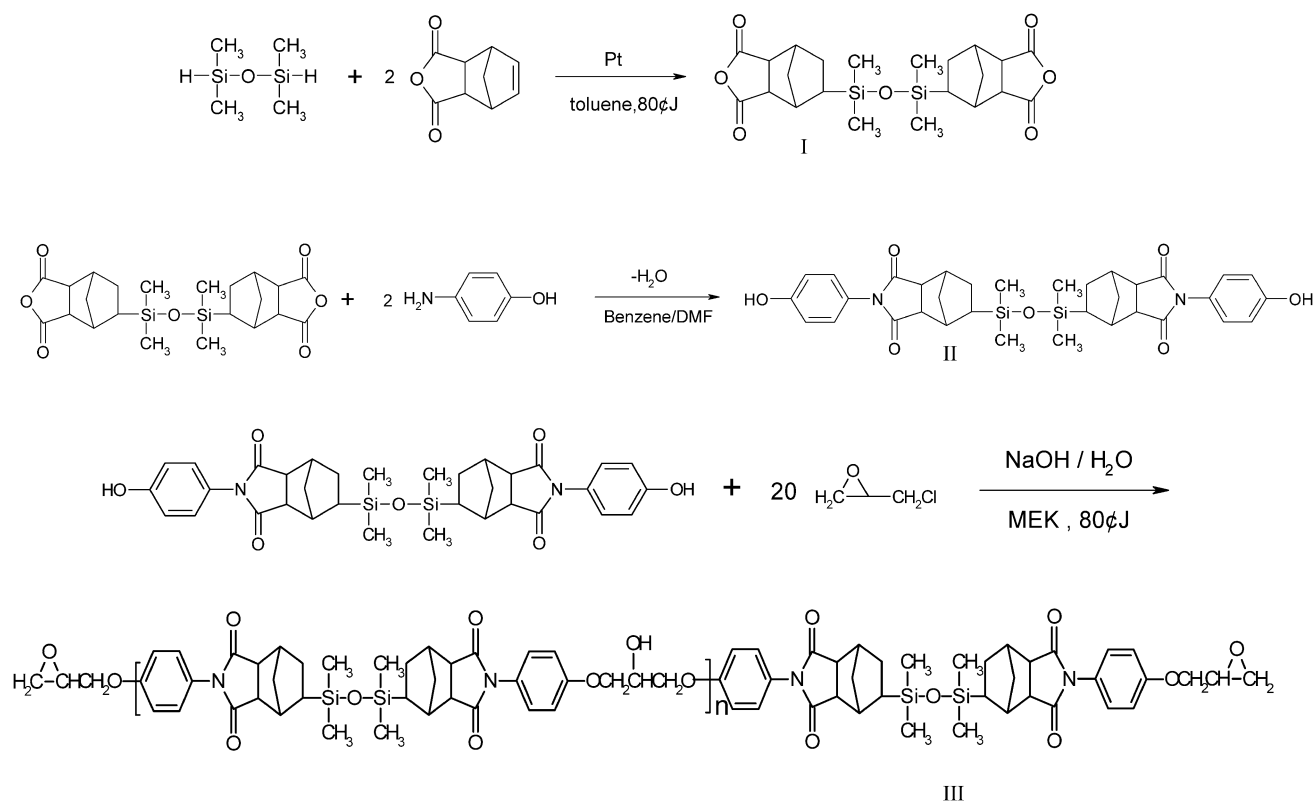
Scheme 1. Synthesis of compounds I, II and III.

Synthesis of 5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disiloxanediallyl)-bis-norborane-2,3-dicarboxylic Anhydride (I)

The synthesis of siloxane-containing dianhydride (I) was done according to the method reported in literature [23]. The chemical structure of this white product was confirmed with ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR (CDCl$_3$, ppm) shows δ: 0.03–0.05 (m, 12H), 0.65 (t, 2H), 1.55–1.66 (m, 8H), 2.73–2.78 (m, 2H), 2.84 (m, 2H), 3.39–3.43 (m, 4H). ^{13}C-NMR (CDCl$_3$, ppm) shows δ: −1.20–0.94, 25.75, 26.74, 40.32, 41.00–41.03, 41.64, 49.46, 52.62, 171.98–172.25.

