Research Article

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Synthesis and performance enhancement of novel polybenzoxazines with low surface free energy

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Abstract

A new siloxane-imide-containing benzoxazine, BZ-A6, has been successfully synthesized. The thermal properties of the polybenzoxazine (PBZ) prepared from BZ-A6 (PBZ-A6) are superior to those of conventional PBZs lacking siloxane groups. The normally brittle PBZs are toughened significantly as a result of adding siloxane-imide moieties. Moreover, the thermal and UV stabilities of the surface free energy of PBZ-A6 are dramatically improved over the conventional bisphenol-A-type PBZ. Siloxane-imide PBZs are more suitable for application as low-surface-free-energy materials that are highly resistant to temperature and UV radiation. PBZ-A6 may also be useful in weather-resistant and self-cleaning coating materials because of its low surface free energy and good thermal and UV resistance.

Keywords: benzoxazine; siloxane-imide modification; surface free energy; thermal stability; UV stability; weather resistance

INTRODUCTION

Polybenzoxazines (PBZs) synthesized through ring-opening polymerizations of cyclic benzoxazine monomers are new types of phenolic resins.[1–3] Fig. 1 displays the structure of a typical benzoxazine monomer, Ba, which can be prepared through the reaction of bisphenol-A, aniline and formaldehyde.[4–6] In addition to possessing the excellent thermal and non-flammable properties of traditional phenolic resins, PBZs also exhibit high molecular design flexibility, low moisture absorption and no by-product release upon curing.[2,3,7–11]

In previous studies, we have developed a new class of PBZs that exhibit extremely low surface free energies – even lower than that of pure Teflon® ($\gamma_s = 21\ \mathrm{mJ\ m^{-2}}$) – as a result of strong intramolecular hydrogen bonding.[12–15] Furthermore, we have applied such low-surface-free-energy PBZs as efficient mold-release agents for silicon molds[16] and as stable superhydrophobic surfaces.[13] Typically, the surface free energies of PBZ systems increase steadily upon increasing thermal curing time and UV exposure time, indicating that PBZs lose stability during thermal treatment or UV exposure, mainly due to the formation of carbonyl-containing species during UV exposure.[15,17] To overcome this problem, we have incorporated siloxane segments into benzoxazines to improve their surface free energy during high-temperature storage.[18,19] In this study, we incorporated a longer siloxane segment into benzoxazines and produced thermally crosslinked polymers, which possess extremely low surface free energies, improved thermal stability and UV resistance relative to those of PBZs without the siloxane group.

PBZs possess many advantageous characteristics; however, their brittleness limits their broader applications. Toughening of PBZs has been achieved previously through the incorporation of other polymers, such as liquid rubber,[20] polyurethane[21] and polyimide.[22] Liu *et al.*[23] found that the addition of soft segments in PBZs, such as silicon-containing benzoxazine units, showed significant toughness improvement but it also resulted in poorer thermal properties. Takeichi and co-workers[24,25] prepared polybenzoxazine (PBa)–polydimethylsiloxane hybrids *in situ* to overcome the brittle and thermal properties of PBZs; nevertheless, the preparation of homogeneous opaque hybrid films using sol–gel processing was complicated and by-products might have been produced. In the study reported here, we incorporated the siloxane-imide-containing BZ-A1 and BZ-A6 into benzoxazines. The resulting polymers (PBZ-A1 and PBZ-A6) after thermal crosslinking possessed low surface free energy and superior thermal and UV resistance relative to those of PBZs lacking the siloxane-imide group. PBZ-A6 exhibited high flexibility, high glass transition temperature (T_g) of 186.4 °C and good thermal and UV stability. We believe PBZ-A6 has the potential to be used in applications requiring self-cleaning and weather-resistance characteristics.

