

New Investigation of 1-Substituted Imidazole Derivatives as Thermal Latent Catalysts for Epoxy-Phenolic Resins

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ABSTRACT: Novel 1-substituted imidazole derivatives (4–10) were synthesized by imidazole and the corresponding substituted reagents (chloromethylpivalate, diphenylphosphinichloride, di-*tert*-butyldicarbonate, 1,1'-oxalylchloride, pyrazine, phneylisocyanat, and *p*-toluensulfonylchloride). Polymerization of diglycidyl ether of bisphenol A (DGEBA) with 1-substituted imidazole derivatives, two commercial available catalysts (imidazole and 1-cyanoethyl-2-ethyl-4-methylimidazole) and *N*-benzylpyrazinium hexafluoroantimonate were investigated as model reactions of epoxy resin systems with respect to the thermal latency and storage stability of the catalysts. The catalytic activity of 1-substituted imidazole derivatives 4–10 depended on the steric and withdrawing electronic effect of the substitution groups. To characterize the cure activation energy and the viscosity-storage time, the order of thermally latent activity is 1-tosylimidazole (6) > 1,1'-oxalyl-diimidazole (8) > *N*-ben-

zylpyrazinium hexafluoroantimonate (BPH, 3) > 1-tritylimidazole (9) > *N*-phenyl-imidazole-1-carboxamide (5) > 3-(diphenylphosphinoyl)imidazole (7) > *tert*-butyl-1*H*-imidazole-1-carboxylate (4) > 1-cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ, 2) > 1-[(pivalyloxy)methyl]imidazol (10) > imidazole (1). In comparison with commercially available catalysts imidazole (1) and 1-cyanoethyl-2-ethyl-4-methylimidazole (2) and a cationic latent catalyst *N*-benzylpyrazinium hexafluoroantimonate (BPH, 3) as the standard compounds, in addition to 1-[(pivalyloxy)methyl]imidazole (10), the 1-substituted imidazole derivatives (4–9) revealed better thermal latency. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3292–3300, 2007

Key words: 1-substituted imidazole derivatives; catalysts; epoxy-phenolic resins; polymerization; thermal latency; thermosets; resins

INTRODUCTION

Epoxy resins are widely used in the electronics industry as molding and sealing compounds for electronic packaging. These thermosetting resins have an especially useful variety of properties including excellent insulating characteristic, good adhesive properties, outstanding chemical resistance, retention of properties under severe operating conditions, low moisture adsorption, and no reaction by-products that could cause void formation or act as plasticizers.^{1–7} Although the biphenyl type epoxy resins are of great advantage for highly reliable electronic molding compounds (EMC) with good adhesion and high toughness and for use of high filter loadings,^{8–10} their low molecular weight epoxy resin system has low storage stability at room temperature. Hence, latent catalysts

for these systems need to be developed to improve the pot life at room temperature.⁶

Catalysts are used in most molding compound formulations to reduce the in-mold time and extremely important for adhesives, paints, coating, molding resins, insulation materials, and matrices for composite materials.^{11,12} Three types of catalysts were usually applied in the molding compound of electronic industries, which contain a series of imidazole, diazabicyclic derivatives (DBN and DBU) and phenolic compounds.^{13,14} Sometimes, the mixture compounds of diazabicyclic derivatives and phenolic compounds were also applied in the manufacture production.^{13,14} Imidazole are used as epoxy curing agents owing to their fast catalytic action and also the fine mechanical properties, which they produce in the cured resin.^{15–18} Some imidazoles are high effective epoxy-curing agents and have superior physical properties (e.g., better heat resistance, lower tensile elongation, a higher modulus and a wider range of cure temperature) than amine-cured system,^{19,20} but unmodified imidazoles have low stability when mixed with epoxides (curing occurs slowly at room temperature) making them unsuitable for use in one-pot compositions. Because of the strong reactivity of these catalysts, the

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molding compounds must be stored at low temperature to prolong the pot-life. Much work has been carried out on stabilizing imidazoles for use as latent epoxy-curing agents and approach involves the preparation of metal-imidazole complex^{21,22} and 1,3-disubstitutedimidazolium salts.²³ As a result, the modified imidazoles have attracted much attention as latent catalysts to maintain the long pot-life and improve the physical properties, as well as the cure reaction at high temperature.

A perfect latent catalyst for molding compound should have the following properties: (1) rapid cure at a moderately elevated temperature (100–175°C), (2) indefinite storage life for the catalyzed resin, and (3) no adverse effect on the properties of the cured material.²⁴ Latent catalysts in an epoxy resin system can be classified into two groups: thermal^{25,26} and cationic latent catalyst.^{27–31} A few of pure thermal latent catalysts were developed and reported in the recent research because of the poor catalyzed reactivity. Most of cationic latent catalysts were published in recent year in which the reactivity of cationic latent catalysts were enhanced by the nucleophilicity of counterion (BF_4^- , PF_6^- , AsF_6^- , and SbF_6^-).³¹ The acidic species (HBF_4 , HPF_6 , HAsF_6 , and HSbF_6) would be released while the curing polymerization. The acidic species would be damaged by the electronic products. In this work, we provide a series of the novel 1-substituted imidazole derivatives as the latent catalysts. Because of the 1-substituted imidazoles contain the strong withdrawing groups (carboxamide, carboxylate, diphenylphosphinoyl, oxalyl, and *p*-toluenesulfonyl) or bulky protecting group (pivalyloxymethyl and trityl), which would be stabilized and modulated the reactivity of imidazole at room temperature. Nevertheless, the 1-substituted imidazoles' own weak bonds, (C–N, N–S, N–P, and N–P), in the structure would be decomposed and released the imidazolyl anion at a moderately elevated temperature (100–175°C) to attack the epoxy resins and catalyze the polymerization.

