ORIGINAL ARTICLE

Curing acceleration of cyanate ester resin by a phenolic compound having a tertiary amino group at the ortho-position

Keisuke Izu[1] · Yuichiro Tokoro[1] · Toshiyuki Oyama [1]

Abstract

To develop a novel organic catalyst that can effectively cure cyanate ester resins, the effects of incorporating various phenolic compounds on the curing of bisphenol A dicyanate (BADCY) was investigated. Differential scanning calorimetry (DSC) and Fourier transform infrared (FT-IR) spectroscopy analyses revealed that *o*-(dimethylamino)methylphenol (*o*-DAMP) was a highly effective catalyst for accelerating the curing of BADCY, and the addition of *o*-DAMP reduced the final curing temperature of BADCY to 180 °C. The promoting effect of *o*-DAMP was found to be due to the presence of an acidic phenolic OH group and a basic (dimethylamino)methyl group at the ortho-positions of the molecule. The addition of *o*-DAMP improved the modulus, strength and fracture toughness (K_{IC}) of the cured BADCY resins. The mechanical and thermal properties of the cured resins could be adjusted by changing the amount of *o*-DAMP.

Introduction

Cyanate ester resin is a high-performance thermosetting resin that forms a networked polymer by the cyclotrimerization reaction of cyanate ester groups to give a cured product with high heat resistance, low water absorption and high electrical insulation (Scheme 1) [1–5]. Based on these properties, cyanate ester resin is expected to be a promising candidate in many advanced applications, such as the high-performance encapsulating resin for electronic devices including SiC power semiconductor devices, high-temperature adhesives and structural materials for the aerospace industry [6–14].

However, cyanate ester resin has the disadvantage that the curing of the resin requires prolonged high temperatures (250 °C or higher), and such curing can damage the product to which the resin is applied. To overcome this

disadvantage, catalysts are usually added to the curing system to promote the polymerization of the resin. The most common catalysts are mixtures of carboxylates or chelate salts of transition metal ions (Cu^{2+}, Co^{2+}, Zn^{2+}, etc.) and cocatalysts (such as *p*-nonylphenol) [7], but curing at 230 °C or higher is usually required even in the presence of such catalysts. Furthermore, the metal ions in the catalyst remain in the cured resin, and these residual metal ions can adversely affect the properties of the cured resin. For these reasons, attempts have been made to promote the curing of cyanate ester resin by adding catalysts that do not contain metal ions [13–19]. In particular, the addition of active hydrogen compounds containing alcoholic and phenolic –OH and –NH_2 groups that can react with cyanate ester groups has been widely studied [13–16]. For example, Ma et al. reported that the addition of poly(ethylene glycol) promotes the polymerization of cyanate ester resins [15], and Lin et al. cured cyanate ester resin at a final curing temperature of 200 °C by adding a polymeric microsphere with phenolic –OH or –NH_2 groups [14]. However, to our knowledge, few studies have successfully cured cyanate ester resin at a final curing temperature below 200 °C in the absence of metal ions.

Thus, we explored a novel nonmetallic catalyst that could cure a cyanate ester resin below 200 °C by using bisphenol A dicyanate (BADCY) as a typical cyanate ester resin. In this study, we focused on compounds having phenolic OH groups because they are readily available in

✉ Toshiyuki Oyama
 oyama-toshiyuki-wz@ynu.ac.jp

1 Department of Chemistry and Life Science, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
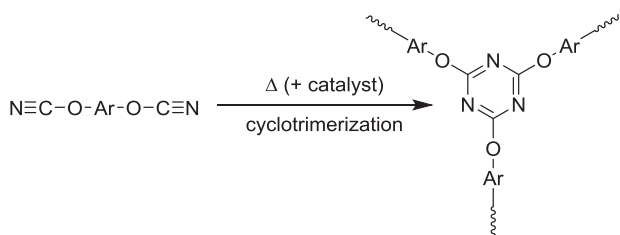
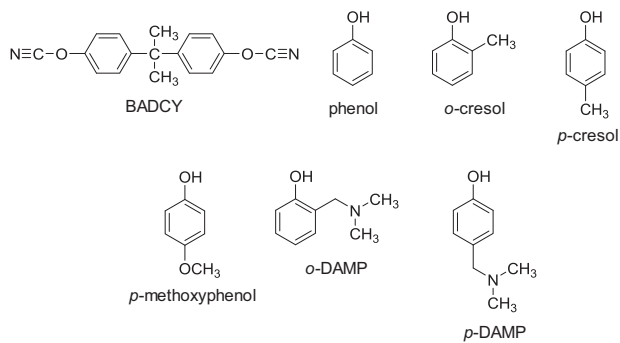**Scheme 1** Cyclotrimerization of cyanate ester resin