Synthesis of N,N'-bis-(4-hydroxylphenyl)-5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disiloxanediallyl)-bis-norborane-2,3-dicarboximide (II)

The siloxane-containing dianhydride (I) (30 g, 0.065 mole) was dissolved in 90 ml DMF. 4-aminophenol (14.9 g, 0.136 mole) in 40 ml DMF was gradually added. The solution was stirred for 8 hours at 0 °C, followed by imidization using Dean-Stark instrument. After vacuum drying, compound II in solid powder was obtained (38 g, mp. = 123 °C, yield: 91%) (Scheme 1). ^{1}H-NMR (CDCl$_3$, ppm) δ: 0.01–0.02 (m, 12H), 0.61 (m, 2H), 1.54–1.62 (m, 8H), 2.74 (m, 2H), 2.78 (m, 2H), 3.12–3.17 (m, 4H), 6.70–6.73 (d, 4H), 6.90–6.94 (d, 4H), 7.42 (s, 2H). ^{13}C-NMR (CDCl$_3$, ppm) δ: −0.88, −0.84, 25.64, 26.54, 39.70, 40.57, 41.33, 48.54, 51.09, 116.16, 123.45, 127.81, 156.62, 178.57, 178.60, 178.82.

Synthesis of N,N'-diglycidylether-bis-(4-phenyl)-5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disloxanediallyl)-bis-norborane-2,3-dicarboximide (III)

The synthesis of siloxane- and imide-modified epoxy (III) was silimar to the previous experiment [24]. A three-necked flask equipped with a stirrer and an addition funnel was filled with a solution of II (12.88 g, 0.02 mole) and epichlorohydrin (37 g, 0.4 mole). NaOH solution (1.6 g NaOH (0.04 mole) in 3.2 ml H$_2$O) was added gradually to the mixture, and stirring continued for 6 hours at 65 °C. The product was extracted three times with toluene. After removing the solvent and residual reactants by vacuum drying, the siloxane- and imide-modified epoxy (III) with an epoxy equivalent weight of 477 g/eq. was obtained (92.6% of yield, mp. = 100–103 °C). ^{1}H-NMR (CDCl$_3$, ppm) δ: 0.01–0.16, 0.63, 1.54–1.64, .69–2.87, 3.20–3.21, 3.29–3.30, 3.92–3.94, 4.18–4.22, 6.93–6.97, 7.09–7.12. ^{13}C-NMR (CDCl$_3$, ppm) δ: −0.85, 25.62, 26.54, 39.76, 40.62, 41.33, 44.50, 48.50, 49.90, 51.07, 68.95, 115.17, 125.00, 127.72, 158.30, 177.35–177.57.

Preparation of Epoxy Curing Systems

The siloxane- and imide-modified epoxy (III) with dianhydride (I) in equivalent ratios of 1/1 and 1/0.8, respectively, together with 1 phr of 2-ethyl-4-methyl-1-ethylcyanoimidazole were dissolved in acetone and were vacuum dried at 50 °C to obtain the well mixed blends. For a comparison, the controlled systems of similar blend for bisphenol F epoxy in place of III were prepared exactly by the same formulation and procedure.

Characterizations

Dynamic Differential Scanning Calorimetry (DSC)

Prior to the DSC runs, the temperature and heat of reaction were calibrated by indium and zinc standards. Samples (4–10 mg) were placed in DSC (DSC7, Perkin-Elmer) and dynamic curing reaction was conducted at four heating rates (3 °C/min, 5 °C/min, 10 °C/min and 15 °C/min).

Thermogravimetric Analysis (TGA)

Thermal stability of the cured epoxy samples were investigated, using a Du Pont TA 2950 thermogravimetric analyzer. The system was operated in temperature range from 50 to 800° under nitrogen and air respectively, at a heating rate of 10 °C/min.

Thermal–Mechanical Properties

The precured epoxy in released film was placed in aluminium pan, and was cured according to the curing profile: 130 °C/30 min + 150 °C/180 min + 200 °C/30 min. Thermal mechanical behavior was investigated by TMA (TA 2940, Dupont) and dynamic mechanical analysis was performed using a Dupont DMA2980 with a dual cantilever head on cured film with dimensions of 60 × 8 × 0.1 mm at a frequency of 1 Hz and heating rate of 3 °C/min from 30 °C to 300 °C.

