

# Synthesis and characterization of a novel siloxane-imide-containing polybenzoxazine

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## Abstract

A novel siloxane-imide-containing polybenzoxazine based on *N,N'*-bis(*N*-phenyl-3,4-dihydro-2*H*-benzo[1,3]oxazine)-5,5'-bis(1,1',3,3'-tetramethyldisiloxane-1,3-diyl)-bis(norborane-2,3-dicarboximide) (BZ-A1) was successfully synthesized. The thermal properties of BZ-A1 are superior to those of conventional polybenzoxazines lacking siloxane groups. Polymerized BZ-A1 possesses extremely low surface free energy ( $\gamma_s = 15.1 \text{ mJ m}^{-2}$ ) after curing at 230 °C for 1 h. Moreover, the surface free energy of polymerized BZ-A1 is more stable than conventional bisphenol A-type polybenzoxazine during thermal curing and annealing processes, indicating that polymerized BZ-A1 is more suitable for applications requiring low surface free energy materials for high temperatures over long periods of time.

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**Keywords:** polybenzoxazine; benzoxazine; siloxane; surface free energy; thermal stability; BZ-A1

## INTRODUCTION

The diverse applications of thermosetting polymers have attracted much interest.<sup>1–4</sup> Polybenzoxazines (PBZs) are some of these materials that have attracted great interest from both academia and industry because of their superior properties.<sup>5–8</sup> Benzoxazine monomers, formed from amines and phenol in the presence of formaldehyde, were first synthesized by Holly and Cope.<sup>9</sup> Later, a bifunctional benzoxazine precursor was synthesized by Ning and Ishida<sup>5</sup> and the resulting polymers possessed high mechanical integrity. Benzoxazine monomers can be prepared readily from inexpensive raw materials.<sup>10–13</sup> PBZs possess unique properties such as low water absorption (despite the large number of OH groups present in the backbone structure),<sup>12,13</sup> high moduli,<sup>14</sup> excellent resistance to chemicals,<sup>15</sup> near-zero volumetric shrinkage/expansion upon polymerization<sup>16</sup> and high glass transition temperatures ( $T_g$ ).<sup>17</sup>

In our previous study, a new class of PBZ was developed which exhibited extremely low surface free energies – even lower than that of pure Teflon – through strong intramolecular hydrogen bonding.<sup>18–21</sup> Furthermore, we applied the low surface free energy PBZ material as an efficient mold-release agent for silicon molds<sup>22</sup> and a stable superhydrophobic surface.<sup>19</sup> Typically, the surface free energy of the PBZ system decreases initially and then increases steadily upon increasing the curing time, indicating that the surface free energy of PBZs is not stable during curing and annealing processes.

In order to overcome this problem, we designed a siloxane segment into benzoxazine to improve the stability of surface free energy during high-temperature storage.<sup>23</sup> However, Liu *et al.*<sup>24</sup> found that the addition of soft segments of bis-propyltetramethyldisiloxane in benzoxazines usually results in lower  $T_g$  and poorer thermal properties. Ardhyananta *et al.*<sup>25</sup> developed a polymerized bifunctional bisphenol A-type

benzoxazine (PBa)–polydimethylsiloxane (PDMS) hybrid system using the sol–gel process to increase  $T_g$  to above 200 °C. Poly(imide-siloxane) selected to blend into PBa to increase  $T_g$  was also discussed by Takeichi *et al.*<sup>26</sup> An imide-containing structure incorporated into benzoxazine can improve the thermal properties of PBZs.<sup>23</sup> In the study reported here, we formulated a benzoxazine containing a siloxane-imide segment: *N,N'*-bis(*N*-phenyl-3,4-dihydro-2*H*-benzo[1,3]oxazine)-5,5'-bis(1,1',3,3'-tetramethyldisiloxane-1,3-diyl)-bis(norborane-2,3-dicarboximide) (BZ-A1). It possesses a relatively low surface free energy and better thermal properties than those PBZs lacking siloxane groups after thermal crosslinking. Furthermore, the surface free energy of the polymerized BZ-A1 is more stable during high-temperature thermal curing processes.

## EXPERIMENTAL

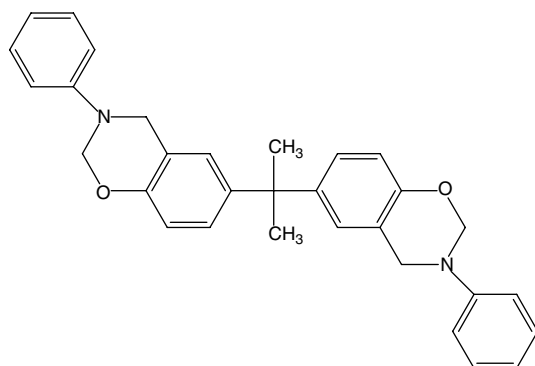
### Materials

1,4-Dioxane and paraformaldehyde (95%) were purchased from TEDIA (USA) and Showa Chemicals (Japan), respectively. Ethyl acetate (99.9%) was used as received from Mallinckrodt Inc. (USA). Aniline (99%), ethylene glycol ( $\geq 99\%$ ) and diiodomethane (99%) were obtained from Aldrich (USA). Bifunctional bisphenol A-type benzoxazine (Ba; Fig. 1) was purchased from Shikoku Chemicals (Japan).

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**Figure 1.** Structure of the bifunctional bisphenol A-type benzoxazine Ba.