Fig. 1 Chemical structures of the compounds used in this study

various structures. To enhance the reactivity of the phenolic OH groups toward cyanate ester groups, we examined the addition of phenolic compounds having electron-donating groups and the activation of the phenolic OH groups by acid-base interactions. The resins were cured using the most effective catalyst in various amounts, and their thermal and mechanical properties were also investigated.

Experimental

Materials

The structures of the compounds used in this study are shown in Fig. 1. BADCY was kindly donated by Mitsubishi Gas Chemical Company, Inc (Tokyo, Japan). o-(Dimethylamino)methylphenol (o-DAMP) (containing 22 mol% phenol) and p-cresol were purchased from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan). Phenol, o-cresol and p-methoxyphenol were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). p-(Dimethylamino)methylphenol (p-DAMP) was synthesized according to the literature [20].

Preparation of the cured resins

The preparation of the cured product of BADCY by using o-DAMP as the catalyst with a ratio between OCN in BADCY and OH in o-DAMP of 1.0:0.05 is described as a typical example. BADCY (9.53 g, 68.4 mmol of OCN) was

melted at 100 °C for 20 min and then naturally cooled to 90 °C. o-DAMP (0.465 mL, 3.42 mmol of OH) was added to the melted BADCY and mixed at 90 °C for 1 min. The resulting mixture was molded to aluminum metal casting plates preheated at 90 °C and then degassed under reduced pressure for 20 min at this temperature. The molded and degassed mixture was heated at 120 °C/2 h + 150 °C/2 h + 180 °C/6 h to give a cured resin.

Measurement

Differential scanning calorimetry (DSC) analysis was performed on a DSC-60 (Shimadzu Corp. (Kyoto, Japan)) at a heating rate of 10 °C/min under a nitrogen atmosphere to evaluate the effects of phenolic compounds on the curing of BADCY. The exothermic onset temperatures (T_{onset}s) were determined from the intersections of the tangents of the DSC thermograms. Fourier transform infrared (FT-IR) spectra were acquired with a SPECTRUM ONE system (PerkinElmer Inc. (Waltham, MA, USA)) to examine the progress of the reaction in the actual curing process when preparing the cured products. Specimens for measuring the mechanical properties were prepared by cutting the obtained cured resins with a diamond saw and polishing the cut surface with sandpaper (P240, 800 and 800/2400). The flexural properties of the specimens were measured by a three-point bending test with an AG-X 10 kN universal testing machine (Shimadzu Corp.) at a crosshead speed of 2 mm/min according to JIS K7203. The critical stress intensity factor (K_{IC}), as an index of fracture toughness, was measured with an AG-X 10 kN universal testing machine (Shimadzu Corp.) at a crosshead speed of 10 mm/min according to ASTM D5045. Dynamic mechanical analysis (DMA) was performed on a DMS6100 system (SII Nano-Technology Inc. (Tokyo, Japan)) at a heating rate of 5 °C/min and a frequency of 1.0 Hz under an air atmosphere. Thermogravimetric analysis (TGA) was performed on a TGA-50 instrument (Shimadzu Corp.) at a heating rate of 10 °C/min under a nitrogen atmosphere.

Results and discussion

Effects of adding various phenolic compounds on the reaction behavior of BADCY

DSC analyses of the mixtures between BADCY and various phenolic compounds were performed at a ratio of OCN/OH = 1.0/0.05 to investigate the effects of the structures of the phenolic compounds on the reaction behavior. The results of the DSC analyses are shown in Fig. 2, and their T_{onset}s and peak temperatures (T_{peak}s) are provided in Table 1. BADCY itself showed T_{onset} and T_{peak} at 271 °C and 311 °C,
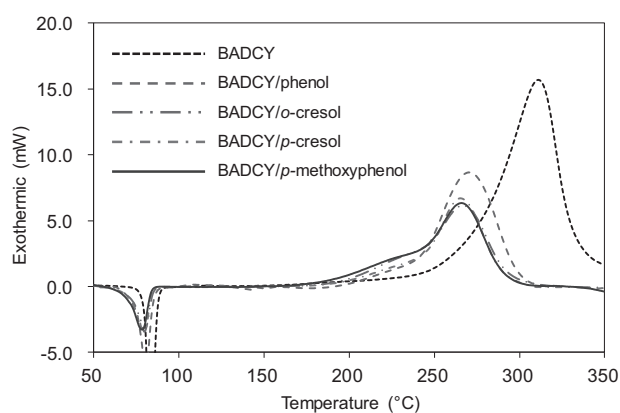
Fig. 2 DSC thermograms of BADCYs in the absence and presence of phenolic compounds (OCN/OH = 1.0/0.05)