EXPERIMENTAL

Diglycidylether of bisphenol A (DGEBA, ZX-1059) was purchased from Tohto Kasei. 1-Cyanoethyl-2-ethyl-4-methylimidazole (**2**, 2E4MZ-CN) was purchased from Shikoku Chemical. *N*-Benzylpyrazinium hexafluoroantimonate (BPH, **3**) and 1-substituted imidazole derivatives **4–10** were prepared by following the previously reported procedure^{27–39} and the physical properties and spectroscopic characteristics were consistent with the published data.

N-Benzylpyrazinium hexafluoroantimonate (**3**, BPH)²⁷

¹H NMR (DMSO-*d*₆, 300 MHz) δ 5.91 (s, 2H, CH₂), 7.47 (m, 3H, ArH), 7.59 (m, 2H, ArH), 9.29 (s, 2H,

Py-H), 9.54 (s, 2H, Py-H); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 64.59, 129.68, 129.89, 130.20, 133.14, 137.42, 151.60; IR (neat) 3114 (m), 1445 (m), 1157 (m), 666 (m) cm⁻¹.

tert-Butyl-imidazole-1-carboxylate (**4**)³³

¹H NMR (CDCl₃, 300 MHz) δ 1.62 (s, 9H, 3 × CH₃), 7.04 (d, *J* = 2.0 Hz, 1H), 7.37 (d, *J* = 2.0 Hz, 1H), 8.08 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 27.56, 85.20, 116.84, 129.95, 136.77, 146.81; IR (neat) 3138 (m), 2988 (m), 1747 (s, C=O), 1469 (m), 1383 (m), 1288 (s), 1253 (m), 1150 (m), 1002 (m), 771 (m) cm⁻¹; MS *m/z* (relative intensity) 170 (M+, 10), 169 (100), 155 (10), 154 (35), 138 (13), 137 (28), 136 (22), 113 (49), 71 (10), 67 (10), 57 (58), 55 (23).

N-phenyl-imidazole-1-carboxamide (**5**)³⁴

¹H NMR (DMSO-*d*₆, 300 MHz) δ 7.21–7.59 (m, 7H, ArH + imidazole), 8.35 (s, 1H), 9.57 (b, 1H, NH); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 117.56, 121.55, 125.88, 129.57, 130.14, 136.48, 137.04, 147.34; IR (neat) 3321 (b), 1731 (s), 1650 (m), 1553 (m), 1488 (m), 1448 (m), 1319 (m), 1230 (m), 1076 (m), 753 (m), 696 (m) cm⁻¹; MS *m/z* (relative intensity) 188 (M+, 3), 97 (6), 95 (8), 91 (8), 85 (6), 83 (10), 81 (13), 79 (10), 77 (10), 73 (10), 71 (17), 69 (100), 67 (25), 57 (59), 56 (10), 55 (77).

1-Tosylimidazole (**6**)³⁵

¹H NMR (CDCl₃, 300 MHz) δ 2.39 (s, 3H, ArH), 7.04 (s, 1H), 7.26 (s, 1H), 7.32 (d, *J* = 9.0 Hz, 2H), 7.78 (d, *J* = 9.0 Hz, 2H), 7.97 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 22.12, 117.84, 127.76, 130.84, 131.82, 135.33, 137.04, 146.74; IR (neat) 3171 (s), 3107 (m), 1594 (m), 1464 (m), 1380 (m), 1152 (m), 1046 (841), 801 (m), 678 (m), 587 (m) cm⁻¹; MS *m/z* (relative intensity) 224 (M+, 14), 223 (100), 155 (23), 137 (9), 91 (35), 77 (10), 69 (35), 57 (11), 55 (14), 41 (9).

3-(Diphenylphosphinoyl)imidazole (**7**)³⁶

¹H NMR (CDCl₃, 300 MHz) δ 6.69 (s, 2H), 7.21–7.26 (m, 6H), 7.69–7.75 (m, 5H, ArH + imidazole), 12.27 (b, 1H, OH); ¹³C NMR (CDCl₃, 75 MHz) δ 119.35, 128.42, 128.58, 130.79, 131.45, 131.58, 133.01; IR (neat) 3413 (b), 1965 (m), 1650 (m), 1440 (m), 1133 (s), 1102 (m), 729 (m), 559 (m) cm⁻¹; MS *m/z* (relative intensity) 287 (M+, 4), 220 (2), 219 (12), 201 (2), 141 (3), 137 (3), 77 (3), 70 (5), 69 (100).