### Synthesis of siloxane-containing dihydroxyl compound

Siloxane-imide-containing dianhydride (A1) and siloxane-containing dihydroxyl compound (A1-OH) were synthesized according to the method reported by Li *et al.*<sup>27</sup> (Scheme 1). A light brown powder, A1-OH, was obtained in 88% yield. The chemical structure of A1-OH was confirmed from <sup>1</sup>H NMR and Fourier transform infrared (FTIR) spectral analyses. <sup>1</sup>H NMR (CDCl<sub>3</sub>;  $\delta$ , ppm): 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). FTIR: 1789 and 1720 cm<sup>-1</sup> (imide), 3100–3500 cm<sup>-1</sup> (OH).

### Synthesis of BZ-A1

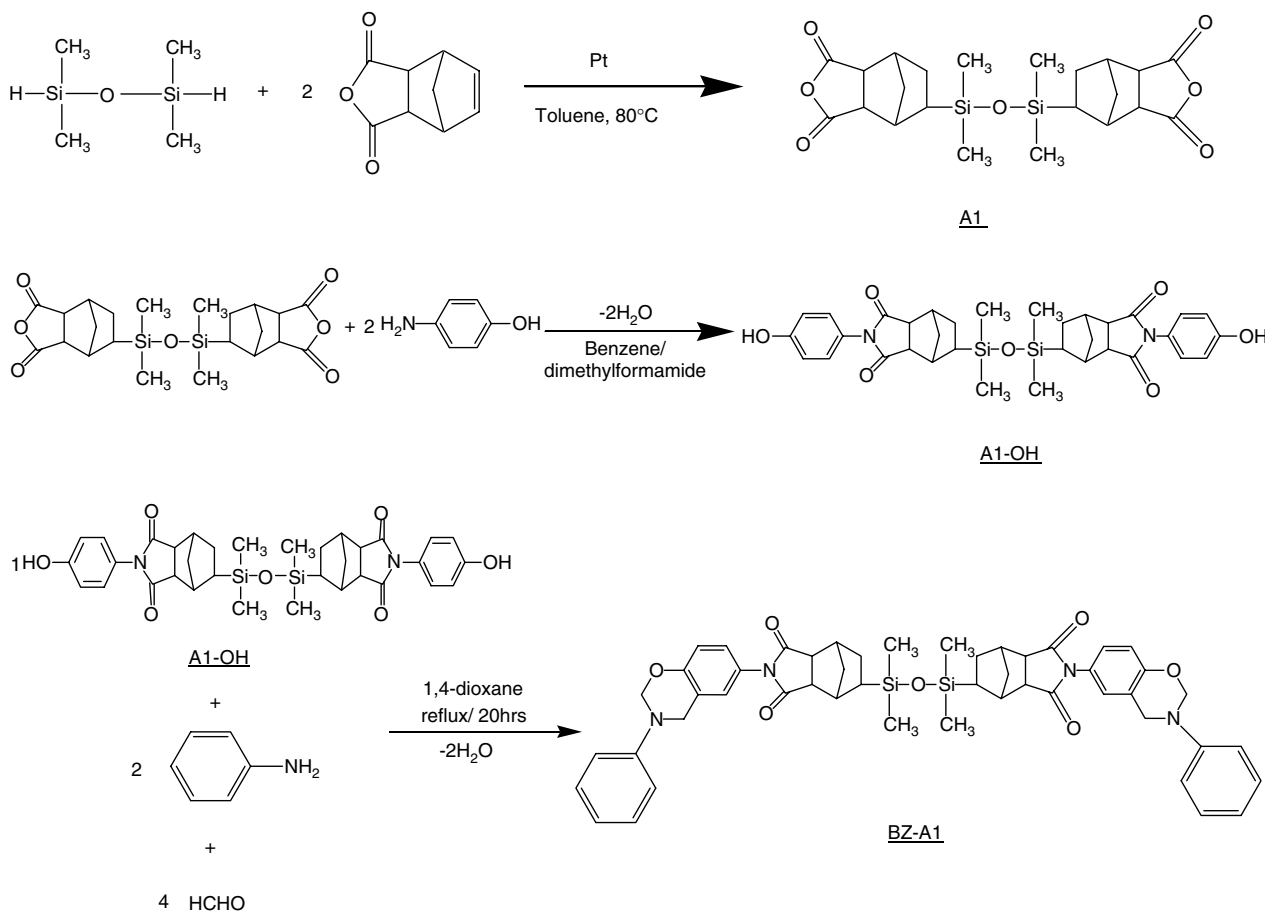
Aniline (1.88 g, 0.02 mol) was added dropwise into a mixture of A1-OH (6.44 g, 0.01 mol), paraformaldehyde (1.26 g, 0.04 mol) and 1,4-dioxane (100 mL) in a 250 mL round-bottom flask equipped with a magnetic stirrer bar. The mixture was then heated under reflux at 115 °C for 20 h, and it gradually became homogeneous, turning dark brown. The resulting mixture was filtered and the solvent was evaporated under vacuum. The residue was dissolved in ethyl acetate and washed five times sequentially with 1 N aqueous NaOH and distilled water. Evaporation of the solvent and vacuum drying in an oven provided BZ-A1 as a brown powder (73.0% yield).