Fig. 3 DSC thermograms of BADCYs in the absence and presence of phenol, o-DAMP and p-DAMP (OCN/OH = 1.0/0.05)

Table 1 The results of the DSC analysis of the mixtures between BADCY and phenolic compounds[a]

Phenolic compound	OH/OCN	T_{onset} [°C]	T_{peak} [°C]
None	–	271	311
phenol	0.05	197	272
o-cresol	0.05	187	267
p-cresol	0.05	189	265
p-methoxyphenol	0.05	173	266
o-DAMP[b]	0.05	108	141, 194
p-DAMP[b]	0.05	142	208
o-DAMP[b]	0.03	110	144, 242
o-DAMP[b]	0.07	103	136, 183
o-DAMP[b]	0.09	108	136, 186

[a]Heating rate: 10 °C/min, under N_2 (50 mL/min)

[b]Containing 22 mol% phenol

respectively, while T_{onset} and T_{peak} of BADCY/phenol were observed at 197 °C and 272 °C. These results indicate that the addition of phenol promotes the curing of the cyanate ester resin, as reported in the previous literature [13, 16].

The addition of phenolic compounds with electron-donating groups, which are expected to increase the nucleophilicity of the phenolic OH groups, was then examined. The DSC analysis of the mixtures between BADCY and o-cresol, p-cresol or p-methoxyphenol caused further decreases in T_{onset}s (Fig. 2 and Table 1). In particular, the T_{onset} of BADCY/p-methoxyphenol was at 173 °C, which is 24 °C lower than that of BADCY/phenol. On the other hand, it was found that their T_{peak}s hardly changed. These results suggest that the introduction of electron-donating groups into the phenol structure does not sufficiently promote the curing of cyanate ester resins.

Then, we investigated the use of acid-base interactions to enhance the reactivity of the phenolic OH groups. The effects of the addition of o-DAMP, which possesses both phenolic OH and tertiary amino groups, on the exothermic
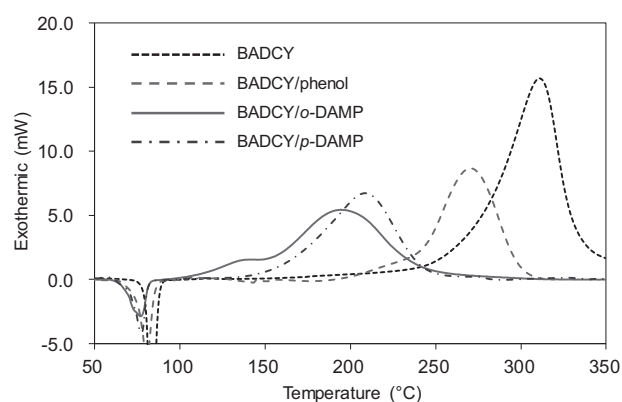
behavior of BADCY were examined. The acid-base interactions between the phenolic OH and (dimethylamino) methyl groups are expected to enhance the nucleophilicity of the hydroxyl group by attracting the proton of the OH to the amino group, thereby promoting the reaction between the phenolic OH and the cyanate ester groups. The results of the DSC analyses with and without o-DAMP are shown in Fig. 3 and Table 1. The T_{onset} and the main T_{peak} of BADCY/o-DAMP were at 108 °C and 194 °C, and these temperatures were found to be 89 °C and 78 °C lower than those of BADCY/phenol, respectively. This result indicates that the activation of the phenolic OH groups by acid-base interactions is effective for promoting the curing of cyanate ester resins.