EXPERIMENTAL

Materials

5-Norbornene-2,3-dicarboxylic anhydride (nadic anhydride) was purchased from Alfa Aesar (USA). Hydride-terminated

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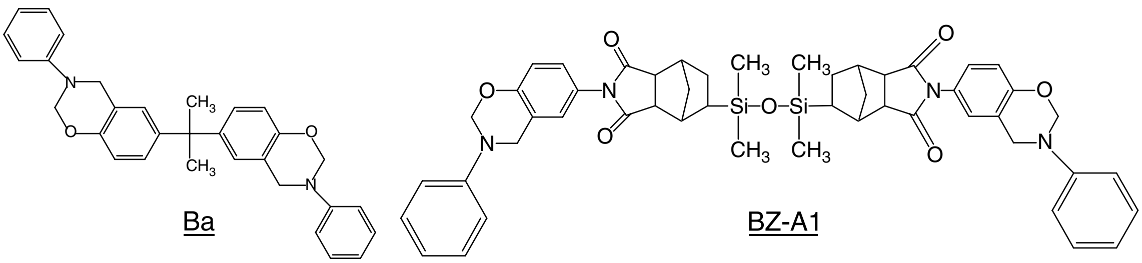
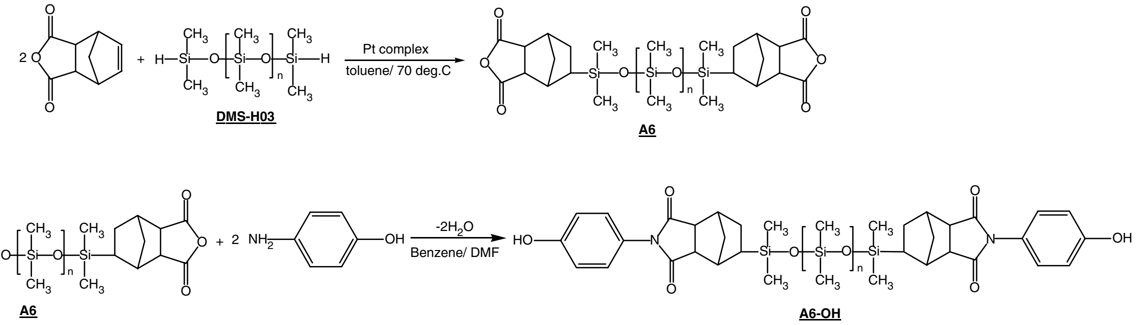


Figure 1. Structures of bi-functional bisphenol-A-type benzoxazine (Ba) and siloxane-imide-containing benzoxazine (BZ-A1).



Scheme 1. Syntheses of A6 and A6-OH.

polydimethylsiloxane (DMS-H03) was purchased from Gelest (USA) with a number-average molecular weight of *ca* 400–500 g mol^{-1}. Platinum divinyltetramethyldisiloxane complex was purchased from Gelest (USA). All chemicals were purified prior to use. 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 (USA). Aniline (99%), ethylene glycol (EG; $\geq$99%) and diiodomethane (DIM; 99%) were obtained from Aldrich (USA). The bifunctional bisphenol-A-type benzoxazine Ba (Fig. 1) was purchased from Shikoku Chemicals (Japan). The siloxane-imide-containing benzoxazine BZ-A1 (Fig. 1) was prepared according to a reported method.[19]

Synthesis of dinoborane anhydride-terminated polydimethylsiloxane (A6)

The synthesis of the siloxane-imide-containing dianhydride A1 has been reported in the literature.[26,27] The higher molecular weight siloxane-imide-containing dianhydride A6 was prepared with reference to these previous methods. Platinum catalyst (0.8 mL) was added dropwise into a solution of nadic anhydride (82.1 g) in toluene (400 mL) in a three-necked round-bottom flask while stirring with a magnetic bar. DMS-H03 (112.5 g) was gradually added into the solution and then heated to 70 °C for 48 h (Scheme 1). The resulting mixture was filtered and the solvent was evaporated under vacuum. After the removal of residue nadic anhydride, A6 was obtained as a transparent liquid (yield of 75.0%).