Chemical Resistance [25]

The cured samples (4 to 5 g) were immersed in 10% NaOH and 10% HCl respectively, and was stirred at 25 °C for 60 hours. The samples were washed and vacuum dried for 24 hours at 120 °C. Then, the dried samples were powdered and added into soxhlet extractor. After 24 hours of continuous extraction with acetone, the residual powder was dried by heating under vacuum and the undissolved and dry fraction was calculated by $W_1/W_0 \times 100\%$, where W_0 and W_1 are the initial, and residual weights, respectively, of the sample.

Mapping SEM

The cured specimens were fractured under liquid nitrogen. A LEO-1530 scanning electron microscope and EDS Phoenix was used for the morphological observation of the fracture surface.

Results and Discussions

Kinetic Analyses

The results of dynamic DSC revealed that the conversion at exothermal peak of two formulations based on III were very consistent, and their maximum exothermic peaks were higher than those of the corresponding bisphenol F/I systems, as shown in Figure 1 and Table 1. Kinetic study was done by following the Kissinger's method using dynamic DSC data [26–28] to calculate the activation energy from

$$2.303 \, d\log(\Phi/T_m^2)/d(1/T_m) = -E/R, \qquad (1)$$

where T_m is the temperature corresponding to the exothermal peak at a specific heating rate, Φ. The activation energy, E, is obtained from the slope of the plot of $\log(\Phi/T_m^2)$ against $1/T_m$. The calculated activation energy of the two III/I systems was less than that of the corresponding bisphenol F/I system, presumably because this homopolymer (III) contains more imide groups (a tertiary amine) in the polymer main chain, which have pronounced catalytic effect on the curing reaction of epoxy. The catalytic effect of tertiary amine on the curing reaction of epoxy is well known in literature [29, 30]. The activation energy of epoxy cure by aromatic diamine, in A. Moroni, J. Mijovic and E. M. Pearce's
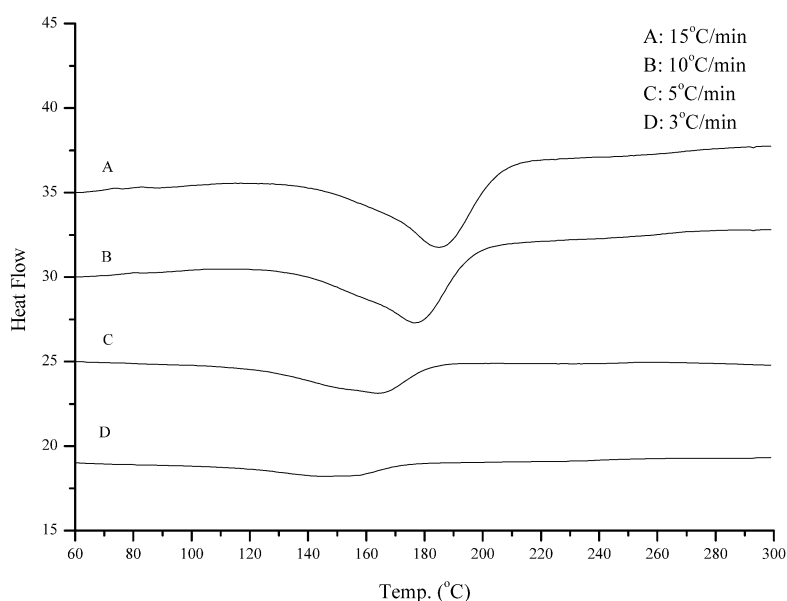

Figure 1. Typical dynamic DSC of III/I = 1/1.

Table 1. Curing dynamic DSC

		Heating rate (°C/min)					
		15	10	5	3	E_a (Kcal/Mole)	R^2
830LVP/I = 1/1	T_{peak} (°C)[a]	176.3	168.71	153.33	143.41	17.27	0.9904
	Yield at peak (%)[b]	56.74	55.55	54.95	55.31		
830LVP/I = 1/0.8	T_{peak} (°C)[a]	177.51	167.03	152.98	144.23	16.41	0.9903
	Yield at peak (%)[b]	57.8	58.3	59.42	59.7		
III/I = 1/1	T_{peak} (°C)[a]	185.52	177.73	164.28	147.27	14.40	0.9906
	Yield at peak (%)[b]	69.01	70.61	69.94	67.53		
III/I = 1/0.8	T_{peak} (°C)[a]	178.25	169.85	157.65	136.65	12.44	0.9894
	Yield at peak (%)[b]	69.83	69.72	71.05	68.93		