To further investigate the effects of introducing a (dimethylamino)methyl group on phenolic compounds, BADCY/p-DAMP was analyzed by DSC (Fig. 3, Table 1). The exothermic behavior of BADCY/p-DAMP was found to be different from that of BADCY/o-DAMP, with the T_{onset} and T_{peak} of the former being 34 °C and 14 °C higher than those of the latter, respectively. This result demonstrates that introducing a tertiary amino group at the ortho-position of the phenolic OH group is more effective for curing than introducing the same group at the para-position. We also measured FT-IR spectra of the mixtures of BADCY with o-DAMP, p-DAMP and phenol before the DSC measurements to elucidate the mechanism of the reaction promotion. The results are shown in Fig. 4, and the absorption of iminocarbonate (–O–C(=NH)–O–) [11, 15, 21, 22] at 1680 cm^{-1} appeared in the spectra of BADCY/o-DAMP and BADCY/p-DAMP, while no such absorption was observed in the spectrum of BADCY/phenol. This indicates that both the intramolecular acid-base interaction of o-DAMP and the intermolecular acid-base interaction of p-DAMP can effectively promote the reaction between the phenolic OH and cyanate ester to form an iminocarbonate group.

These results suggest that the acid-base interactions caused by the introduction of a tertiary amino group may promote the reaction between OCN and phenolic OH groups to form an iminocarbonate that can be cyclotrimerized with another two monomers (Scheme 2a). In addition, when the tertiary amino group is located ortho to the OH group, intramolecular cyclization between the iminocarbonate and the tertiary amino group would further form an
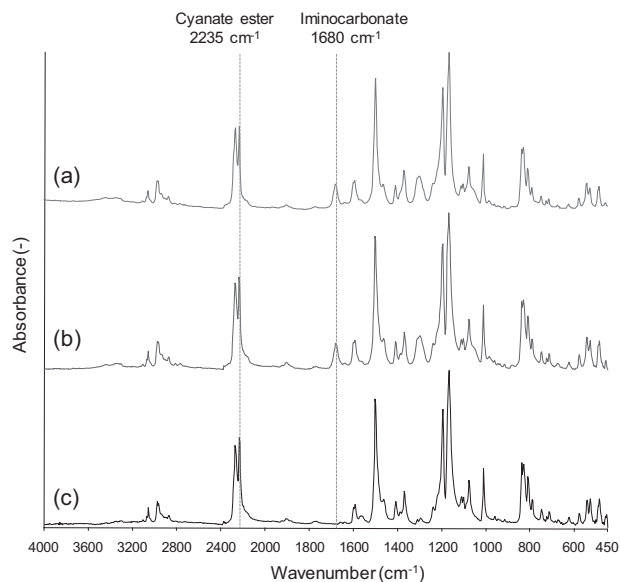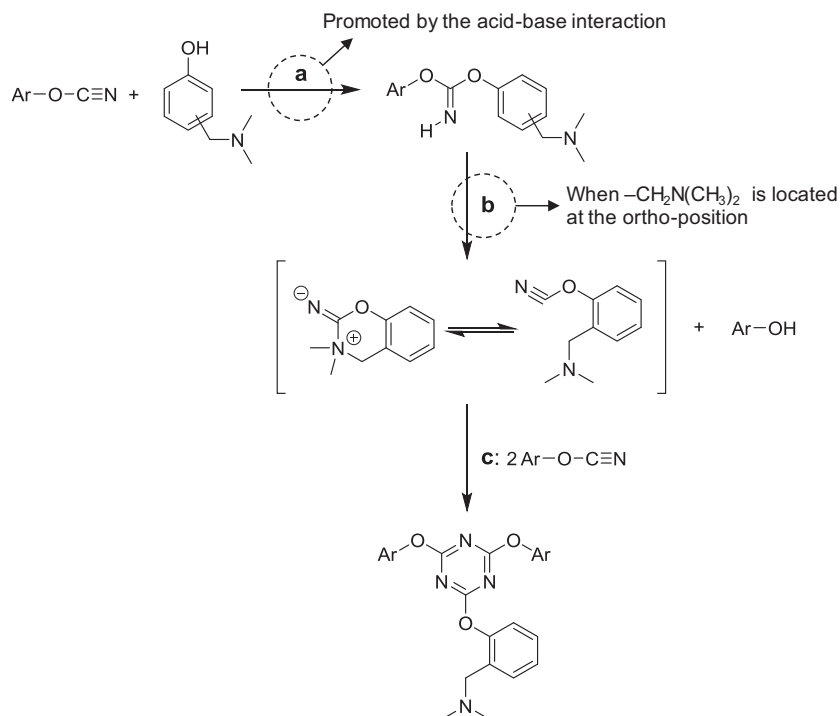