### Contact angle measurements

The surface free energy of polymer samples was determined through contact angle goniometry at 25 °C using a Krüss GH-100 goniometer interfaced with image-capture software. Deionized water, ethylene glycol and diiodomethane were used as standards. To obtain reliable contact angle data, at least three droplets (5  $\mu$ L each) were dispensed at different regions of the same piece of film; at least two pieces of film were used. Thus, at least six advancing contact angles were averaged for each type of film and each type of liquid.

### Preparation of PBZ films

An aliquot (1 mL) of benzoxazine monomer (BZ-A1 or Ba; 0.5 g) solution in tetrahydrofuran (THF; 10 mL) was filtered at room



**Scheme 1.** Preparation of BZ-A1 monomer from A1 and A1-OH.

**Table 1.** Curing conditions for PBZs

	Ba	BZ-A1
Curing conditions	200 °C for 2 h + 230 °C for 2 h	200 °C for 2 h + 230 °C for 2 h
	200 °C for 2 h + 230 °C for 4 h	200 °C for 2 h + 230 °C for 4 h
	200 °C for 2 h + 230 °C for 6 h	200 °C for 2 h + 230 °C for 6 h

temperature through a 0.2 μm syringe filter (poly(vinylidene fluoride) membrane, Millipore Co.) and then spin-coated (1500 rpm, 45 s) onto a glass slide (100 mm × 100 mm × 1 mm). The sample was then cured in an oven at a desired temperature for a desired period of time.

### Preparation of siloxane-imide-containing PBZ

Ba and BZ-A1 were subjected to the curing schedule listed in Table 1. After completing the curing process, samples were slowly cooled to room temperature. No catalyst was used in these experiments.

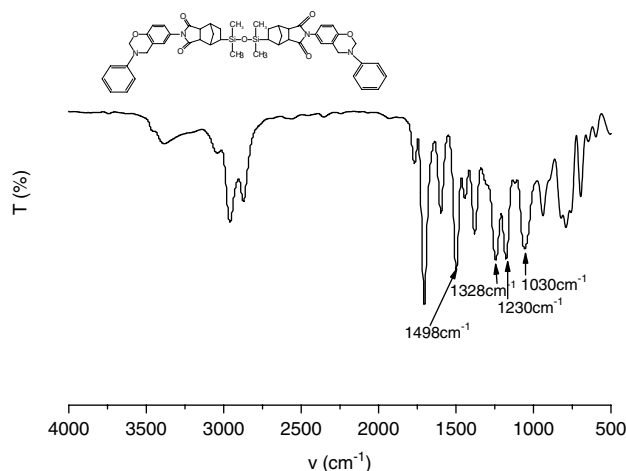
### Characterization

FTIR spectra were recorded using a Nicolet Avatar 320 FTIR spectrophotometer. Samples were prepared by casting BZ-A1 monomer solutions directly onto a potassium bromide plate and evaporating the THF at 50 °C under vacuum. The spectrometer was operated in transmission mode utilizing 32 scans at a resolution of 2 cm<sup>-1</sup>. <sup>1</sup>H NMR spectra were recorded using a Varian UNITY Inova-400 NMR spectrometer operating at a proton frequency of 400 MHz and with CDCl<sub>3</sub> as the solvent. Molecular weights were determined using a TRIO-2000 liquid chromatography/mass spectrometry (LC-MS) apparatus and a DB-5 MS column. DSC was performed using a TA Instruments DSC-Q10 apparatus operated at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere (gas flow rate of 40 mL min<sup>-1</sup>). Benzoxazine samples of approximately 5 mg were scanned in hermetic aluminium sample pans. TGA was performed using a TA Instruments TGA-Q500 apparatus operated at a heating rate of 20 °C min<sup>-1</sup> under an atmosphere of nitrogen or air. An energy-dispersive spectrometry (EDS) system was used for elemental testing, which was carried out using an LEO-1530 FE-SEM system.

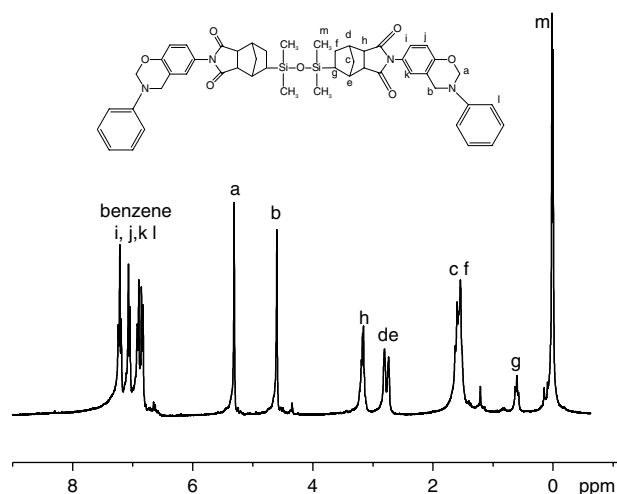
## RESULTS AND DISCUSSION

### Synthesis of BZ-A1

BZ-A1 was prepared according to Scheme 1 and its chemical structure was confirmed using FTIR and <sup>1</sup>H NMR spectroscopies and LC-MS. The FTIR spectrum of BZ-A1 (Fig. 2) displays characteristic absorptions of a benzoxazine structure at 1498 and 1030 cm<sup>-1</sup> (vibrations of trisubstituted benzene ring), 1328 cm<sup>-1</sup> (CH<sub>2</sub> wagging of the oxazine unit) and 1230 cm<sup>-1</sup> (asymmetric C–O–C stretching). The <sup>1</sup>H NMR spectrum of BZ-A1 (Fig. 3) displays signals of aromatic protons at 6.60–7.40 ppm and characteristic peaks attributed to methylene units (oxazine Ar–CH<sub>2</sub>–N) at 5.30 and 4.60 ppm. LC-MS (Fig. 4) provides a molecular weight of 881.1 g mol<sup>-1</sup>, consistent with the calculated formula weight.



