

Preparation, Characterization, and Polymerization of Novel Maleimidobenzoxazine Containing Carboxylic Moiety and Its Curing Behaviors with Epoxy Resin

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Received 28 September 2009; accepted 24 March 2010

DOI 10.1002/app.32503

Published online 24 May 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel benzoxazine containing maleimide and carboxylic moieties, 1-[3-(4-carboxylphenyl)-3,4-dihydro-2H-benzo[e][1,3]-oxazin-6-yl]maleimide (Mal-Bz-Co), was synthesized and the structure was identified by $^1\text{H-NMR}$ and FTIR. Mal-Bz-Co exhibited good solubility in common organic solvents. The cure behavior of Mal-Bz-Co and cocure behavior of Mal-Bz-Co with *o*-cresol formaldehyde epoxy resin were investigated by differential scanning calorimetry. Results indicated that Mal-Bz-Co showed a single curing exothermic peak at about 238.3°C. However, the maximum curing tempera-

ture (T_p) decreased to 146.1°C when Mal-Bz-Co cocured with *o*-cresol formaldehyde epoxy resin in the molar ratio of 1 : 1. The T_p was about 92°C lower than that of Mal-Bz-Co. Thermogravimetric analysis showed that high-decomposition temperature and char yield were observed for the cured resins of Mal-Bz-Co and Mal-Bz-Co/*o*-CFER. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 705–710, 2010

Key words: benzoxazine; maleimide; carboxylic; epoxy resin; thermal properties

INTRODUCTION

Phenolic resin is used widely as an industrial material because of its good heat resistance, electrical insulation, dimensional stability, flame resistance, and chemical resistance.¹ However, a number of shortcomings are also associated with these materials. For example, they are brittle, they have poor shelf life, and they release by-products such as water and ammonia compounds during the curing process, which sometimes affect the properties of cured resins by forming micro voids.²

In recent years, a new type of phenolic resin, called polybenzoxazine, has attracted considerable attention because of its capability to overcome the aforementioned shortcomings.³ No need of strong acidic or basic catalysts and no generation of by-products during the curing process are attractive properties of polybenzoxazines.⁴ In addition, polybenzoxazines also exhibit some unique properties such as high flexibility in molecular design, low-moisture absorption, good thermal stability, electrical property, and excellent resistance to chemicals

and UV light, superior dimensional stability according to the low-volumetric shrinkage on curing.^{5–7} Furthermore, benzoxazine is a new kind of high-performance composite matrix and polybenzoxazine can be used as resin matrix for resin transfer molding (RTM) technology.⁸

According to the high flexibility in molecular design, some functional moieties could be incorporated into the benzoxazine monomer to improve its properties. Incorporation of the maleimide functionality into monofunctional benzoxazine resulted in an increase of char yield and glass transition temperature. Furthermore, the benzoxazine compound with a maleimide pendant show attractive processing and thermal properties.^{9–11}

From a processing point of view, a benzoxazine monomer with low-polymerization temperature is highly desired.¹¹ Benzoxazine can cure at elevated temperature without catalysts, but it can also cure at lower temperature in the presence of catalysts such as acid, which is because of the strong basicity of the N and O atoms by Lewis definition makes the ring very likely to be opened via a cationic mechanism.¹² Carboxylic acid can effectively catalyze the thermal curing of benzoxazine at lower temperature. Therefore, incorporation of the carboxylic moieties into benzoxazine can lower the curing temperature and improve the properties of the produced polymers.^{13,14}

Despite their high moduli and T_g , the polybenzoxazines have been shown to display surprisingly low-

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Contract grant sponsor: Planned Science and Technology Project of Hunan Province; contract grant number: 2008FJ3208.