Fig. 4 FT-IR spectra of (**a**) BADCY/*o*-DAMP, (**b**) BADCY/*p*-DAMP and (**c**) BADCY/phenol before the DSC measurements (OCN/OH = 1.0/0.05)

intermediate with a six-membered ring structure (Scheme 2b), and this reactive intermediate would readily react with two more OCN groups to give a triazine ring with an *o*-DAMP moiety (Scheme 2c). The resulting product has two basic groups (the triazine ring [23] and the (dimethylamino)methyl group), and these are expected to promote the reaction between the cyanate ester and the Ar–OH released during the reaction in Scheme 2 by intermolecular acid-base interactions, which accelerates the overall curing reaction of this system [24, 25]. Although direct spectral evidence of the incorporation of *o*-DAMP into the network of BADCY has not been obtained, the crosslink density of the cured resin decreased as the amount of *o*-DAMP was increased, which suggests the incorporation of *o*-DAMP into the polymer network (see the section "Properties of the BADCYs cured in the presence of *o*-DAMP as a catalyst").

The effects of the amount of *o*-DAMP on the reaction behavior were also investigated by using DSC analysis. The results are shown in Fig. S1 and Table 1, and it was confirmed that the T_{peak} of BADCY/*o*-DAMP decreased as the amount of *o*-DAMP increased.

Curing behavior of the BADCY/*o*-DAMP system

We then examined the curing behavior of BADCY/*o*-DAMP under stepwise heating, which is commonly used in the actual preparation of cured cyanate ester resin products. The cured resins were prepared under stepwise heating conditions with final curing temperatures of 170 and 180 °C, and the progress of the curing was monitored based

Scheme 2 Presumed curing mechanism of cyanate ester resin in the presence of *o*-DAMP

Fig. 5 FT-IR spectra of BADCY/*o*-DAMPs cured at (a) 120 °C/2 h + 150 °C/2 h + 170 °C/6 h and (**b**) 120 °C/ 2 h + 150 °C/2 h + 180 °C/ 6 h (OCN/OH = 1.0/0.05)
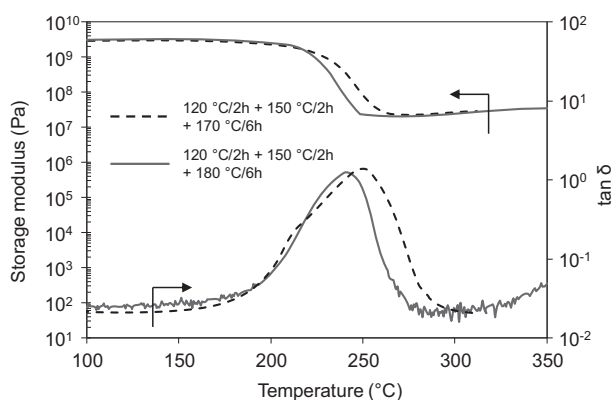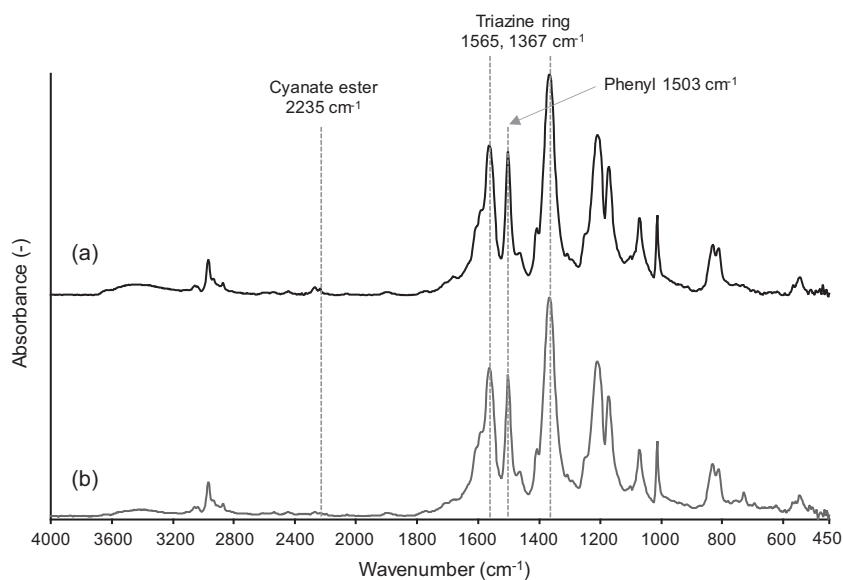