[a] The temperature at the maximum heat flow of dynamic DSC.
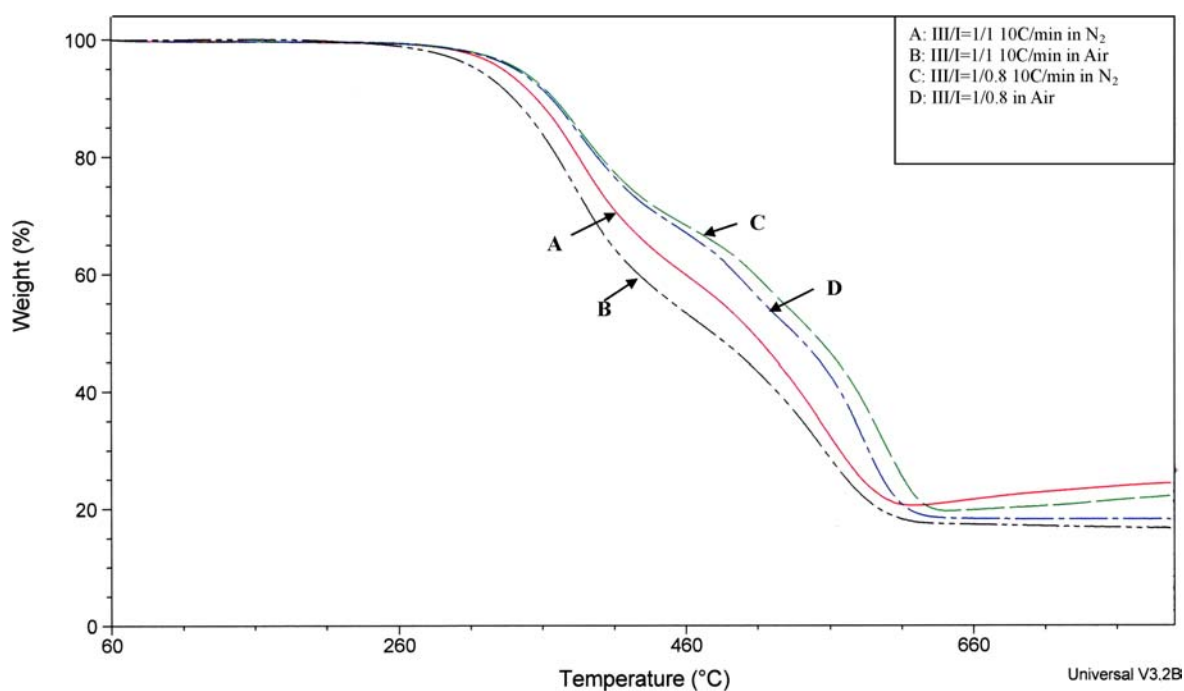[b] The reaction conversion at peak temperature.

Figure 2. TGA of III/I systems.

study, was reported something around 22.4 Kcal/mole [31], while the activation energy for our siloxane- and imide-modified epoxy III cured by siloxane-modified dianhydride (I), in the presence of tertiary amine is much lower, around 14.40 to 12.44 Kcal/mole. It is found that the blend III/I = 1/0.8 exhibits lower activation energy than III/I = 1/1, simply because III/I = 1/0.8 contains less equivalent ratio of reactants.

Thermal Stability

Figure 2 shows the TGA thermograms of the samples (III/I = 1/1 and 1/0.8) in nitrogen (Curves A, C) and in air atmosphere (Curves B, D). It is found that both samples are stable up to approximately 300 °C, while samples in nitrogen atmosphere indicate a little better thermal stability on the on-set of weight loss and char yield than those in air atmosphere.