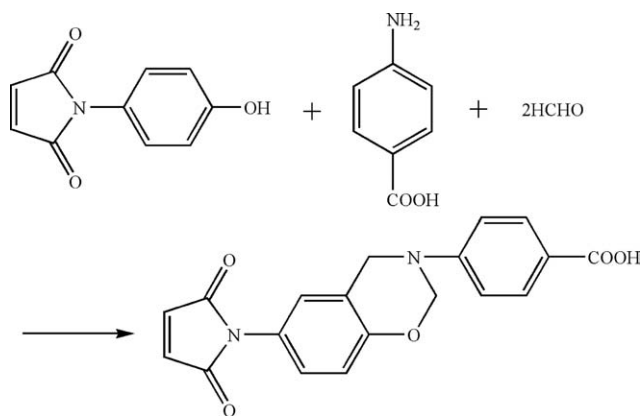


Figure 1 Preparation of Mal-Bz-Co.

crosslink densities in comparison with ordinary thermosetting resins, which is due to the strong hydrogen bonding restricting segmental mobility and impeding network formation.^{7,15} Curing of the benzoxazine with epoxy may allow the network structure to achieve a higher crosslink density. The phenolic groups, which were produced during the ring-opening polymerization of benzoxazines, have been shown to react with epoxy resins at elevated temperatures.^{15–17} Furthermore, curing of the benzoxazine with epoxy can improve the toughness of the produced polymers.^{18,19}

Therefore, benzoxazine containing maleimide and carboxyl moieties was synthesized in this article. The curing behavior of the benzoxazine, the curing behavior of the benzoxazine/epoxy blends, and the properties of the cured resins were discussed.

EXPERIMENTAL

Materials

4-Aminophenol, maleic anhydride, isopropanol, *N,N*-dimethylformamide (DMF), tetrahydrofuran, dioxane, 1,2,4,5-benzotetracarboxylic acid dianhydride (PMDA) 4-aminobenzoic acid, paraformaldehyde, and 1,2,3,6-tetrahydro-3,6-methanophthalic anhydride (MA) were purchased from Shanghai Chemistry Reagent Company. All chemicals used were AR grade and used as received. *o*-Cresol formaldehyde epoxy resin (*o*-CFER, melting point: 73°C) was kindly supplied by Baling Petrochemical Corporation of China.

Measurements

Fourier transform infrared (FTIR) spectra were obtained with a WQF-410 spectrophotometer (Beijing Second Optical Instrument Factory). Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded on a INOVA-400 instrument (Siemens Company of German). Differential scanning calorimetry

(DSC) and thermogravimetric analysis (TGA) were conducted with a NETZSCH STA 449C at a heating rate of 10°C/min under argon atmosphere.

Synthesis of *N*-(4-hydroxyphenyl) maleimide (HPM)

The HPM was synthesized according to Liu et al.^{20,21} The product was yellow needles with melting point 179°C. ¹H-NMR (400 MHz, CDCl₃, 298 K), ppm: δ = 5.15 (s, -OH), 6.85 (2H, -CH=CH-), 6.9–7.2 (4H, Ar); IR (KBr, cm⁻¹): 3480 (Ph-OH), 1705 (C=O), 1602 and 1518 (Ph and C=C of maleimide), 1385 (C-N stretching).

Synthesis of 1-[3-(4-carboxylphenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl] maleimide (Mal-Bz-Co)

A mixture of HPM (10 mmol, 1.89 g), 4-aminobenzoic acid (10 mmol, 1.37 g), paraformaldehyde (20 mmol, 0.60 g), and isopropanol (20 mL) was added to a flask and stirred at 80°C for 8 h. The reaction is shown in Figure 1. The product was filtered, washed with isopropanol (to remove the unreacted reagents), and vacuum dried. Then the primary product was dissolved in dioxane. By-product (the triazine intermediate²²) was filtered out, and the solvent of the filtrate was evaporated by vacuum distillation. The last product was vacuum dried, and 1.8 g Mal-Bz-Co was obtained.