Fig. 6 DMA results of BADCY/*o*-DAMPs cured under different conditions (OCN/OH = 1.0/0.05)

on the decrease in the absorption of the OCN group at 2235 cm^{-1} relative to the absorption of the phenyl group at 1503 cm^{-1} in the FT-IR spectra (Fig. 5). The ratio between the absorptions of the OCN and phenyl groups ($A_{\text{-OCN}}/A_{\text{-phenyl}}$) in the cured resin prepared at a final curing temperature of 180 °C was 0.027, while the $A_{\text{-OCN}}/A_{\text{-phenyl}}$ of the cured resin prepared at a final curing temperature of 170 °C was 0.046. These results suggest that the progress of the curing is better when the final curing temperature is 180 °C. We also conducted DMA of the cured resins to evaluate the effect of the final curing temperatures on the properties of the cured resins (Fig. 6). In the tan δ plot of the resin cured at a final curing temperature of 180 °C, a single peak was observed at 241 °C, which suggests sufficient curing of the resin. However, a shoulder peak was observed at 220 °C along with the main peak at 250 °C in the tan δ plot of the resin cured at a final temperature of 170 °C. The appearance of the two peaks indicates insufficient curing under these

conditions; that is, the original T_g of the cured resin would be 220 °C, and when the measuring temperature of the DMA exceeds this temperature, the remaining OCN groups would react again to raise the T_g. The results of the FT-IR and DMA measurements show that the utilization of *o*-DAMP as a catalyst enables the production of a sufficiently cured BADCY at a final curing temperature of 180 ° C, which is lower than the curing temperatures required with existing catalysts.

The FT-IR spectra of the BADCY/*o*-DAMP system were then acquired at each curing step to examine the curing behavior in detail (Fig. 7). The intensities of the absorptions of OCN at 2235 cm^{-1} and iminocarbonate group at 1680 cm^{-1} decreased, and the absorptions assignable to triazine ring at 1565 and 1367 cm^{-1} increased in intensity as the curing proceeded. The FT-IR spectra of BADCY without a catalyst were also measured at each curing step (Fig. S2), and the change in $A_{\text{-OCN}}/A_{\text{-phenyl}}$ for each curing step in BADCY/*o*-DAMP was compared with the changes in BADCY without a catalyst (Fig. 8). The $A_{\text{-OCN}}/A_{\text{-phenyl}}$ of BADCY/*o*-DAMP was found to be much smaller than that of BADCY without a catalyst from the early stages of curing. In addition, the increase in the absorptions of the triazine ring in BADCY/*o*-DAMP was larger than that in BADCY without a catalyst from the early stages of curing, especially at 120 °C/2 h and 120 °C/2 h + 150 °C/2 h (see Figs. 7 and S2). These results suggest that the addition of *o*-DAMP is a very effective strategy for promoting the curing of cyanate ester resins.

Furthermore, the effect of the amount of *o*-DAMP on the curing of BADCY was investigated. The FT-IR spectra of the BADCYs cured up to a final curing temperature of 180 °C with different amounts of *o*-DAMP were measured, and the results are shown in Fig. S3. In all the spectra, large

Fig. 7 FT-IR spectra of BADCY/*o*-DAMP at each curing step (OCN/OH = 1.0/0.05); (i) before curing, (ii) after 120 °C/2 h, (iii) after 120 °C/2 h + 150 °C/2 h, (iv) after 120 °C/2 h + 150 °C/2 h + 180 °C/2 h, and (v) after 120 °C/2 h + 150 °C/2 h + 180 °C/6 h