1,1'-Oxalyldiimidazole (**8**)³⁷

¹H NMR (D₂O-*d*₂, 300 MHz) δ 7.21 (s, 4H), 8.40 (s, 2H); ¹³C NMR (D₂O-*d*₂, 75 MHz) δ 119.40, 133.89, 173.57; IR (neat) 3421 (b, OH), 1953 (s, C=O), 1310 (m), 769 (m), 623 (m) cm⁻¹; MS *m/z* (relative

TABLE I
Synthesis of Latent Catalysts by the Reaction of Imidazole with Different Protecting Agents

Catalyst	Protecting agents	Yield ^a (%)
4	diterbutyldicarbonate	92
5	phenylisocyanate	82
6	<i>p</i> -toluenesulfonylchloride	85
7	diphenylphosphinic chloride	95
8	oxalylchloride	92
9	triphenylmethylchloride	90
10	chloromethylpivalate	66

^a The yield was provided after the purification by chromatography or recrystallization.

intensity) 223 (M⁺, 5), 222 (24) 183 (75), 155 (16), 154 (65), 153 (8), 137 (100), 136 (55), 135 (12), 124 (7), 120 (8), 107 (20), 105 (8), 91 (12), 90 (13), 89 (24), 85 (8).

1-Triylimidazole (9)³⁸

¹H NMR (CDCl₃, 300 MHz) δ 6.83 (s, 1H), 7.07 (s, 1H), 7.14–7.33 (m, 15H, ArH), 7.47 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 75.18, 121.67, 128.00, 128.20, 128.27, 129.74, 138.97, 142.46; IR (neat) 3080 (m), 1594 (m), 1487 (m), 1437 (m), 1290 (m), 1069 (m), 751 (m), 694 (m) cm⁻¹; MS *m/z* (relative intensity) 171 (M⁺, 22), 170 (100), 165 (66), 136 (23), 107 (21), 95 (28), 91 (40), 89 (29), 83 (31), 81 (40), 79 (28), 77 (52), 73 (23).

1-Pivalyloxymethylimidazol (10)³⁹

¹H NMR (CDCl₃, 300 MHz) δ 1.08 (s, 9H, 3 × CH₃), 5.77 (s, 2H), 6.96 (s, 1H), 7.00 (s, 1H) 7.59 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 27.15, 39.07, 67.95, 119.87, 130.30, 138.61, 178.00; IR (neat) 3631 (m), 3114 (m), 2976 (s), 1739 (s, C=O), 1504 (m), 1278 (m), 1124 (s), 979 (m), 736 (m), 655 (m) cm⁻¹; MS *m/z* (relative intensity) 184 (M⁺, 11), 183 (100), 182 (6), 153 (7), 97 (2), 85 (12), 83 (2), 82 (3), 81 (6), 69 (19).

RESULTS AND DISCUSSION

Preparation of *N*-benzylpyrazinium hexafluoroantimonate (3) and 1-substituted imidazole derivatives (4–10)

Two commercially available catalysts imidazole 1 and 1-cyanoethyl-2-ethyl-4-methylimidazole 2 (2E4MZ-CN) were used as the comparison standards. *N*-Benzylpyrazinium hexafluoroantimonate 3²⁷ and 1-substituted imidazole derivatives 4–10^{33–39} were prepared by reported method. A series of the 1-substituted imidazole derivatives (4–10) were synthesized by the use of imidazole and the protecting agents, which contain the strong withdrawing groups (carboxamide, carboxylate, diphenylphosphinoxy, oxalyl, and *p*-toluenesulfonyl) or bulky group

(pivalyloxymethyl and trityl). The synthetic results of 4–10 were tabulated in the Table I and the structures of compounds 1–10 were shown in the Scheme 1. The isolated yields and spectroscopic characteristics were consistent with those of published data.

Measurement of pot-life⁴⁰

Sample preparation procedure

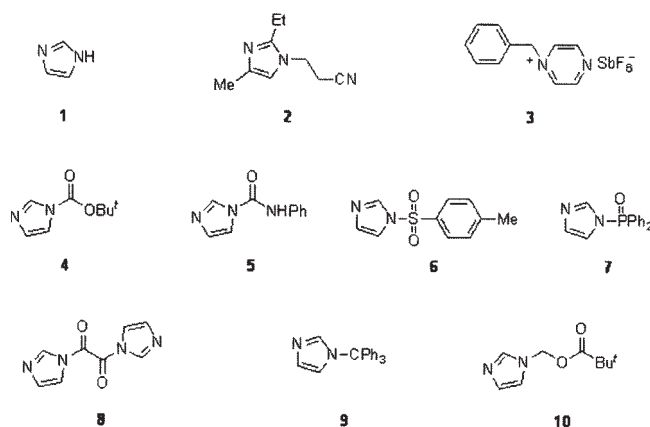
The catalyst level was set to 0.5%, percent by the weight of biglycidylether of bisphenol A epoxy resin (DGEBA, ZX-1059 supplied by Tohto Kasei of Japan, see Scheme 2). The epoxide equivalent weight of DGEBA was 160–170 g/equiv and the viscosity was 2000–3000 cp. The procedure of preparing samples included sample mixing using a high shear blender and sample degassing using a vacuum oven. All of the samples were stored in glass vials at room temperature between viscosity measurements. The glass vials were rotated using a rotator at about 10 rpm all the time to keep the filler from settling (Scheme 2).

Measurement of viscosity

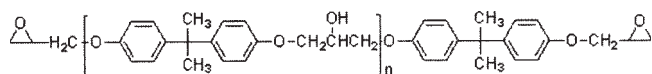
The viscosities of the samples were measured periodically using a Viscometer (Brook Field Instruments, model DV-II+) with parallel plate geometry and Spindle (model SC4-21). The gap was set to 250 μ. The test was done at 25°C for 600 h. The test method used is listed as follows:

1. Preshear at 10 S⁻¹ for 30 s;
2. Stepped ramp of shear rate 0.1–20 S⁻¹ by 25 points, with tolerance no more 5% (up curve);
3. Stopped ramp of shear rate from 20 to 0.1 S⁻¹ by 25 points, with tolerance no more than 5% (down curve).