Blending sample preparation

Blends of Mal-Bz-Co/*o*-CFER were prepared with molar ratios of 1 : 2, 1 : 1, and 2 : 1 for DSC studies and 1 : 1 for FTIR studies and thermal property determinations. The structure of *o*-CFER was shown in Figure 2. The two materials were weighed and dissolved in tetrahydrofuran together. The solution was placed onto a piece of metal plate. After most of the solvent was removed under ambient atmosphere at 60°C, the metal plate was placed into a vacuum oven at 60°C for 24 h to remove the residual solvent. After that, the vacuum oven was subjected to a step curing procedure as follows: 100°C (2 h), and 130°C (2 h), 170°C (2 h). The step cure procedure was according to the DSC studies of the materials. Then

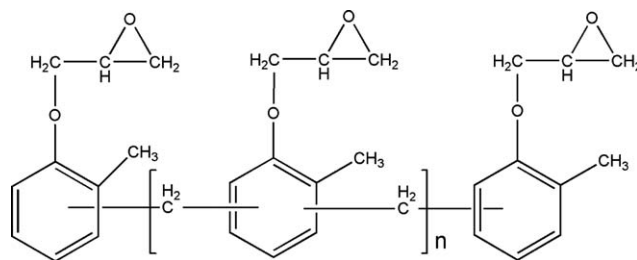


Figure 2 Structure of *o*-cresol formaldehyde epoxy resin.

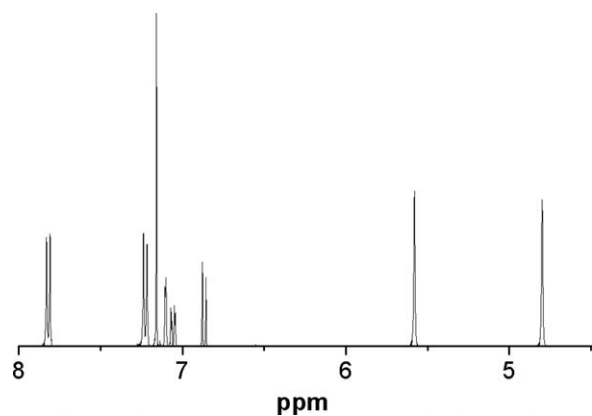


Figure 3 $^1\text{H-NMR}$ of Mal-Bz-Co in $\text{DMSO-}d_6$.

the samples were slowly cooled to room temperature over several hours.

RESULTS AND DISCUSSION

Preparation of Mal-Bz-Co

Mal-Bz-Co was prepared from HPM, paraformaldehyde, and 4-aminobenzoic acid by the solution method (Fig. 1). As found in the $^1\text{H-NMR}$ of the primary product, the primary impurity is triazine intermediate. However, it was found that the triazine intermediate was not soluble in the common organic solvents such as acetone, tetrahydrofuran, dioxane, and DMF. Mal-Bz-Co showed good solubility in these solvents. So the triazine intermediate could be removed according to the difference of solubility.

The chemical structure of Mal-Bz-Co was identified by $^1\text{H-NMR}$ and FTIR. As shown in Figure 3, the oxazine ring was characterized with the absorption peaks at 4.80 ppm (2H, $-\text{Ph-CH}_2-\text{N}-$) and 5.58 ppm (2H, $-\text{O-CH}_2-\text{N}-$).^{9-11,23,24} The absorption peaks at 6.85 ppm and 6.90 ppm (2H) were assigned to the protons of the maleimide group,

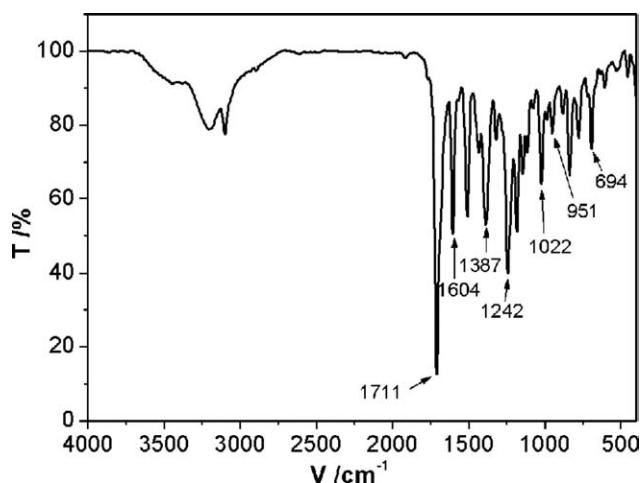


Figure 4 FTIR spectrum of Mal-Bz-Co.