Table 2. Chemical resistant data

	Without testing (%)	After HCL testing (%)	Afer NaOH testing (%)
III/I = 1/1	97.1	96.8	96.6
III/I = 1/0.8	97.6	96.9	96.4
830LVP/I = 1/1	96.4	95.8	95.3
830LVP/I = 1/0.8	97.7	96.2	95.8

Chemical Resistance

Chemical resistance was tested according to the method designed for use of substrates and materials in interconnecting and packaging electronic circuits [25]. Data in Table 2 reveal that all four crosslinked materials were cured nearly completely and exhibited excellent chemical resistant to alkali and acid, mainly because the siloxane segment exhibits not only water-repellant, but is inert to chemicals as well [32].
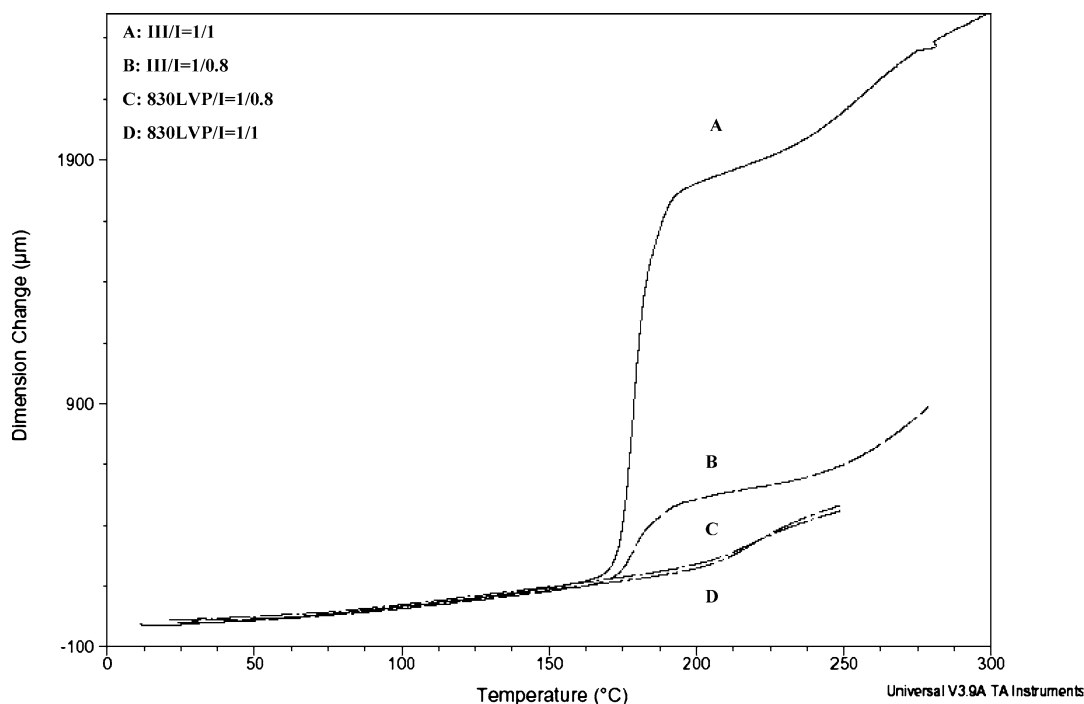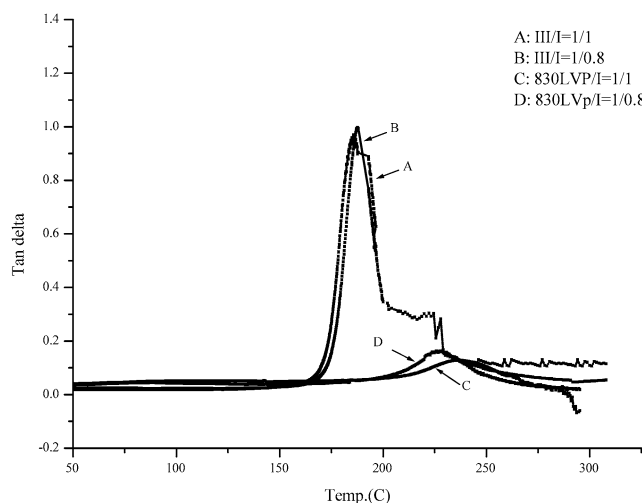
A: III/I=1/1
B: III/I=1/0.8
C: 830LVP/I=1/0.8
D: 830LVP/I=1/1

Figure 3. TMA of 830LVP/I and III/I systems.

A: III/I=1/1
B: III/I=1/0.8
C: 830LVP/I=1/1
D: 830LVp/I=1/0.8

Figure 4. Dampimg curve of 830LVP/I and III/I.