The down curve was used to calculate the viscosity for each sample.



Scheme 1 The structure of BPH (3) and imidazole derivatives (1, 2, and 4–10).



Scheme 2 Diglycidylether of bisphenol A, (DGEBA, ZX-1059)

Figure 1 show the viscosity–shear rate relationship of the DGEBA epoxy resin containing different catalyst compounds (1–10) stored at room temperature. The figure showed that among the 10 compounds tested, five compounds of 1-substituted imidazole derivatives and *N*-benzylpyrazinium hexafluoroantimonate (BPH, 3) showed better room-temperature latency than others. These five compounds were *N*-phenyl-imidazole-1-carboxamide (5), 1-tosylimidazole (6), 3-(diphenylphosphinoyl)imidazole (7), 1,1'-oxalyldiimidazole (8), and 1-tritylimidazole (9). Compounds 5–8 containing the strong withdrawing groups could be a good way to develop as highly latent catalysts. On the other hand, compound 9 protected by trityl bulky group could also enhance the latency property. 1-Cyanoethyl-2-ethyl-4-methylimidazole (2, 2E4MZ-CN) is a commercial latent catalyst, but the latency is no good at room temperature. *tert*-Butyl-imidazole-1-carboxylate (4) and 1-pivalyloxymethylimidazole (10) were poor case approach because of the weak bond O–(C=O) in carbamate or carbonate, which are easily broken to lead the active imidazole moiety at room temperature.⁴¹

Differential thermometry analysis (TG/DTA)

All scanning TG/DTA studies of the curing behavior were performed with Perkin Elemer Instruments Pyris Diamond at heating rate 10°C/min under N₂. High purity indium and zinc were used to calibrate the calorimeter. TG/DTA studies of the cure of

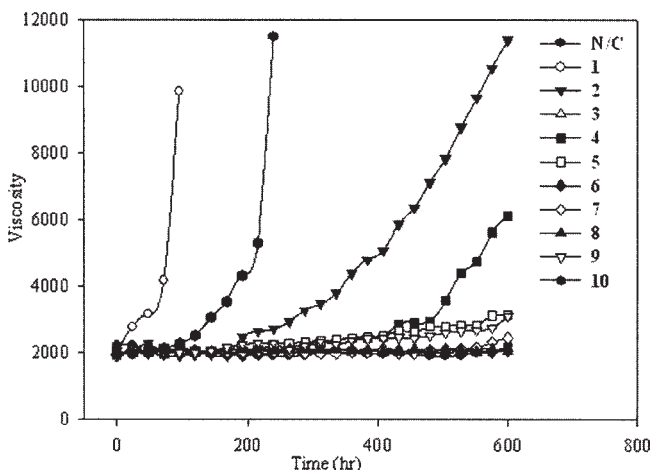


Figure 1 Viscosity-storage time plot of DGEBA epoxy resin without catalyst and with catalysts compounds (1–10) at 10 S⁻¹ shear rate (N/C stands for no catalyst).

TABLE II
The Exotherm Onset, Main Peak, and Total Heat of DGEBA with 1-Substituted Imidazole Catalysts (5–9) at a Concentration of 1, 2, 3, and 5 wt %

Catalyst	Concentration (wt %)	Exotherm onset (°C)	Exotherm peak (°C)	Total heat (J/g)
1	1	83	124	383
	2	70	120	930
	3	63	116	862
2	1	142	160	64
	2	139	155	131
	3	122	155	463
3	5	117	152	797
	1	144	229	404
	2	130	225	802
4	3	125	223	886
	1	134	162	96
	2	134	162	113
5	3	132	161	273
	5	131	160	316
	1	91	130	138
6	2	86	130	241
	3	82	128	489
	5	71	126	898
7	1	171	232	30
	2	159	221	46
	3	154	218	71
8	5	147	214	100
	1	122	160	30
	2	121	155	49
9	3	120	156	61
	5	118	153	96
	1	118	172	188
10	2	111	169	385
	3	106	162	498
	5	103	144	701
10	1	139	177	51
	2	130	173	80
	3	130	172	150
10	5	128	172	218
	1	144	165	42
	2	141	159	101
10	3	135	157	240
	5	131	156	329

^a The heating rate at 10°C/min.

DGEBA with the 1-substituted imidazole catalysts (1–10) at a concentration of 1, 2, 3, and 5 wt % are performed from 30 to 300°C at heating rate 10°C/min under N₂. Table II show the exotherm onset, exotherm peak, and total heat were observed at all four concentrations, with the peaks shifting towards lower temperatures due to enhanced reaction rate with the increasing of 1-substituted imidazoles (1–10) concentration.⁴² Total heat output indicates that an exothermic reaction, namely polymerization, has taken place. Typical total heat of curing systems of DGEBA with the 1-substituted imidazoles (4–10, 5 wt %) were afforded 95–900 J/g. According to the tosyl and diphenylphosphinoyl protecting groups

are the strong withdrawing groups, the nucleophilic reactivity of imidazolyl group of 1-tosylimidazole (6) and 3-(diphenylphosphinoyl)imidazole (7) would be decreased. Since, the lower total heats (30–100 J/g, 1–5 wt %) were generated in the DGEBA with compounds 6 and 7 curing systems. For compound 4, 5, 8, 9, and 10, the imidazolyl group owns the more strong nucleophilic activity because of the weaker carbonyl withdrawing group or alkoxy group. As a result, they provide the higher exothermic heats (200–800 J/g, 5 wt %). These values of total heat, which are presented in Table II, are consistent with the literature reported data.^{21–23,42,43} However, the total heat output is important since too little indicates that no polymerization occurred and too high heat output signifies that the reaction will not be scaled up to industrial capacity with a satisfactory safety level.²³