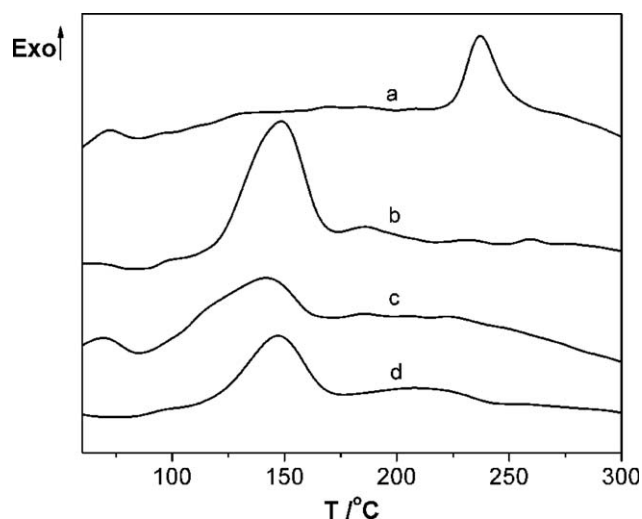


Figure 5 DSC thermograms of Mal-Bz-Co (a) and Mal-Bz-Co/*o*-CFER with molar ratios of 1 : 2 (b), 1 : 1 (c), and 2 : 1 (d).

whereas the peaks at 7.10–7.83 ppm (7H) were assigned to benzene ring. The structure of the monomer was also confirmed by FTIR. The oxazine ring of Mal-Bz-Co was observed with the characteristic absorptions in FTIR spectrum (Fig. 4) at 1242 cm^{-1} (asymmetric stretching of C-O-C), at 1022 cm^{-1} (symmetric stretching of C-O-C), at 1387 cm^{-1} (C-N-C), and at 951 cm^{-1} (oxazine ring).^{25,26} Absorption bands in the FTIR spectrum at 1711 cm^{-1} (stretching of C=O), at 1604 cm^{-1} (stretching of C=C), at 692 cm^{-1} (C=C-H) were assigned to the maleimide group.^{20,21,27}

Mal-Bz-Co was not soluble in methanol, ethanol, and isopropanol. However, Mal-Bz-Co showed good solubility in acetone, tetrahydrofuran, dioxane, and polar aprotic solvents such as DMF and DMSO. The good solubility of Mal-Bz-Co implied its good processibility in solution processes and the possibility of process with epoxy.

Cure behavior of Mal-Bz-Co

DSC was used to study the cure behavior of Mal-Bz-Co, and the DSC scan was shown in Figure 5(a). It

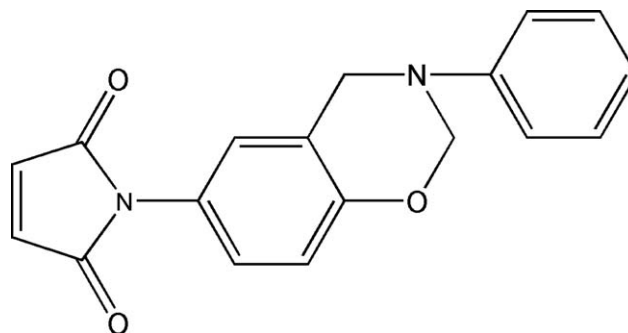


Figure 6 Structure of MIB.

TABLE I
Summary of DSC Results of Mal-Bz-Co
and Mal-Bz-Co/o-CFER

Sample	T_i^a (°C)	T_p^b (°C)	T_f^c (°C)	ΔH^d (J/g)
Mal-Bz-Co	218.6	238.3	257.1	52.65
Mal-Bz-Co/o-CFER (1 : 2)	117.2	146.1	170.2	148.70
Mal-Bz-Co/o-CFER (1 : 1)	110.5	141.5	164.5	81.92
Mal-Bz-Co/o-CFER (2 : 1)	122.8	148.5	172.5	84.40

^a Initial curing temperature.

^b Maximum curing temperature.

^c Final curing temperature.