**Figure 2.** FTIR spectrum of BZ-A1.



**Figure 3.** <sup>1</sup>H NMR spectrum of BZ-A1.

### Curing behavior of BZ-A1

Typically, benzoxazines undergo exothermic ring-opening reactions at ca 200–250 °C, which can be monitored using DSC. The reaction point of Ba is 228.7 °C; the energy of the exothermic ring-opening reaction is 296.0 J g<sup>-1</sup> (Fig. 5). The thermogram of BZ-A1 in Fig. 5 reveals a ring-opening exothermic reaction having an onset temperature at 194.9 °C and a peak point at 232.7 °C. The exothermic energy of BZ-A1 is 173.7 J g<sup>-1</sup>; i.e. it is lower than that of Ba, presumably due to the molecular weight effect, the molecular weight of BZ-A1 (879 g mol<sup>-1</sup>) being significantly higher than that of Ba (462 g mol<sup>-1</sup>). The polymerized forms of Ba (PBa) and BZ-A1 (PBZ-A1) were then cured in an oven under the curing conditions listed in Table 1.

### Thermal stability of the poly(siloxane-co-imide)-containing benzoxazine PBZ-A1

PBZs usually exhibit good thermal properties after polymerization.<sup>28</sup> T<sub>g</sub> of PBZ-A1 after crosslinking is 186.1 °C (Fig. 6), which is substantially higher than that of typical PBZs (T<sub>g</sub> of PBa is 150.0 °C).<sup>14</sup> Liu *et al.*<sup>24</sup> have discussed that the longer and flexible of siloxane segments in the matrix structure results in lower of T<sub>g</sub> (T<sub>g</sub> from tan δ peak of siloxane copolybenzoxazine

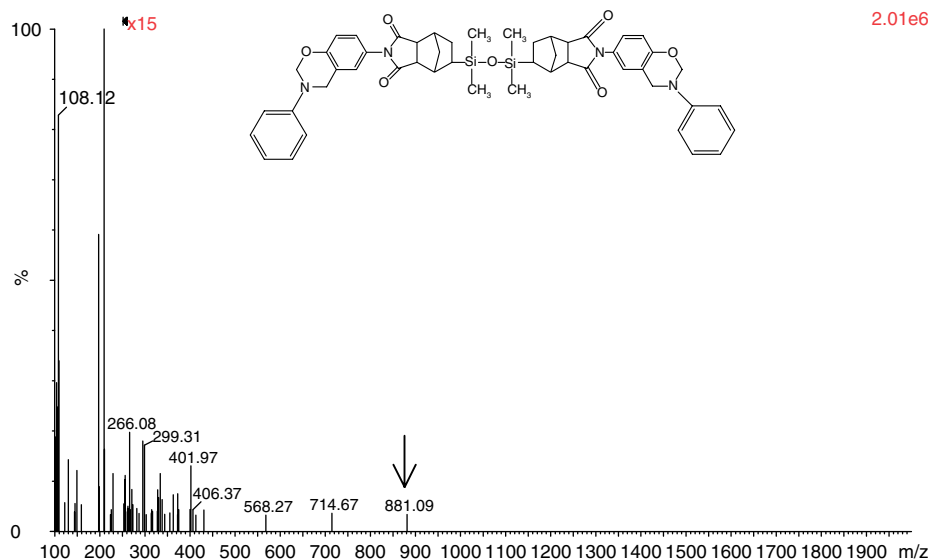


Figure 4. LC-MS spectrum of BZ-A1.

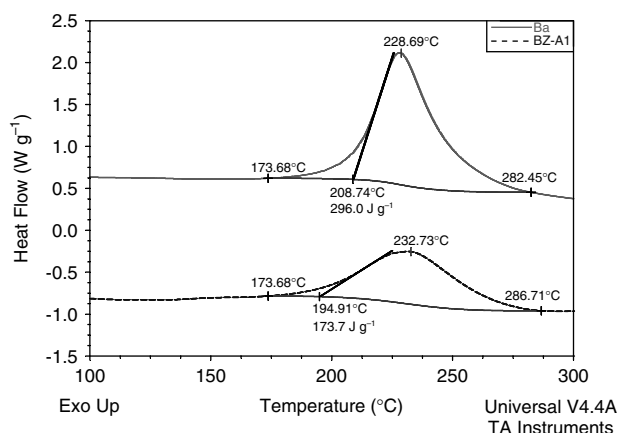


Figure 5. DSC thermograms of Ba and BZ-A1.