Fig. 8 Changes in $A_{-OCN}/A_{-phenyl}$ for each curing step in BADCY/*o*-DAMP (OCN/OH = 1.0/0.05) and BADCY without a catalyst; (i) before curing, (ii) after 120 °C/2 h, (iii) after 120 °C/2 h + 150 °C/2 h, (iv) after 120 °C/2 h + 150 °C/2 h + 180 °C/2 h, and (v) after 120 °C/2 h + 150 °C/2 h + 180 °C/6 h
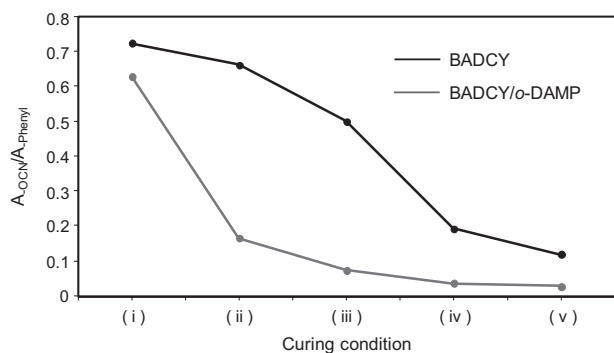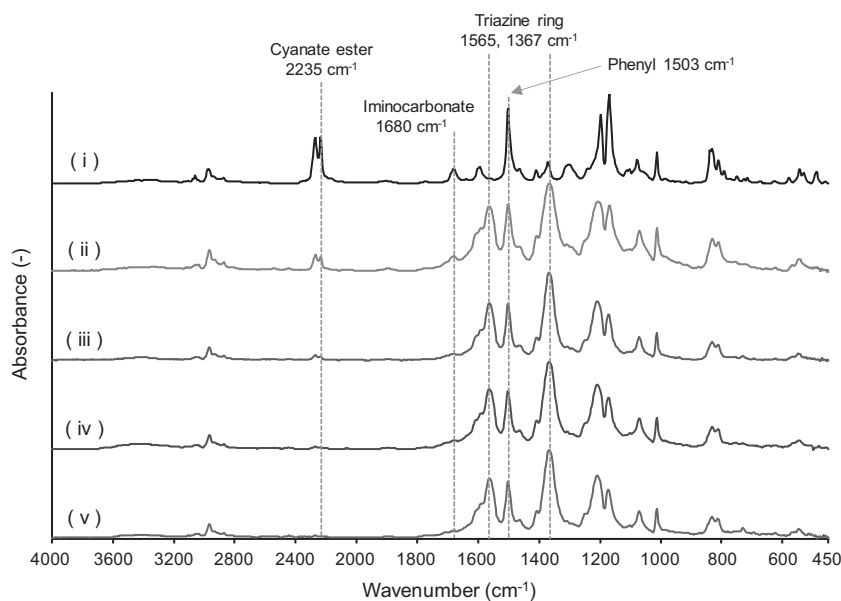

Fig. 9 DMA results of BADCY/*o*-DAMPs with different ratios between OCN in BADCY and OH in *o*-DAMP

absorptions for the triazine ring were observed at 1565 and 1367 cm^{-1}. On the other hand, the absorption of OCN at 2235 cm^{-1} decreased with increasing amount of *o*-DAMP, and it almost completely disappeared when the ratio of OH in *o*-DAMP to OCN in BADCY was 0.05 or more. We also conducted DMA of the BADCYs cured up to a final curing temperature of 180 °C with different amounts of *o*-DAMP (Fig. 9). The numbers at the right of the sample names indicate the ratio of OH in *o*-DAMP to OCN in BADCY. The results of BADCY cured without any catalyst clearly indicated that the resin was not sufficiently cured. The tan δ plot of BADCY/*o*-DAMP0.03 showed a peak at 258 °C with shoulder peaks at lower temperatures. The presence of such peaks suggests insufficient curing of the resin. In other words, the unreacted OCN groups would react at temperatures higher than the shoulder peak temperatures, thereby increasing the T_g of the resin. On the other hand, such
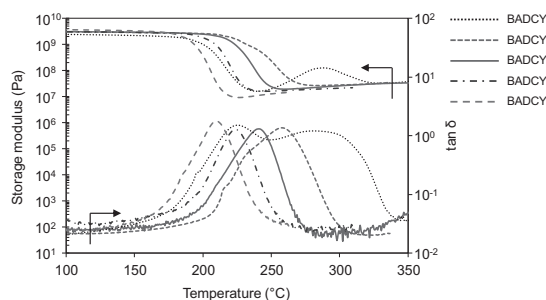
behavior was not observed in the tan δ plots for the cured resins with a ratio of OH in *o*-DAMP to OCN in BADCY was 0.05 or more, and these results were in agreement with those of the FT-IR spectra (Fig. S3). The results of the FT-IR and DMA measurements shown above revealed that BADCY can be sufficiently cured at a final curing temperature of 180 °C by adding *o*-DAMP with a ratio of OH in *o*-DAMP to OCN in BADCY was 0.05 or more.