The chemical structure of the transparent liquid product, A6, was confirmed with ^{1}H NMR spectral analysis (Varian UNITY Inova-400NMR spectrometer) and Fourier transform infrared (FTIR) spectral analysis (PerkinElmer Spectrum One). ^{1}H NMR ($CDCl_3$, 400 MHz; δ, ppm): 0.03–0.05 (12H, $CH_3-Si-CH_3$), 0.65 (2H, –CH–Si–), 1.55–1.66 (8H, cyclopentane CH_2), 3.39–3.43 (4H, –C(=O)). FTIR (KBr; cm^{-1}): 1859, 1778 (anhydride, C=O stretching), 1222 (C–Si stretching), 1078 (Si–O–Si stretching); no 1680 (norborane, C=C stretching) or 2150 (Si–H stretching).

Imidization of A6 to produce A6-OH

4-Aminophenol (5.3 g, 0.0484 mol) in dimethylformamide (DMF; 30 mL) was added gradually to a stirred solution of A6 (16.5 g, 0.022 mol) in DMF (30 mL) in a 250 mL round-bottom flask (Scheme 1). The solution was stirred for 6 h in an ice-bath and the imidization was performed using a Dean–Stark apparatus. A6-OH was obtained as a viscous dark brown liquid after vacuum drying (yield of 86.8%).

^{1}H NMR ($CDCl_3$; δ, ppm): 0.03–0.08 (12H, $CH_3-Si-CH_3$), 0.65 (2H, –CH–Si–), 1.55–1.66 (8H, cyclopentane CH_2), 6.23 (2H, aromatic C–OH), 6.73–6.96 (8H, benzene). FTIR (KBr; cm^{-1}): 1720 (imide), 3100–3500 (OH, broad band).

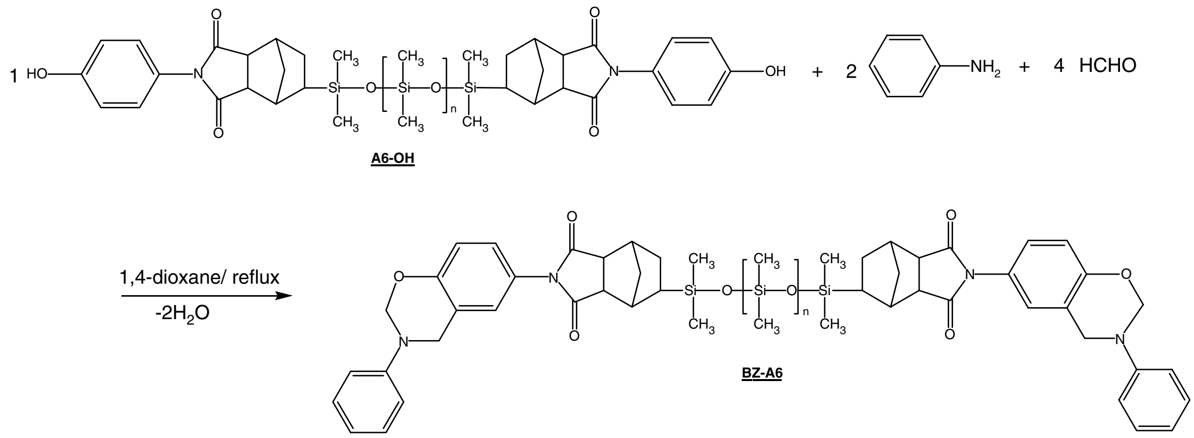
Synthesis of siloxane-imide-containing benzoxazine (BZ-A6)

Aniline (3.8 g, 0.04 mol) was added dropwise into a mixture of A6-OH (18.95 g, 0.02 mol), paraformaldehyde (2.4 g, 0.08 mol) and 1,4-dioxane (120 mL) in a 250 mL round-bottom flask equipped with a magnetic stirrer bar (Scheme 2). The mixture was then heated under reflux at 115 °C for 20 h, gradually becoming homogeneous and turning dark brown. The resulting mixture was filtered and the solvent evaporated under vacuum. The residue was dissolved in ethyl acetate and washed five times sequentially with 0.5 N aqueous NaOH and distilled water. Evaporation of the solvent and vacuum drying in an oven provided BZ-A6 as a viscous dark brown liquid product (yield of 87.7%).