For the compounds *N*-phenyl-imidazole-1-carboxamide (5), 3-(diphenylphosphinoyl)imidazole (7), and 1,1'-oxalyldiimidazole (8) curing system (preceding the dominant exotherm peak which shifts towards lower temperatures with increasing imidazoles concentration), two exotherm peaks can be observed whereas only one exotherm peak was observed for the 1-tosylimidazole (6) and 1-tritylimidazole (9) curing systems. The phenomenon of a lower temperature small peak (or shoulder) have also observed by Heise and Martin^{18,23} and Vogt⁴⁴ with 1,3-unsubstituted imidazoles (2,4-EMI and 1*H*-imidazole, respectively). They attributed this lower temperature peak to the adduct formation steps. Confirmation of this assignment was obtained^{18,41} by noting a gradual increase in the exotherm area of the lower temperature peak (as found in the present work in Figs. 2–4) and simultaneous decrease in that of the main peak

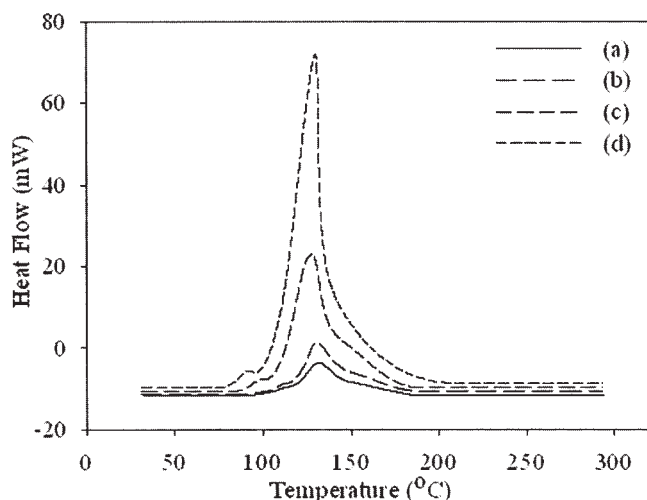


Figure 2 Scanning TA/DTA of the cure of DGEBA at 10°C/min with *N*-phenyl-imidazole-1-carboxamide (5): (a) 1; (b) 2; (c) 3; and (d) 5 wt %.

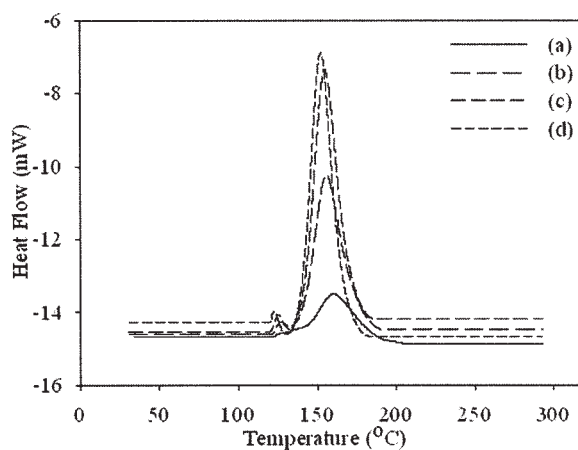


Figure 3 Scanning TA/DTA of the cure of DGEBA at 10°C/min with 3-(diphenylphosphinoyl)imidazole (7): (a) 1; (b) 2; (c) 3; and (d) 5 wt %.

on increasing the new latent imidazoles concentration. Figure 5 shows that only one exotherm peak of curing systems of DGEBA with the 1-tritylimidazole (9) was observed at all four concentrations (1, 2, 3, and 5 wt %), and the commercial latent catalyst 2E4MZ-CN has also only one exotherm peak.

The measurement of glass transition temperature (T_g)

The glass transition temperature is the most important single parameters, which can help to determine the applications and properties of polymer materials.⁴⁵ Glass transition temperature (T_g) of DGEBA/catalyst curing system depend on the amount and property of catalyst,⁴⁶ the epoxide equivalent weight

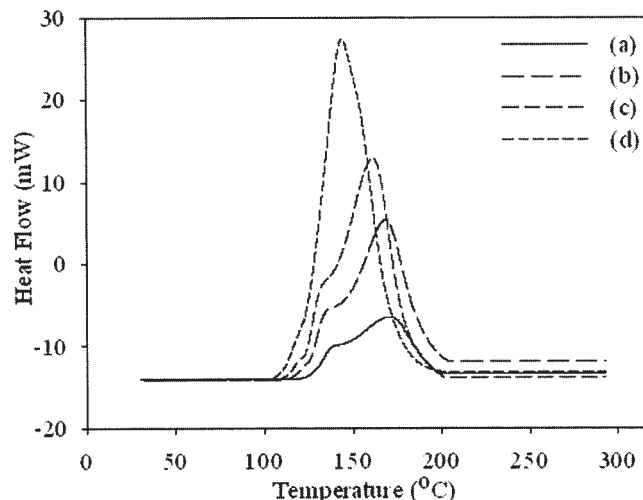


Figure 4 scanning ta/dta of the cure of DGEBA at 10°C/min with 1,1'-oxalyldiimidazole (8): (a) 1; (b) 2; (c) 3; and (d) 5 wt %.