Properties of the BADCYs cured in the presence of *o*-DAMP as a catalyst

The mechanical and thermal properties of the BADCYs cured up to a final curing temperature of 180 °C with varying amounts of *o*-DAMP are shown in Table 2. For comparison, the mechanical properties, crosslink density and T_g of the BADCY cured in the absence of a catalyst by heating to a final curing temperature of 250 °C are also shown in the table. The flexural modulus and the strength of the cured resins were found to be increased by the addition of *o*-DAMP. The fracture toughness (K_{IC}) of BADCY/*o*-DAMP

Table 2 Mechanical and thermal properties of BADCY/o-DAMPs with different ratios between OCN in BADCY and OH in o-DAMP[a]

Sample	Flexural properties		K_{IC} [MN/m$^{3/2}$]	Crosslink density[b,c] [kmol/m^3]	T_g [°C][b]	T_{d5} [°C][d]	Char yield [%][d,e]
	Modulus [GPa]	Strength [MPa]					
BADCY	3.04 ± 0.04[f]	191 ± 4[f]	0.52 ± 0.02[f]	–[g], (1.86)[f]	–[g], (297)[f]	389	35.1
BADCY/o-DAMP0.03	3.61 ± 0.05	204 ± 13	0.65 ± 0.03	(1.96)[g]	(258)[g]	342	30.9
BADCY/o-DAMP0.05	3.70 ± 0.05	199 ± 15	0.66 ± 0.02	1.41	241	310	25.9
BADCY/o-DAMP0.07	3.42 ± 0.13	207 ± 13	0.75 ± 0.05	1.21	224	293	27.9
BADCY/o-DAMP0.09	3.83 ± 0.04	188 ± 13	0.87 ± 0.07	0.75	210	282	25.1

[a]Curing condition: 120 °C/2h + 150 °C/2h + 180 °C/6h

[b]By DMA (heating rate: 5 °C/min, frequency: 1.0 Hz)

[c]Calculated by E′/RT (E′: the smallest value of the storage modulus at the rubbery plateau in DMA)

[d]By TGA (heating rate: 5 °C/min, under N$_2$, 50 mL/min)

[e]At 800 °C

[f]Value of the sample cured at 120 °C/2h + 150 °C/2h + 180 °C/2h + 200 °C/4h + 250 °C/2h

[g]Insufficient curing was suggested in the DMA chart

also increased with increasing amounts of o-DAMP. On the other hand, the T_gs determined from the tan δ peaks of the DMA charts (Fig. 9) and T_{d5}s and char yields obtained from TGA charts (Fig. S4) decreased as the amount of o-DAMP increased. These results indicate that the thermal and mechanical properties of the cured resins can be tuned by changing the amount of o-DAMP, and the most balanced properties were obtained with BADCY/o-DAMP0.05.

The changes in the thermal and mechanical properties shown above can be explained by the decrease in the degree of crosslinking with increasing amounts of o-DAMP. The crosslink density calculated by E′/RT, where E′ is the smallest value of the storage modulus in the rubbery plateau, R is the gas constant and T is the absolute temperature [26–28], actually decreased with increasing amounts of o-DAMP (Table 2). As shown in Scheme 2, o-DAMP is considered to be incorporated into the network structure, and this incorporation reduces the degree of crosslinking, decreasing the thermal properties. On the other hand, the decrease in the degree of crosslinking increases the motion of the chains between the crosslinking points and would allow effective packing of the chains during cooling after curing. As a result, the interactions between the chains in the cured resins would be increased, improving their mechanical properties. A similar relationship between the degree of crosslinking and the packing of the chains has also been reported for epoxy resins [29].

Conclusion

The effect of adding various phenolic compounds on the curing of BADCY was examined, and the introduction of a (dimethylamino)methyl group into the phenolic structure was found to be effective for curing acceleration. The use of o-DAMP with a (dimethylamino)methyl group ortho to the phenolic OH group was particularly effective, and sufficient curing of BADCY at the final curing temperature of 180 °C was achieved by adding o-DAMP at a ratio of OH in o-DAMP to OCN in BADCY was 0.05 or more. The resulting cured products had better mechanical properties, including modulus, strength and fracture toughness than the fully cured BADCY without any catalyst. In addition, the mechanical and thermal properties of the cured BADCY could be adjusted by changing the amount of o-DAMP, which is expected to be suitable for industrial applications. The curing mechanisms and curing kinetics of BADCY in the presence of o-DAMP are currently being investigated in more detail, and the results will be reported elsewhere.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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