^{1}H NMR ($CDCl_3$; δ, ppm): 6.70–7.30 (aromatic protons), 5.35 (OCH_2N), 4.65 ($Ar-CH_2-N$). The spectrum is shown in Fig. 2. FTIR (KBr; cm^{-1}): 1256 (C–O–C stretching), 1178 (C–N–C stretching), 1307 (CH_2, wagging of oxazine), 1502 (trisubstituted benzene ring).

Preparation of PBZ films

A solution of a benzoxazine monomer (Ba, BZ-A1 or BZ-A6; 0.5 g) in tetrahydrofuran (10 mL) was passed through a 0.2 µm syringe filter and then a portion (1 mL) was spin-coated (1500 rpm, 45 s)



Scheme 2. Preparation of BZ-A6.

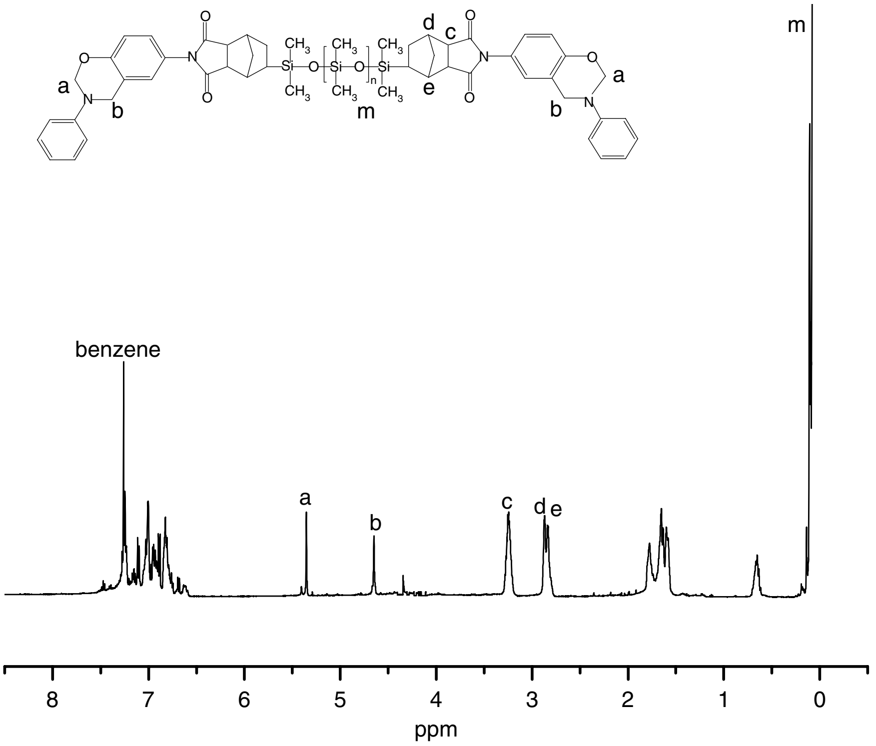


Figure 2. ^{1}H NMR spectrum of BZ-A6.

Table 1. Curing conditions for benzoxazines Ba, BZ-A1 and BZ-A6

Curing conditions	200 °C/2 h + 230 °C/2 h
	200 °C/2 h + 230 °C/4 h
	200 °C/2 h + 230 °C/6 h

onto a glass slide (100 mm × 100 mm × 1 mm). After curing (Table 1), the PBZ thin film was subjected to surface behavior characterizations.