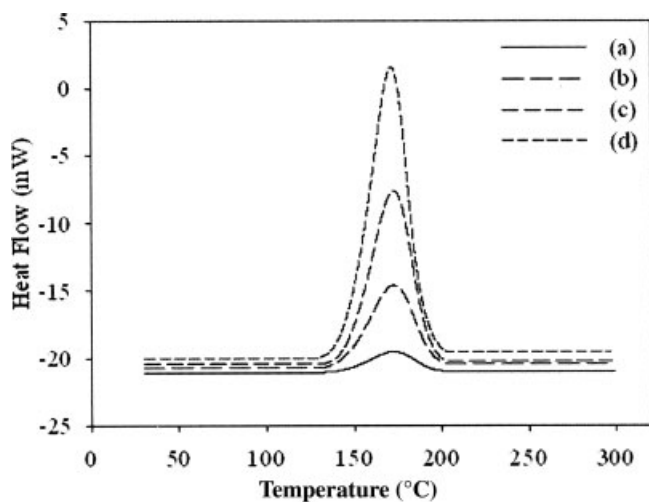


Figure 5 Scanning TA/DTA of the cure of DGEBA at 10°C/min with 1-tritylimidazole (9): (a) 1; (b) 2; (c) 3; and (d) 5 wt %.

of DGEBA and the blending agent (i.e., hardener, and filler⁴⁵).

The glass transition temperature (T_g) studies are performed by using a dynamic differential scanning calorimeter (DSC, Shimadzu Instruments DSC-60), calibrated with indium. The samples were placed in aluminum-sealed pans and were performed under a flow (30 mL/min) of dry N_2 . Temperature scans were performed from 30 to 300°C at heating rate 10°C/min. The amount of sample was limited to 12–15 mg to minimize experimental errors. The glass transition temperature (T_g) of the cure of DGEBA (ZX-1059 supplied by Tohto Kasei of Japan, 160–170 g/equiv) with the 1-substituted imidazole catalysts (4–10) at a concentration of 1 wt % are measured and determined by a second run; the thermogram presents no residual heat. The epoxy (DGEBA) with two of commercially available catalysts (1 and 2) and a cationic latent catalyst (BPH, 3) were also done for comparison purpose.

Lee and Choi⁴⁷ have reported that *N*-benzylpyrazinium salts are excellent thermal initiators for the curing of epoxy resins. They can easily control the initiation and curing process of epoxy systems, and activity of the latent thermal initiator depends on the nature of counteranions, such as PF_6^- , AsF_6^- , SbF_6^- , and BF_4^- .³⁰ In the comparison case, the T_g value of the DGEBA/*N*-benzylpyrazinium hexafluoroantimonate (BPH, 3) system was provided at 75°C because of the lower epoxide equivalent weight (160–170 g/equiv) of DGEBA resin was used in our work. The literature data was reported at 92°C (T_g) by using the higher epoxide equivalent weight (187 g/equiv) of DGEBA resin.²⁸

In DGEBA/1-substituted imidazole derivatives catalysts (1, 2, 5, 6, 7, and 9) curing systems, the T_g indicate that complete or near complete curing sys-

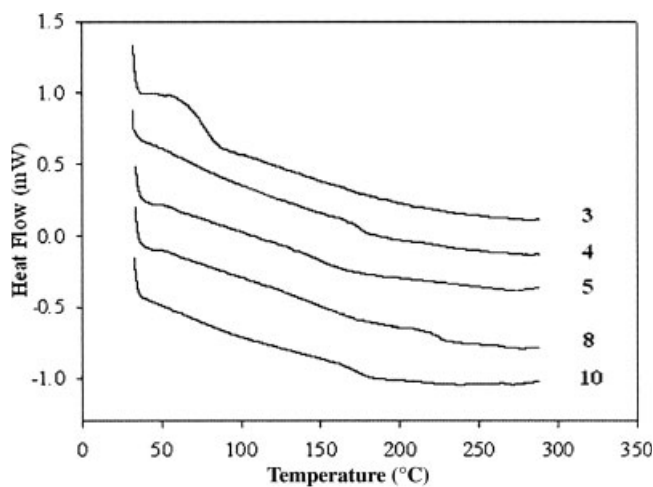


Figure 6 Second run for the DSC thermogram of DGEBA with of BHP(3) or 1-substituted imidazole catalysts (4, 8, and 10) curing systems as a concentration of curing systems at a 1 wt % showing the T_g values.

tems were obtained in the range of about 150–155°C. When we applied DGEBA resin with the 1-substituted imidazole catalysts including carboxyl, dicarbonyl, and pivalyloxymethyl protecting groups in core molecular (4, 8, and 10), the T_g values were increased to 169, 221, and 175°C, respectively, (Fig. 6). Because of the 1-substituted imidazoles (4, 8, and 10) containing the carbonyl or carboxyl group are able to participate the polymerization as a hardener agent (like to acid anhydrides)⁴⁸ to increase the crosslinking density.⁴⁹ As a result, the T_g values are increased and the thermal stabilities are also enhanced in this curing system.