^d Polymerization enthalpy.

was found that there was only one exotherm starting at 218.6°C with a maximum at 238.3°C and no endothermic peak was observed. Therefore, this exother-

mic peak corresponded to the polymerization of benzoxazine via the ring opening of oxazine rings and the addition homopolymerization of maleimide.

To compare the curing behavior of the novel benzoxazine, the benzoxazine compound MIB (Fig. 6) was introduced. The curing behavior of MIB had been researched by Ishida et al.⁹ and they found that the curing temperature of MIB was about 213°C, which was lower than that of Mal-Bz-Co. However, as shown in Figure 5(a), no endothermic peak assigned to the melting behavior of Mal-Bz-Co was observed, which indicated that the high-curing temperature of Mal-Bz-Co was due to its high crystallinity.¹³ This was because that high-crystallinity limited chain motion at low temperature due to the strong intermolecular interaction and steric hindrance. Therefore, the crosslinked reaction could not

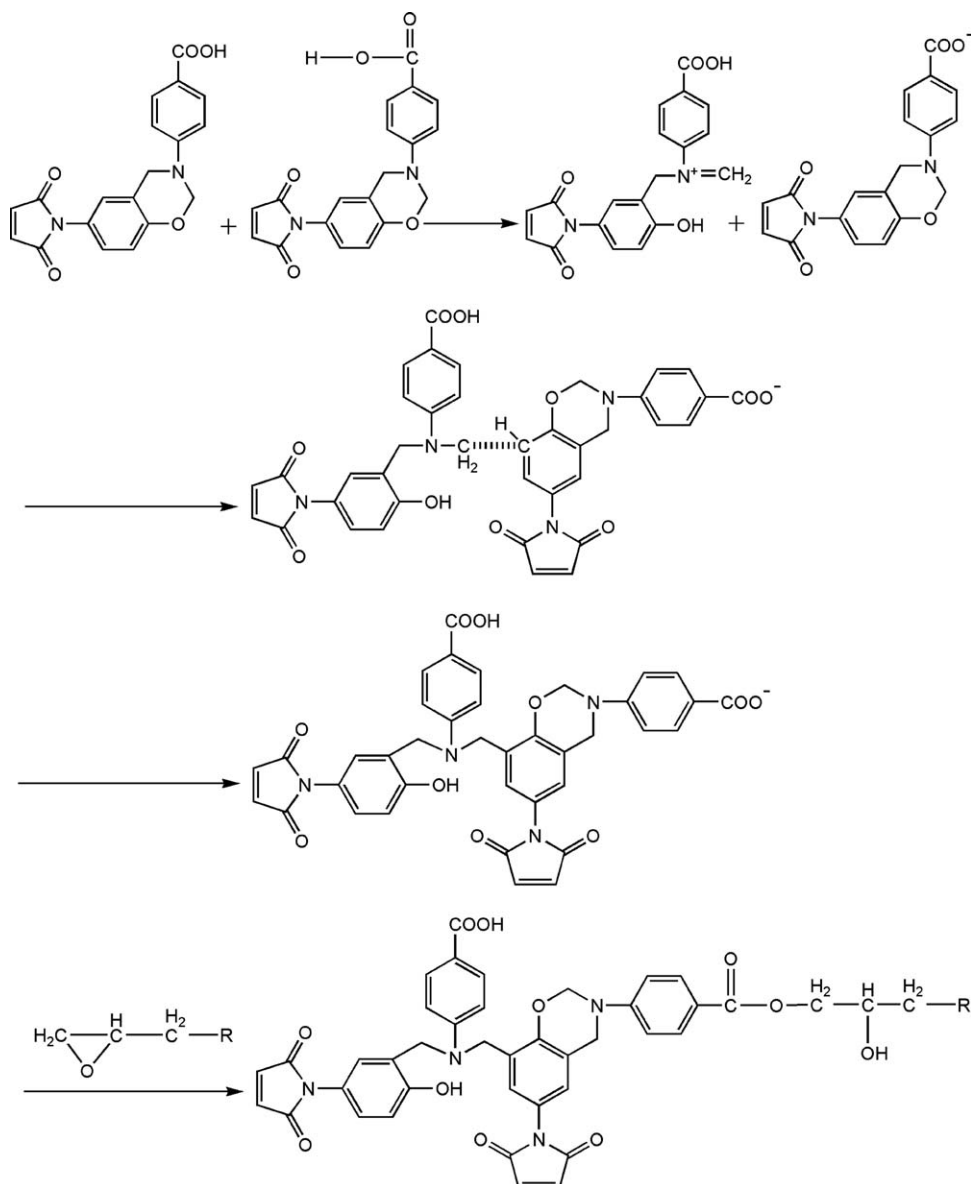


Figure 7 Curing reaction of Mal-Bz-Co/o-CFER system.