The siloxane-imide-containing benzoxazine monomer BZ-A6 was heated at 80 °C in an oven for 1 h. The viscous BZ-A6 was then coated onto a copper foil and cured at the desired temperature and time. A free-standing, flexible PBZ film of BZ-A6 was obtained after etching the copper foil.

Characterization

DSC was performed using a DSC-Q10 (TA Instruments) operated at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. TGA was performed using a TGA-Q500 (TA Instruments) operated at a heating rate of 20 °C min^{-1} under either a nitrogen or air atmosphere. Thermal mechanical properties were investigated using dynamic mechanical analysis (DMA) with a DMA-Q800 (TA Instruments) operated at a heating rate of 2 °C min^{-1} using an applied force of 0.05 N, and a frequency of 1 Hz. UV resistance was investigated using a QUV accelerated weathering tester under UV-A irradiation (351 nm, 1.55 W m^{-2}) at 60 °C (ASTM G153).

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 and injecting a 5 μL liquid drop. Deionized water, EG and DIM were used as

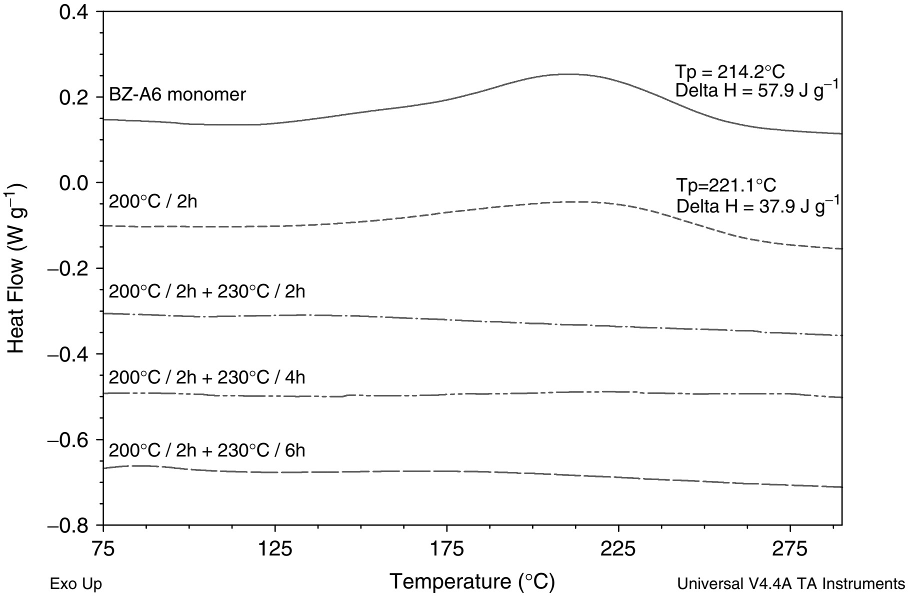


Figure 3. DSC thermograms of BZ-A6 monomer and polymerized BZ-A6 (after curing).

standards to measure the surface free energies. To obtain reliable contact data, at least three droplets were dispensed on different regions of the same piece of film, and at least two pieces of film were used. Thus, at least six advancing contact angles were averaged for each kind of film and each kind of liquid.

RESULTS AND DISCUSSION

Curing behavior of BZ-A6

In general, benzoxazines undergo exothermic ring opening at temperatures of *ca* 200–250 °C,[19,28–30] which can be monitored using DSC. The thermogram of BZ-A6 in Fig. 3 reveals a ring-opening exothermic reaction having an onset temperature at 153.7 °C and a peak maximum at 214.2 °C with exothermic energy of 57.9 J g^{-1}. After curing at 200 °C for 2 h, the reaction heat decreases to 37.9 J g^{-1} from 57.9 J g^{-1}. We performed the polymerization of BZ-A6 using a two-step process: the first step involved benzoxazine ring opening at 200 °C and the second involved post-curing at 230 °C. PBZs were cured in an oven under the curing conditions listed in Table 1.