Figure 7 and Table III shows the conversion of the DGEBA cured by each catalyst (3–9) as a function of the curing temperature obtained from dynamic TG/DTA. As shown Figure 7, the conversion of all

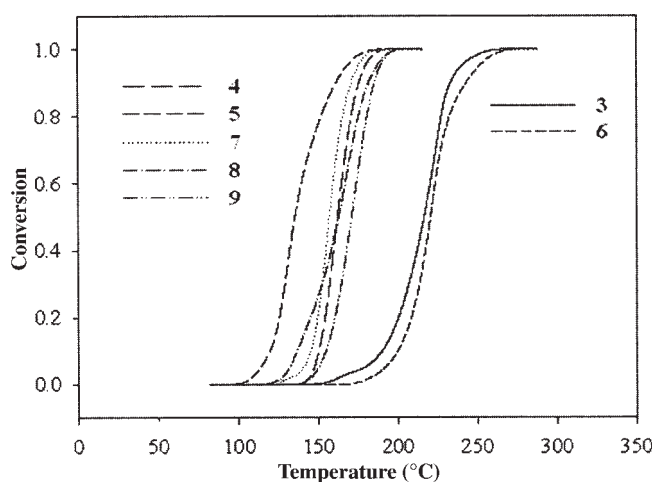


Figure 7 Conversion curves of DGEBA cured by each catalyst (3–9) as a function of the curing temperature.

TABLE III
The Glass Transition Temperature (T_g) Studies
of DGEBA with 1-Substituted Imidazole Catalysts (1–10)
at a Concentration of 1 wt %

Catalyst	Glass transition temperature (T_g , °C) ^a	Conversion (%) ^b
1	151	>99
2	150	>99
3	75	>99
4	169	>99
5	154	>99
6	151	>99
7	152	>99
8	221	>99
9	150	>99
10	175	>99

^a The glass transition temperature was obtained from second run of DSC at the heating rate 10°C/min.

^b The conversion was determined by scan of TG/DTA.

catalysts is rapidly activated at a specific temperature. In the case of DGEBA/the 1-substituted imidazoles (4, 5, 7, 8, and 9), the conversion rapidly increased above 120–145°C and decreased gradually above 180–200°C, whereas the conversion of DGEBA/1-tosylimidazole (6) and DGEBA/BPH increased drastically above 180°C. The reactivity of 1-substituted imidazoles (4, 5, 7, 8, and 9) in this epoxy system is higher than that of 6 and BPH. This is because the imidazole moiety is an efficient catalyst in the curing epoxy resins to provide the good physical and mechanical properties. In the DGEBA/1-tosylimidazole (6) case, the reactivity of imidazole was decreased by the strong withdrawing group (tosyl group). As a result, the conversion happened at above 190°C. Meanwhile, the conversion of DGEBA/1-substituted imidazoles (4–9) systems and DGEBA/BPH showed no significant change below 120 or 180°C, respectively. Thus, it is confirmed that all the catalysts of 1-substituted imidazoles (4–9) have excellent latent thermal properties in the epoxy system down to temperature below 120°C.

The cure activation energy (E_a)

The cure behaviors of DGEBA resin with each catalysts (1–10, 1 wt %) were studied with TG/DTA in the dynamic scanning mode. The TG/DTA scans at the different heating rates allowed us to determine the cure activation energy (E_a) of the overall process by the Kissinger method:^{30,50–51}

$$\ln \left[\frac{\phi}{T_m^2} \right] = -\frac{E_a}{RT_m} + \ln \left[\frac{AR}{E_a} \right] \quad (1)$$

where, ϕ is the heating rate; T_m is the temperature of the maximum exothermic peak; A is the pre-exponential factor; and R is the gas constant (8.314 J/g mole K).

E_a can be obtained from the slope of the graph $\ln(\phi/T_m^2)$ versus $(1/T_m)$ on the basis of the eq. (1). In Figure 8, the experimental values of $\ln(\phi/T_m^2)$ are plotted as a function of the reciprocal cure temperature ($1/T_m$). The activation energies are listed in Table IV.

From the straight lines, the E_a values are obtained in the range of 35–88 kJ/mol for DGEBA/imidazole derivatives (1, 2, and 4–10) and DGEBA/BPH.(3). The results suggested that the order of the cure activation energy (E_a) to run a reactively controlled polymerization was estimated to be 6 (86.4 kJ/mol) > 8 (79.1 kJ/mol) > 3 (69.0 kJ/mol) > 9 (67.3 kJ/mol) > 5 (66.5 kJ/mol) > 7 (61.4 kJ/mol) > 4 (54.1 kJ/mol) > 2 (50.1 kJ/mol) > 10 (45.4 kJ/mol) > 1 (35.2 kJ/mol). This tendency of the E_a values is consistent with the viscosity measurements. We believe the activity order for the thermally latent catalytic systems was estimated to be 6 > 8 > 3 > 9 > 5 > 7 > 4 > 2 > 10 > 1 on the basis of the relationship between the viscosity measurements and the E_a values.