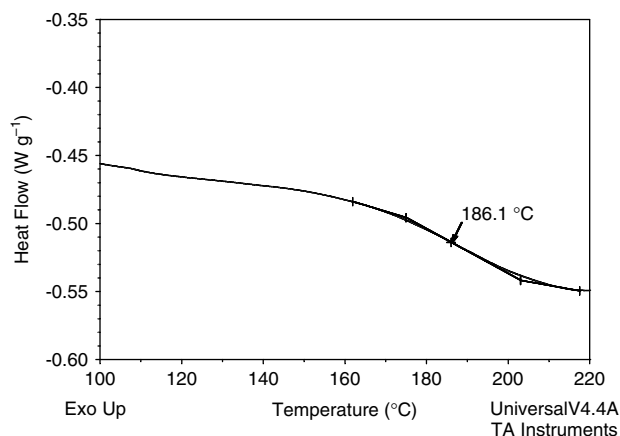


Figure 6. Glass transition temperature of PBZ-A1, determined from the DSC trace.

which named CP-F-Bz/BATMS-Bz-100 is 116 °C). Our PBZ-A1 structure features both siloxane and imide segments in the benzoxazine monomer where the imide segment tends to raise  $T_g$ .

Bisphenol A is one of the phenolic compounds often used as the starting material for the synthesis of PBZs. PBa shows a high decomposition temperature (temperature of 5% weight loss is *ca* 300–330 °C) and high char yield (*ca* 30–42%) as obtained from TGA.<sup>28–32</sup> Liu *et al.*<sup>24</sup> found that the siloxane-containing PBZ CP-F-Bz/BATMS-Bz-100 has  $T_d$  of 369 °C in air. Figure 7 shows TGA thermograms recorded in air; the results are summarized in Table 2. The 5 and 10% weight loss temperatures ( $T_5$  and  $T_{10}$ , respectively) for PBZ-A1 cured at 200 °C for 2 h and 230 °C for 2 h are 380.1 and 441.1 °C, respectively, which are both higher than those of PBa or siloxane-containing PBZ. PBZ-A1 shows higher thermal stability than PBa because of the presence of the siloxane-imide-containing segment. Liu *et al.* used TGA to study a siloxane-containing PBZ, and they found that high thermal stability silica layers were formed during the thermal oxidation process and the layer structure protected the PBZ.<sup>33</sup> PBa–PDMS hybrids were investigated and it was found that introduction of PDMS into PBa results in the improvement of thermal stability of the hybrid.<sup>25</sup>

The better thermal stability of PBZ-A1 with higher decomposition temperature and high char arises from the siloxane and imide groups.

The presence of siloxane-imide groups improves the thermo-oxidative stability of benzoxazine by increasing the char yield to 10–12 wt% in air. This char yield is close to the inorganic content (Si–O–Si, 8.2%) in the BZ-A1 structure. EDS analysis was employed to analyze the elemental composition of the PBZ-A1 residue after TGA testing in air. Figure 8 shows an image of the residue from PBZ-A1 and its EDS trace. The silicon content in the residue is significantly higher than the carbon and oxygen contents, and so the residue from PBZ-A1 after TGA testing in air is primarily inorganic in nature. Thus, the siloxane units of BZ-A1 provide an inorganic content in its structure, therefore improving its thermal stability after crosslinking.

The same phenomena occur in the TGA thermograms recorded under a nitrogen atmosphere (Fig. 9; Table 3).  $T_5$  of PBa is *ca* 328–337 °C under nitrogen atmosphere, whereas that of PBZ-A1 is significantly higher (*ca* 355–362 °C).  $T_5$  and  $T_{10}$  of PBZ-A1 are both higher than those of PBa. PBZ-A1 also features a high

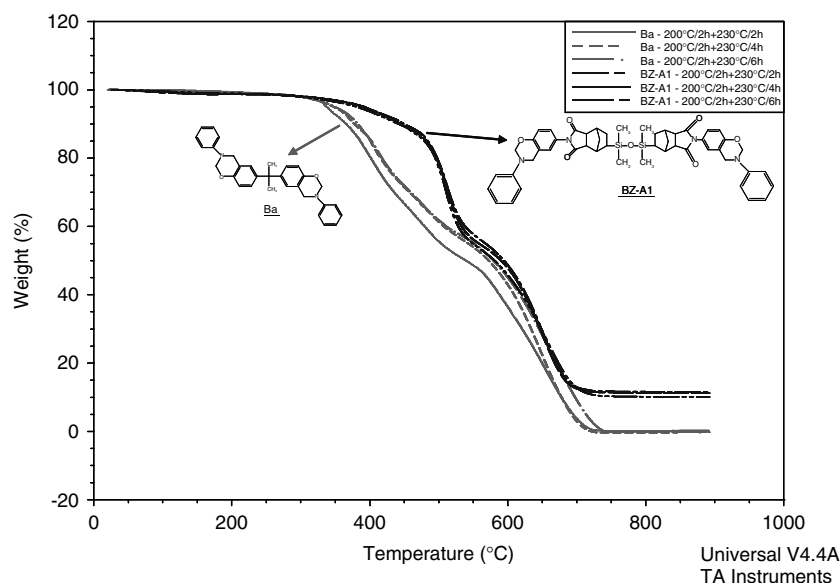


Figure 7. TGA thermograms of PBa and PBZ-A1 (in air).

Table 2. Thermal stabilities of the cured PBZs PBa and PBZ-A1 (in air)					
Polymer	Curing conditions	$T_5^a$ (°C)	$T_{10}^b$ (°C)	$T_d^c$ (°C)	Char yield at 850 °C (%)
Pba	200 °C for 2 h + 230 °C for 2 h	337.3	365.5	349.3	0.2
	200 °C for 2 h + 230 °C for 4 h	347.0	376.8	346.4	-0.3
	200 °C for 2 h + 230 °C for 6 h	349.1	382.1	357.9	-0.1
PBZ-A1	200 °C for 2 h + 230 °C for 2 h	380.1	441.1	472.2	10.1
	200 °C for 2 h + 230 °C for 4 h	389.4	444.2	480.7	11.3
	200 °C for 2 h + 230 °C for 6 h	392.0	449.3	478.1	12.0

<sup>a</sup> Temperature at which the weight loss is 5%.  
<sup>b</sup> Temperature at which the weight loss is 10%.  
<sup>c</sup> Decomposition temperature, onset point temperature.