Thermal stability properties

PBZs usually exhibit good thermal properties.[3] Fig. 3 displays TGA thermograms recorded under air atmosphere. No residue remains after burning PBa at high temperature; the char is almost zero at 850 °C. The char yield of PBZ-A1 at 850 °C is 10–11 wt% and elemental analysis confirms that the residue is inorganic silicon oxide.[19] PBZ-A6 exhibits a higher char yield of 16–17 wt%, presumably due to the longer siloxane chain in the BZ-A6 backbone than that in BZ-A1. Thus, the char yield increases upon increasing the siloxane content in the polymer. PBa starts decomposition, $T_{5\%}$, at *ca* 330–350 °C and it appears that PBZ-A1 has a higher decomposition temperature (380–395 °C; Fig. 4). PBZs containing the siloxane-imide segment in the main chain, PBZ-A1 and PBZ-A6, could show improved thermal stability. The highest $T_{5\%}$ is observed for PBZ-A6. It is thus observed that a longer siloxane chain could make further improvements in the thermal stability since a longer siloxane chain was incorporated into the main chain of PBZ-A6.

TGA reveals that PBa exhibits high decomposition temperature ($T_{5\%}$ of *ca* 300–330 °C) and high char yield (*ca* 30–42%).[3,28,29,31] In a previous study, we found that PBZ-A1 exhibits superior thermal properties relative to PBa.[19] Fig. 5 shows TGA thermograms recorded under nitrogen atmosphere and Table 2 summarizes the results. The 5 and 10% weight loss temperatures ($T_{5\%}$ and $T_{10\%}$, respectively) for PBZ-A6 (437.1 and 481.3 °C, respectively) are the highest among the polymers investigated in this study. The thermal decomposition temperature of PBZ-A6 is in the range 460–471 °C. PBZ-A1 and PBZ-A6 exhibit higher thermal stability than PBa because of the presence of the siloxane-imide-containing segment. Furthermore, the siloxane content of PBZ-A6 is higher than that of PBZ-A1 and the decomposition temperature of PBZ-A6 is accordingly higher. The siloxane-imide-containing PBZs also feature high weight residues after TGA. The highest char yield is 50.9 wt% from PBZ-A6 due to the presence of longer siloxane-imide group. PBZ-A6 exhibits good thermal stability, the highest decomposition temperature and the highest char yield. It appears that incorporating siloxane and imide moieties into the benzoxazine main chain can significantly enhance the thermal properties of PBZs, providing the potential for them to be used as flame-retardant materials.

Dynamic mechanical properties

Figure 6 shows DMA thermograms of PBZ-A6 under three curing conditions and the results are summarized in Table 3. The curing profiles reveal that the storage modulus at room temperature is 600–800 MPa which is much lower than for conventional PBZs. In general, a higher shear storage modulus in the rubbery state indicates a polymer having a high crosslinking density.[23] The storage modulus reaches the highest value after longer post-curing time in the rubbery state at 200 and 220 °C (Table 3). Thus, a longer curing time improves the crosslinking density as would be expected. These results are consistent with the fact that PBZ-A6 exhibits the highest T_g (186.4 °C) of the studied polymers. From a previous study,[24] the storage modulus of the brittle PBa was found