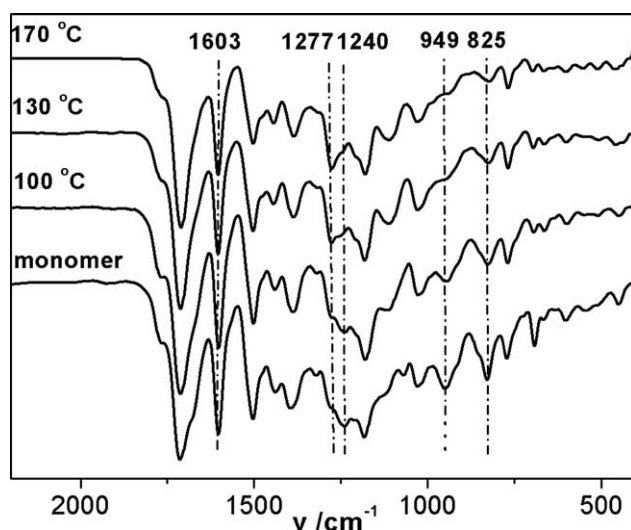


Figure 8 FTIR spectra of Mal-Bz-Co/*o*-CFER after each cure stage.

take place at lower temperature and the curing temperature became higher.

Cocure behavior of Mal-Bz-Co/epoxy

DSC was also used to study the cure behavior of Mal-Bz-Co/*o*-CFER. The DSC scans of Mal-Bz-Co/*o*-CFER mixtures in the molar ratios of 1 : 2, 1 : 1, and 2 : 1 were shown in Figure 5, and the results were summarized in Table I (For comparison, the data of Mal-Bz-Co are summarized in this table together.). As shown in Figure 5, there was only one obvious exotherm in the DSC scans of Mal-Bz-Co/*o*-CFER mixtures, which indicated that the two exothermic peaks corresponding to the polymerization of benzoxazine and epoxy were overlapped. As we could find in Table I, T_{ps} (maximum curing temperatures) of three Mal-Bz-Co/*o*-CFER systems were much lower than that of Mal-Bz-Co. This indicated that the curing temperature of Mal-Bz-Co was greatly decreased when cocured with *o*-CFER.

Furthermore, the curing temperature of the blending system was much lower than most of the benzoxazine/epoxy systems.^{1,17,18,28} The low-curing temperature of the oxazine ring was according to the addition of epoxy, which allowed Mal-Bz-Co dissolve in it when the temperature was higher than the melting point of *o*-CFER. The intermolecular interaction of Mal-Bz-Co was weakened and the chain motion became easier. Therefore, the carboxyl moieties in Mal-Bz-Co could take the effect as catalyzer earlier and the curing temperature of the oxazine ring became lower. The low-curing temperature of epoxy was due to COO—, which was produced in the cationic opening polymerization of benzoxazine and could react with epoxy at low temperature.²⁹