A: III/=1/1
B: III/I=1/0.8
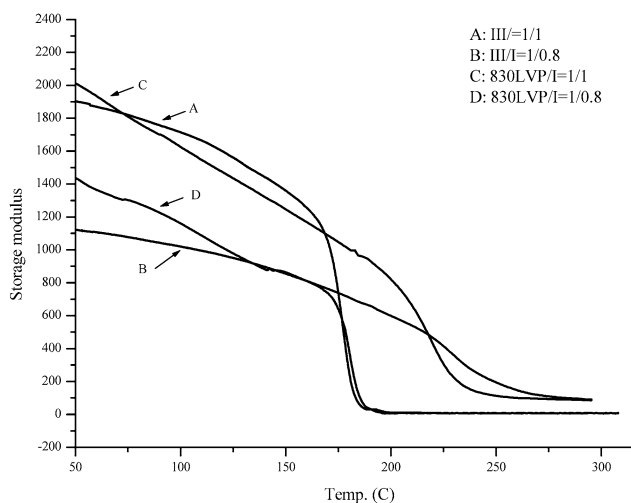C: 830LVP/I=1/1
D: 830LVP/I=1/0.8

Figure 5. Storage modulus of 830LV/I and III/I.

Thermal Mechanical Properties

Thermo-mechanical properties of these four cured materials are given in Figures 3, 4 and 5, and are summarized in Table 3. Coefficient of thermal expansion (CTE) for each of materials was directly read from TMA thermograms (Table 3). Compared with the commercial 830LVP/I system, samples of III/I system show a little better CTE's. The glass transition temperatures, T_g's, of all these materials were higher than 160 °C. It is noted that III/I system indicates lower T_g's than bisphenol F/I system. However, both III/I and bisphenol-F/I systems exhibit excellent flexibility and toughness, because of the presence of siloxane and imide segments in the polymer main chain, as they might be expected.

Dynamic Mechanical Properties

In Figures 4 and 5, the T_g's of the III/I system obtained from DMA study are consistent with those measured by TMA (Figure 3). In addition, the III/I system shows higher damping peaks (tan δ) and higher area of tan δ but lower loss modulus than bisphenol F/I system. Among these materials, III/I = 1/0.8 indicates the lowest storage modulus E' but the highest damping peak (tan δ_{max}), and also the highest area of tan δ, presumably because this formulation contains less crosslinking, due to less equivalent ratio of reactants. All of the DMA data confirm the stress-release and flexibility and toughness enhancement of the III/I systems, due to the presence of siloxane and imide groups in the polymer matrix. Furthermore, it is found that both tan δ and E' curves of III/I systems show a single transition peak,

Table 3. Comparisons of thermal–mechanical properties of III/I and 830LVP/I systems

System	T_g[a] (°C)	CTE[a] (μm/m. °C)	$\tan \delta$ (°C)	Peak height[b]	Area of $\tan \delta$	$E'_{glass.}$ (Mpa)	$E'_{rub.}$ (Mpa)
III/I = 1/1	173.2	97.7	185.6	0.97014	36.8967	1903.71	6.60436
III/I = 1/0.8	171.1	94.7	187.6	0.9964	37.764	1122.02	6.60436
830LVP/I = 1/1	204.1	95.5	227.7	0.163053	14.3721	2012.5	92.1669
830LVP/I = 1/0.8	201.9	95.6	237.2	0.128354	14.9059	1436.93	95.919