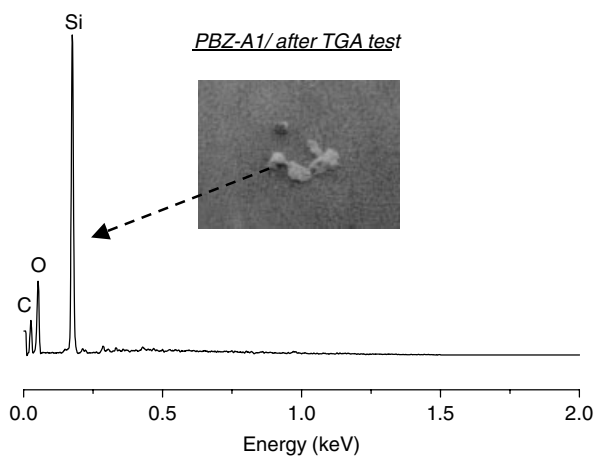


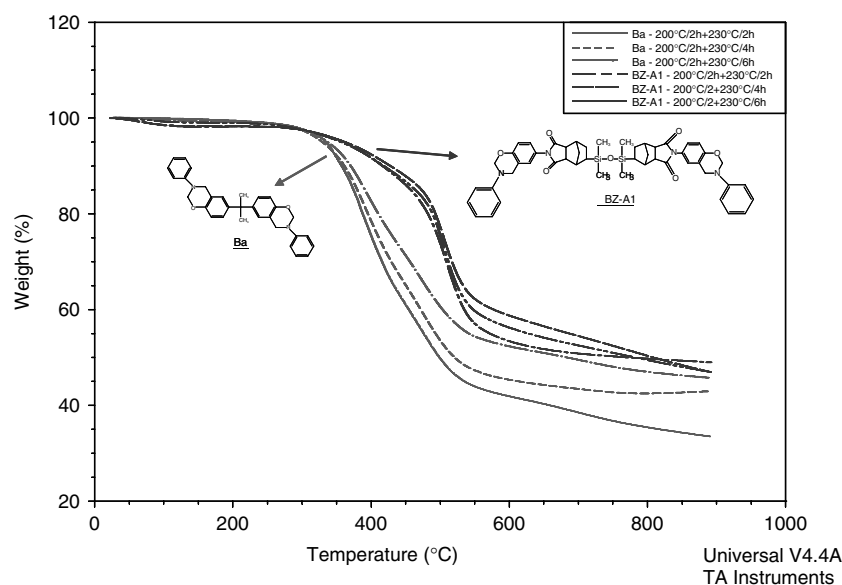
Figure 8. Residue and EDS analysis of PBZ-A1 after TGA.

weight residue after high-temperature decomposition. The char yield of PBZ-A1 after curing at 200 °C for 2 h and then 230 °C for 2 h is high (48%), i.e. it is increased by the presence of the siloxane-imide groups. It appears that PBZ-A1 has potential use as a flame-retardant material.

### Surface behavior of PBZ-A1 and PBa

PBZs feature strong intramolecular hydrogen bonds resulting in extremely low surface free energies, even lower than that of pure Teflon.<sup>18</sup> Some of the intramolecular hydrogen bonds in as-cured samples tend to convert into intermolecular hydrogen bonds upon thermal treatment, thereby resulting in increased hydrophilicity and wettability. To broaden the applications of PBZs, benzoxazine monomers possessing less sensitivity towards thermal treatment are required.

The surface behaviors during the curing process of PBZ-A1 and PBa were characterized after spin-coating films with thicknesses of ca 150 nm. Table 4 lists the advancing contact angles and standard deviations for three different test liquids on the surfaces of PBa and PBZ-A1 films produced using various curing and annealing times. Due to the advancing contact angle being less sensitive to surface roughness and heterogeneity than the receding angle, advancing angle data are commonly used to calculate surface and interfacial tension components.<sup>34,35</sup> At a curing and annealing temperature of 230 °C, the contact angles for both PBa and PBZ-A1 for all test liquids increase initially during the first hour but decrease steadily thereafter (Fig. 10). For the PBa system, curing at 230 °C for 1 h results in the highest contact angles for all three test liquids: 106.1° for water, 82.5° for ethylene glycol and 84.3° for diiodomethane. For the PBZ-A1 system, similar trends are observed by curing and



**Figure 9.** TGA thermograms of Ba and BZ-A1 (under nitrogen).

**Table 3.** Thermal stabilities of the cured PBZs PBa and PBZ-A1 (under nitrogen)

Polymer	Curing conditions	$T_5^a$ (°C)	$T_{10}^b$ (°C)	$T_d^c$ (°C)	Char yield at 850 °C (%)
Pba	200 °C for 2 h + 230 °C for 2 h	334.6	356.8	344.2	34.3
	200 °C for 2 h + 230 °C for 4 h	328.8	360.7	342.7	42.7
	200 °C for 2 h + 230 °C for 6 h	336.5	369.8	341.6	46.3
PBZ-A1	200 °C for 2 h + 230 °C for 2 h	355.7	417.8	452.9	48.0
	200 °C for 2 h + 230 °C for 4 h	361.5	427.2	448.4	48.4
	200 °C for 2 h + 230 °C for 6 h	358.5	415.8	446.5	49.3

<sup>a</sup> Temperature at which the weight loss is 5%.