The curing reaction of Mal-Bz-Co/*o*-CFER system was shown in Figure 7.^{29,30}

To determine that all moieties participated in the curing reaction, the curing reaction of Mal-Bz-Co/*o*-CFER (1 : 1) was investigated by FTIR.³¹ As shown in Figure 8, the absorption peak of epoxy overlapped with that of oxazine ring at 949 cm^{-1} . However, the absorption band at 949 cm^{-1} was decreased with the increased curing temperature and was almost disappeared after the second-stage curing (130°C/2 h), which showed the oxazine rings and epoxy rings were opened. Furthermore, the absorption peak at 1240 cm^{-1} corresponding to the asymmetric stretching of C—O—C of the oxazine ring decreased with the increased temperature, which also showed the oxazine ring was opened. The maleimide polymerization could be monitored by the bands at 1603 cm^{-1} and 825 cm^{-1} which corresponded to the C=C stretching vibration and C—H wag of the vinylene group, respectively.³² As shown in Figure 8, the absorption bands at 1603 cm^{-1} and 825 cm^{-1} were decreased with the increased curing temperature but not disappeared, which showed the maleimide moieties were not completely cured. Besides, an obvious absorption peak at 1277 cm^{-1} appeared during the polymerization which corresponded to the stretching of carboxylic ester (OC—O—C). The carboxylic ester was obtained by the reaction of COO— and epoxy, which was showed in the curing reaction as stated above.

Thermal properties of the cured resins

TGA was used to probe the thermal stability of the cured resins. TGA thermograms of pure Mal-Bz-Co resin and Mal-Bz-Co/*o*-CFER resin (1 : 1) were shown in Figure 9 and the results were summarized

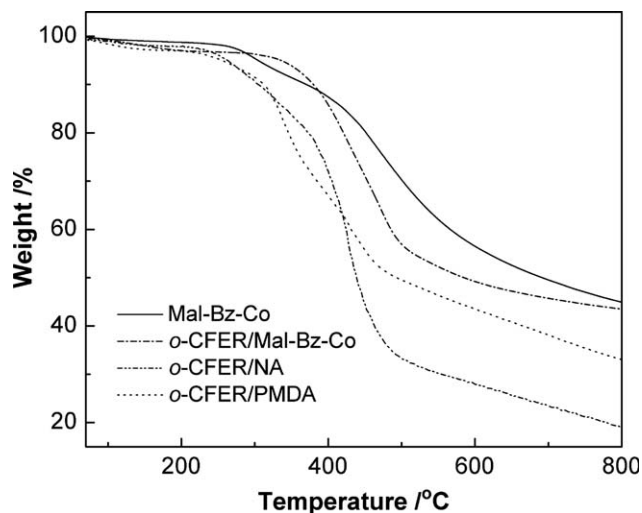


Figure 9 TGA thermograms of different cure systems.

TABLE II
Summary of TGA Results of Mal-Bz-Co,
Mal-Bz-Co/*o*-CFER, NA/*o*-CFER, and PMDA/*o*-CFER
Cure Systems

Cure system	T_{10}^a (°C)	γ_c^b (%)
Mal-Bz-Co	370	44.9
Mal-Bz-Co/ <i>o</i> -CFER	380	43.4
PMDA/ <i>o</i> -CFER	304	33.0
NA/ <i>o</i> -CFER	312	19.1

^a Degradation temperature of loss 10 wt % by TGA analysis.

^b Char yield at 800°C.

in Table II. To compare the thermal properties of the cured resins, two commercial curing agents PMDA and NA were used to cure *o*-CFER and the TGA results were also shown in Figure 9. As shown in Table II, the char yield at 800°C of the cured Mal-Bz-Co was 44.9%, whereas that of the Mal-Bz-Co/*o*-CFER in the molar ratio of 1 : 1 was 43.4%. However, the char yield of the *o*-CFER cured with PMDA and NA were 33.0% and 19.1%, respectively. This indicated that the incorporation of Mal-Bz-Co greatly improved the thermal properties of the cured resins. The T_{10} of the cured Mal-Bz-Co was 370°C, which increased to 380°C when cocured with *o*-CFER. This was resulted to the addition of *o*-CFER, which could promote the polymerization of Mal-Bz-Co and increase the crosslink density. Although the TGA traces did not reach a constant weight percentage, the results of TGA showed that the novel materials exhibited excellent thermal properties.

CONCLUSIONS

A novel benzoxazine named Mal-Bz-Co containing maleimide and carboxylic moieties was synthesized to show attractive processing and thermal properties when cocured with *o*-CFER. Mal-Bz-Co showed a single curing exothermic peak at 238.3°C but decreased to 146.1°C when cocured with *o*-CFER in the molar ratio of 1 : 1. FTIR showed that the oxazine rings and epoxy rings were almost completely cured after Mal-Bz-Co/*o*-CFER (1 : 1) was disposed at 130°C for 2 h. High-char yield of 43.4% at 800°C

of the cocured resin indicated its good thermal stability.