[a] T_g's and CTE's obtained from TMA thermograms; CTE means the coefficient of thermal expansion.
[b] Peak height was measured from damping curve of DMA thermograms.
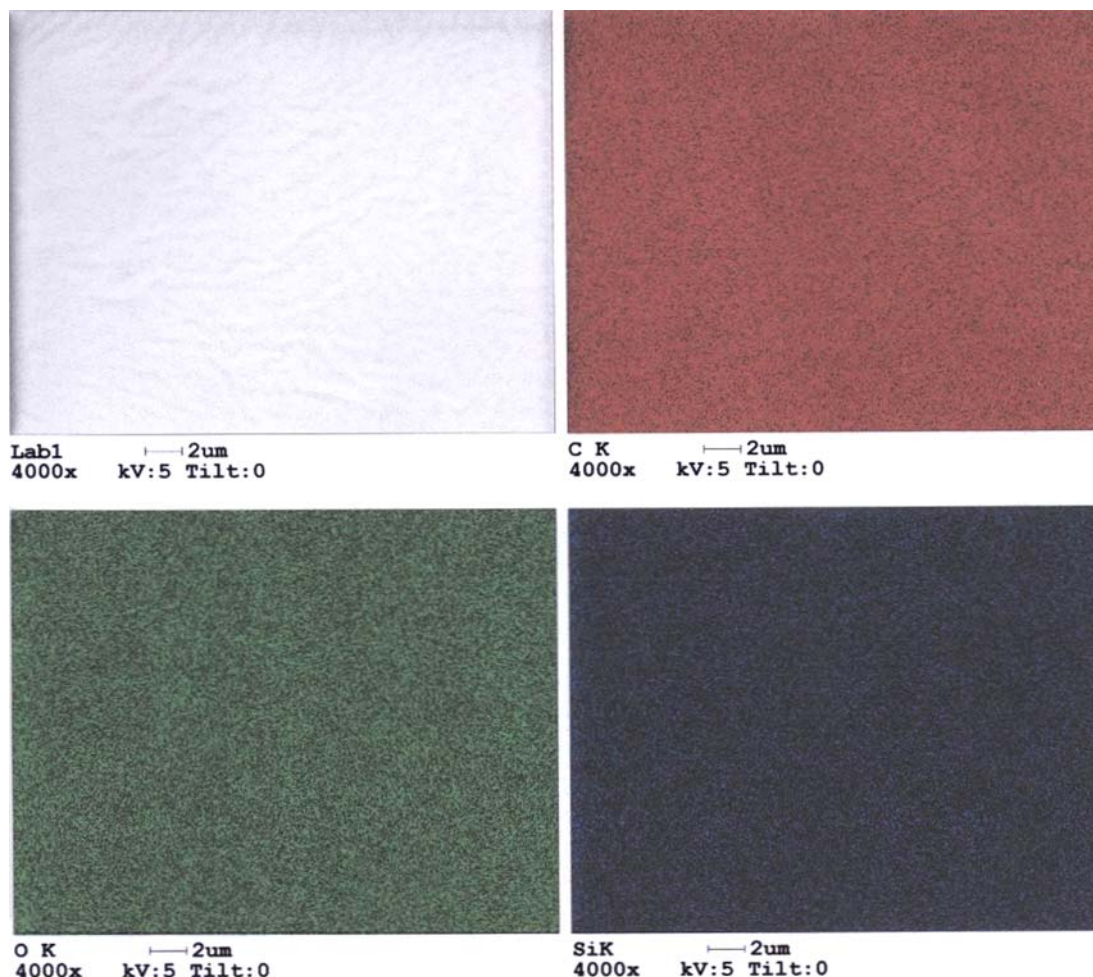

Figure 6. Typical mapping SEM of III/I = 1/1: (a) SEM; (b) C-Mapping SEM; (c) O-Mapping SEM, and (d) Si-Mapping SEM.

implying good compatibility of the system. It can be inferred that siloxane moiety was uniformly dispersed in the crosslinked network and there was no phase separation in the cured materials. This inference was confirmed by the SEM photos of cured materials, and the carbon-mapping SEM, oxygen-mapping SEM, and silicone-mapping SEM (Figure 6). It is obvious that all mapping SEM photos indicate compatibility and good homeogeneity of the materials.

Conclusion

A novel siloxane- and imide-containing epoxy resin was synthesized and the structure was characterized with ^{1}H-NMR and ^{13}C-NMR. This siloxane- and imide-modified epoxy (III) was cured with siloxane-containing dianhydride (I). Kinetic study revealed that the tertiary amine on the imide group in this epoxy (III) played a catalytic effect during epoxy cure, with III/I system indicating a relatively lower activation energy than bisphenol-F/I system. Among all the homogeneous and compatible systems, the III/I cured systems posses more contents of siloxane and imide groups and exhibited excemellent chemical resistance and thermo-mechanical properties, which is considered as a permissive material for electronic applications. The performance of electronic application for high density printing circuit board based on this material will be reported elsewhere.

Acknowledgement

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