<sup>b</sup> Temperature at which the weight loss is 10%.

<sup>c</sup> Decomposition temperature, onset point temperature.

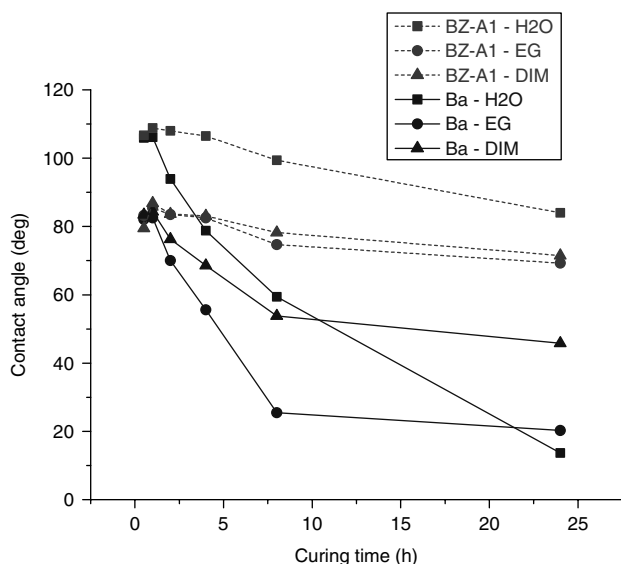
**Table 4.** Contact angles and surface free energies of the cured and annealed PBa and PBZ-A1

Polymer	Curing conditions		Contact angle (°)			Surface free energy, $\gamma_s$ (mJ m <sup>-2</sup> )
	Temperature (°C)	Time (h)	Water	Ethylene glycol	Diiodomethane	
Pba	230	0.5	105.9	82.1	83.4	17.0
		1	106.1	82.5	84.3	16.6
		2	93.9	70.0	76.3	22.5
		4	78.8	55.6	68.6	30.0
		8	59.4	25.5	53.8	43.6
		24	13.7	20.3	45.8	42.6
PBZ-A1	230	0.5	106.7	83.2	79.5	18.5
		1	108.8	85.4	86.8	15.1
		2	108.0	83.5	83.6	16.6
		4	106.5	82.5	83.1	17.0
		8	99.4	74.7	78.2	20.4
		24	84.0	69.3	71.5	24.6

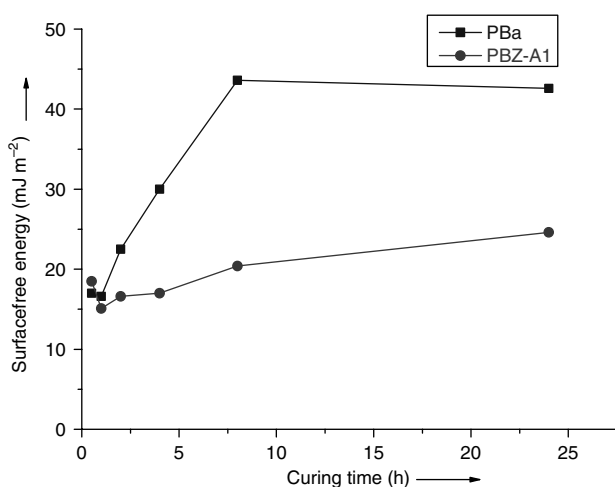
annealing at 230 °C, except that the contact angles are all higher than those for the PBa system. Curing at 230 °C for 1 h also provides the highest contact angles for all three of the test liquids: 108.8° for water, 85.4° for ethylene glycol and 86.8° for diiodomethane. The contact angle for water on PBa is initially 105.9° but decreases

markedly to 13.7° after curing for 24 h. In contrast, the contact angle for water on PBZ-A1 is initially 106.7°, reaching 108.8° after curing for 1 h and decreasing very slowly to 84.0° after curing for 24 h. Indeed, the contact angles for water on PBZ-A1 are all higher than those on PBa for all curing times, suggesting that the





**Figure 10.** Contact angles of PBZs after various curing times (EG, ethylene glycol; DIM, diiodomethane).



**Figure 11.** Surface free energies of PBZs after various curing and annealing times at 230 °C.

good thermal stability of the siloxane-imide-containing segment in BZ-A1 is able to improve the stability of the surface free energy during curing and annealing at high temperatures for long periods of time.

The three-liquid method of van Oss *et al.*<sup>36</sup> was employed to calculate the surface free energy ( $\gamma_s$ ) and the results are summarized in Table 4. When the curing temperature for the PBa system is 230 °C, the surface free energy decreases initially and then increases steadily with curing time (Fig. 11). The lowest surface free energy (16.6 mJ m<sup>-2</sup>) is obtained when curing at 230 °C for 1 h which then increases to 42.6 mJ m<sup>-2</sup> upon increasing the curing or annealing time. In this system, curing at 230 °C for 1 h provides the lowest surface free energy of 15.1 mJ m<sup>-2</sup> – a value that is even lower than those of Teflon<sup>37</sup> (21 mJ m<sup>-2</sup>) and PBa (16.6 mJ m<sup>-2</sup>), determined using the same liquids. The low surface free energy of PBZ-A1 may arise from the combination of benzoxazine groups and siloxane-containing segments. The incorporation of the siloxane segment in benzoxazine improves

the thermal stability while maintaining the low surface free energy after high-temperature thermal annealing for periods of time.