References

- Kimura, H.; Matsumoto, A.; Ohtsuka, K. *J Appl Polym Sci* 2008, 109, 1248.
- Ghosh, N. N.; Kiskan B.; Yagic Y. *Prog Polym Sci* 2007, 32, 1344.
- Men, W. W.; Lu, Z. J. *J Appl Polym Sci* 2007, 106, 2769.
- Liu, Y. L.; Chou, C. I. *J Polym Sci Part A: Polym Chem* 2005, 43, 5267.
- Ishida, H.; Allen, D. J. *J Polym Sci Part B: Polym Phys* 1996, 34, 1019.
- Kim, H. D.; Ishida, H. *J Appl Polym Sci* 2001, 79, 1207.
- Ishida, H.; Low, H. Y. *Macromolecules* 1997, 30, 1099.
- Xiang, H.; Ling, H.; Wang, J.; Song, L.; Gu, Y. *Polym Compos* 2005, 26, 563.
- Ishida, H.; Ohba, S. *Polymer* 2005, 46, 5588.
- Agag, T.; Takeichi, T. *J Polym Sci Part A: Polym Chem* 2006, 44, 1424.
- Liu, Y. L.; Yu, J. M.; Chou, C. I. *J Polym Sci Part A: Polym Chem* 2004, 42, 5954.
- Wang, Y. X.; Ishida, H. *Polymer* 1999, 40, 4563.
- Andreu, R.; Reina, J. A.; Ronda, J. C. *J Polym Sci Part A: Polym Chem* 2008, 46, 6091.
- Liu, Y. L.; Yu, J. M. *J Polym Sci Part A: Polym Chem* 2006, 44, 1890.
- Rao, B. S.; Reddy, K. R.; Pathak S. K.; Pasala, A. R. *Polym Int* 2005, 54, 1371.
- Ishida, H.; Allen, D. J. *Polymer* 1996, 37, 4487.
- Kimura, H.; Matsumoto, A.; Hasegawa, K.; Ohtsuka, K.; Fukuda, A. *J Appl Polym Sci* 1998, 68, 1903.
- Ishida, H.; Ohba, S. *J Appl Polym Sci* 2006, 101, 1670.
- Rimduisit, S.; Pirstpindvong, S.; Tanthapanichakoon, W.; Damrongsakkul, S. *Polym Eng Sci* 2005, 45, 288.
- Wu, C. S.; Liu, Y. L.; Hsu, K. Y. *Polymer* 2003, 44, 565.
- Liu, Y. L.; Chen, Y. J.; Wei, W. L. *Polymer* 2003, 44, 6465.
- Brunovska, Z.; Liu, J. P.; Ishida, H. *Macromolecules* 1999, 200, 1745.
- Agag, T.; Takeichi, T. *Macromolecules* 2001, 34, 7257.
- Agag, T.; Takeichi, T. *Macromolecules* 2003, 36, 6010.
- Dunkers, J.; Ishida, H. *Spectrochim Acta* 1995, 51A, 855.
- Dunkers, J.; Ishida, H. *Spectrochim Acta* 1995, 51A, 1061.
- Liu, Y. L.; Chen, Y. J. *Polymer* 2004, 45, 1797.
- Jain, R.; Narula, A. K.; Choudhary, V. *J Appl Polym Sci* 2007, 106, 3327.
- Ma, Z. G.; Gao, J. G. *J Phys Chem B* 2006, 110, 12380.
- Dunkers, J.; Ishida, H. *J Polym Sci Part A: Polym Chem* 1999, 37, 1913.
- Gărea, S. A.; Iovu, H.; Nicolescu, A.; Deleanu, C. *Polym Test* 2007, 26, 162.
- Giulio, C. D.; Gautier, M.; Jasse, B. F. *J Appl Polym Sci* 1984, 29, 1771.