The water-absorption properties

DGEBA resin with 1-substituted imidazoles (4–9, 1 wt %) were mixed and cured at 150°C for 7–8 h to study the water-absorption. The specimens of $3 \times 7 \times 50$ mm³ size were exposed to humid environments (72 h at 80°C/80% R.H.). The resulting moisture absorptions are low than 1% wt. When the same size specimens were cooking in the boiling water for 48 h, the average water-absorptions are lower than 0.7% wt.

CONCLUSIONS

In this work, we successful develop a series of 1-substituted imidazole derivatives (4–10) containing imidazole moiety to imitate the polymerization in the molding temperature (100–175°C) due to the imidazole

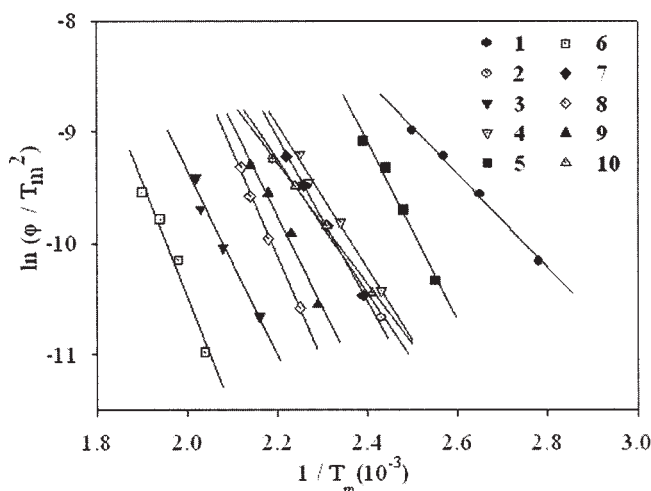


Figure 8 $\ln(\phi/T_m^2)$ versus $(1/T_m)$ Plot for determining the cure activation energy.

TABLE IV
Cure Activation Energy (E_a) Obtained by the Kissinger Equation

Catalyst	Kinetic factors	Heating rate ($^{\circ}\text{C}/\text{min}$)				Slope	E_a (kJ/mol)
		5	10	15	20		
1	$1/T_m$	2.78	2.65	2.57	2.50	-4.23	35.2
	$\ln(\varphi/T_m^2)$	-10.16	-9.56	-9.22	-8.99		
2	$1/T_m$	2.43	2.31	2.25	2.19	-6.02	50.1
	$\ln(\varphi/T_m^2)$	-10.67	-9.84	-9.49	-9.25		
3	$1/T_m$	2.16	2.08	2.03	2.02	-8.33	69.0
	$\ln(\varphi/T_m^2)$	-10.66	-10.04	-9.69	-9.41		
4	$1/T_m$	2.43	2.34	2.27	2.25	-6.50	54.1
	$\ln(\varphi/T_m^2)$	-10.43	-9.81	-9.46	-9.20		
5	$1/T_m$	2.55	2.48	2.44	2.39	-8.00	66.5
	$\ln(\varphi/T_m^2)$	-10.33	-9.70	-9.32	-9.08		
6	$1/T_m$	2.04	1.98	1.94	1.90	-10.39	86.4
	$\ln(\varphi/T_m^2)$	-10.78	-10.15	-9.78	-9.54		
7	$1/T_m$	2.39	2.31	2.26	2.22	-7.39	61.4
	$\ln(\varphi/T_m^2)$	-10.47	-9.84	-9.48	-9.22		
8	$1/T_m$	2.25	2.18	2.14	2.12	-9.52	79.1
	$\ln(\varphi/T_m^2)$	-10.58	-9.96	-9.58	-9.32		
9	$1/T_m$	2.29	2.23	2.18	2.14	-8.31	67.3
	$\ln(\varphi/T_m^2)$	-10.55	-9.91	-9.55	-9.30		
10	$1/T_m$	2.41	2.31	2.24	2.19	-5.46	45.4
	$\ln(\varphi/T_m^2)$	-10.45	-9.84	-9.49	-9.25		

moiety is extensively utilized in the curing epoxy resins to provide the good physical and mechanical properties. To base on the studies of the viscosity and E_a measurement, the activity order of the thermally latent catalytic systems was estimated to be $6 > 8 > 3 > 9 > 5 > 7 > 4 > 2 > 10 > 1$. The thermal latent properties of 4-9 are better than no modify imidazole 1 or the commercial latent catalyst 1-cyanoethyl-2-ethyl-4-methylimidazole 2 (2E4MZ-CN) and similar to the cationic latent catalyst 3 (BHP). Whatever, 1-substituted imidazole derivatives (4-10) were efficient catalysts for DGEBA resin to undergo thermal cure reaction without the generation of the harmful species. But, most of cationic latent catalysts would be released the acidic species by-product (HBF_4 , HPF_6 , HAsF_6 , and HSbF_6) and damaged the electronic products while the curing polymerization due to the reactivity of is enhanced by the nucleophilicity of counterion (e.g., BF_4^- , PF_6^- , AsF_6^- , and SbF_6^-).

The T_g values of 1-substituted imidazole derivatives (4-10, $> 150^{\circ}\text{C}$) are better or similar the commercial available catalysts 1 (imidazole), 2 (2E4MZ-CN), and the cationic latent catalysts 3 (BHP, 75°C). Since, the designed 1-substituted imidazole catalysts 4-10 are very stable at room temperature and prolong the pot-life of DGEBA resin could provide a degree of low storage stability and good handling because of the low reactivity at ambient temperature.

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