## CONCLUSIONS

A novel siloxane-imide-containing benzoxazine (BZ-A1) was synthesized. The product from the curing of BZ-A1 (PBZ-A1) possesses extremely low surface free energy and improved thermal stability. This newly developed PBZ-A1 shows better stability of surface free energy under thermal curing and annealing, maintaining its low surface free energy compared with the conventional PBa.

## REFERENCES

- 1 Drockenmuller E, Li LYT, Ryu DY, Harth E, Russell TP, Kim HC, *et al*, *J Polym Sci A: Polym Chem* **43**:1028 (2005).
- 2 Huang CC, Yang MS and Liang M, *J Polym Sci A: Polym Chem* **44**:5875 (2006).
- 3 Wooster TJ, Abrol S, Hey JM and MacFarlane DR, *J Polym Sci A: Polym Chem* **43**:5072 (2005).
- 4 Liu YL and Hsieh CY, *J Polym Sci A: Polym Chem* **44**:905 (2006).
- 5 Ning X and Ishida H, *J Polym Sci A: Polym Chem* **32**:1121 (1994).
- 6 Takeichi T, Komiya I and Takayama Y, *Kyoka-Purasutikkus* **43**:109 (1997).
- 7 Wang YX and Ishida H, *Polymer* **40**:4563 (1999).
- 8 Macko JA and Ishida H, *Polymer* **42**:227 (2001).
- 9 Holly FW and Cope AC, *J Am Chem Soc* **66**:1875 (1944).
- 10 Burke WJ, Murdoch KC and Ec G, *J Am Chem Soc* **76**:1677 (1954).
- 11 Burke WJ, Glennie ELM and Weatherbee C, *J Org Chem* **24**:909 (1964).
- 12 Furukawa N, *Jpn Kokai Tokkyo Koho* **18**:2004 (2004).
- 13 Wang YX and Ishida H, *Polym Mater Sci Eng* **80**:211 (1999).
- 14 Ishida H and Allen DJ, *J Polym Sci B: Polym Phys* **34**:1019 (1996).
- 15 Kim HD and Ishida H, *J Appl Polym Sci* **79**:1207 (2001).
- 16 Ishida H and Low HY, *Macromolecules* **30**:1099 (1997).
- 17 Ishida H and Rodriguez Y, *Polymer* **36**:3151 (1995).
- 18 Wang CF, Su YC, Kuo SW, Huang CF, Sheen YC and Chang FC, *Angew Chem Int Ed* **45**:2248 (2006).
- 19 Wang CF, Wang YT, Tung PH, Kuo SW, Lin CH, Sheen YC, *et al*, *Langmuir* **22**:8289 (2006).
- 20 Liao CS, Wu JS, Wang CF and Chang FC, *Macromol Rapid Commun* **29**:56 (2008).
- 21 Liao CS, Wang CF, Lin HC, Chou HY and Chang FC, *J Phys Chem C* **112**:16189 (2008).
- 22 Wang CF, Chiou SF, Ko FH, Chen JK, Chou CT, Huang CF, *et al*, *Langmuir* **23**:5868 (2007).
- 23 Chen KC, Li HT, Chen WB and Huang SC, presented at the 11th Pacific Polymer Conference, Cairns, 6–10 December (2009).
- 24 Liu YL, Hsu CW and Chou CI, *J Polym Sci A: Polym Chem* **45**:1007 (2007).
- 25 Ardhyanta H, Wahid MH, Sasaki M, Agag T, Kawachi T, Ismail H, *et al*, *Polymer* **49**:4585 (2008).
- 26 Takeichi T, Agag T and Zeidam R, *J Polym Sci A: Polym Chem* **39**:2633 (2001).
- 27 Li HT, Chuang HR, Wang MW and Lin MS, *Polym Int* **54**:1416 (2005).
- 28 Ghosh NN, Kiskan B and Yagci Y, *Prog Polym Sci* **32**:1344 (2007).
- 29 Hemvichian K and Ishida H, *Polymer* **43**:4391 (2002).
- 30 Agag T and Takeichi T, *Macromolecules* **36**:6010 (2003).
- 31 Takeichi T, Kano T and Agag T, *Polymer* **46**:12172 (2005).
- 32 Choi SW, Ohba S, Brunovska Z, Hemvichian K and Ishida H, *Polym Degrad Stab* **91**:1166 (2006).
- 33 Liu YL, Chiu YC and Wu CS, *J Appl Polym Sci* **87**:404 (2003).
- 34 Good RJ and van Oss CJ, in *Modern Approaches to Wettability: Theory and Applications*, ed. by Schrader ME and Loeb GI. Plenum Press, New York, pp. 1–27 (1992).
- 35 Drelich J, Miller JD and Good RJ, *J Colloid Interface Sci* **179**:37 (1996).
- 36 van Oss CJ, Chaudhury MK and Good RJ, *Chem Rev* **88**:927 (1988).
- 37 Takei YG, Aoki T, Sanui K, Ogata N, Sakurai Y and Okano T, *Macromolecules* **27**:6163 (1994).