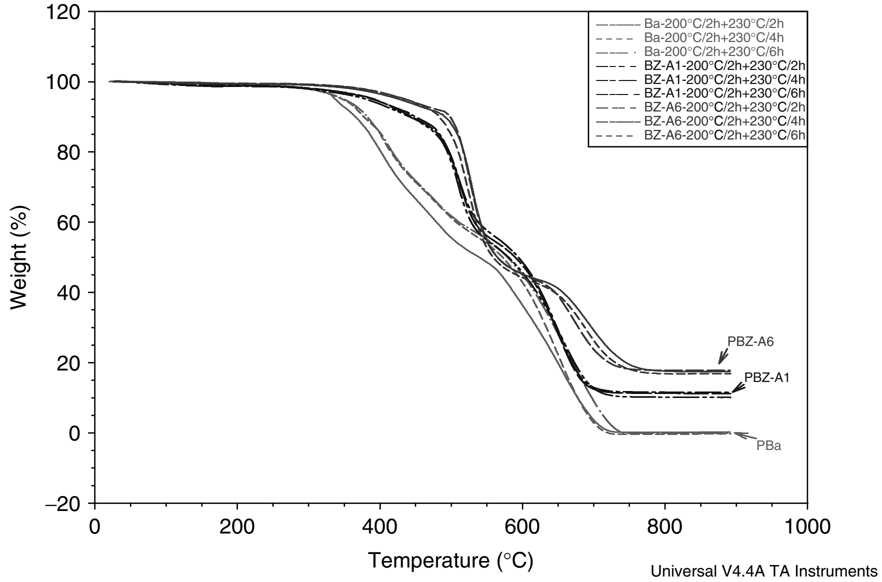


Figure 4. TGA thermograms of PBa, PBZ-A1 and PBZ-A6 (in air).

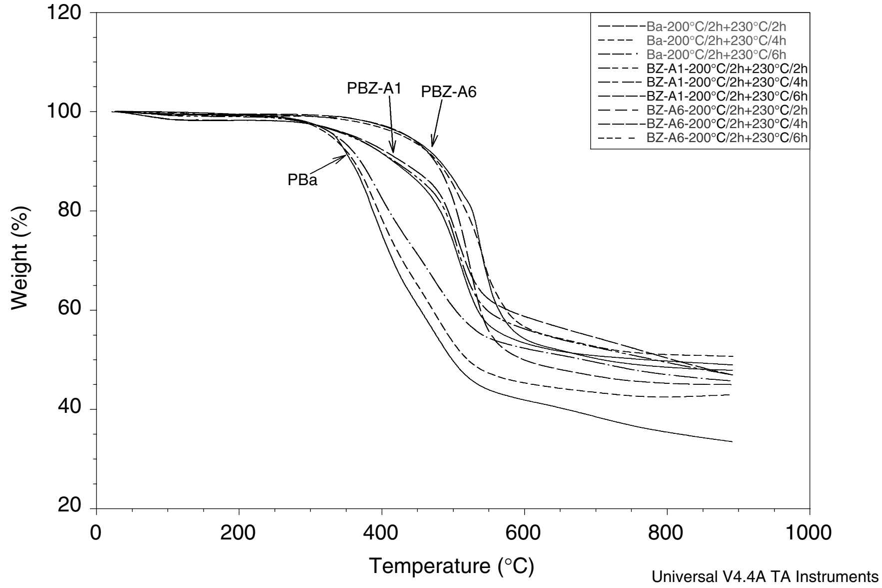


Figure 5. TGA thermograms of PBa, PBZ-A1 and PBZ-A6 (in nitrogen).

Table 2. Thermal stability of cured PBZs PBa, PBZ-A1 and PBZ-A6 (in nitrogen)[a]

	Curing time (h)					
Polymer	First step at 200 °C	Second step at 230 °C	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_d (°C)	Char yield at 850 °C (%)
Pba	2	2	334.6	356.8	344.2	34.3
		4	328.8	360.7	342.7	42.7
		6	336.5	369.8	341.6	46.3
PBZ-A1	2	2	355.7	417.8	452.9	48.0
		4	361.5	427.2	448.4	48.4
		6	358.5	415.8	446.5	49.3
PBZ-A6	2	2	437.1	474.2	471.0	45.1
		4	437.2	481.3	459.9	48.1
		6	430.6	477.4	463.7	50.9

[a] $T_{5\%}$, temperature at which the weight loss reached 5%; $T_{10\%}$, temperature at which the weight loss reached 10%; T_d, decomposition temperature.

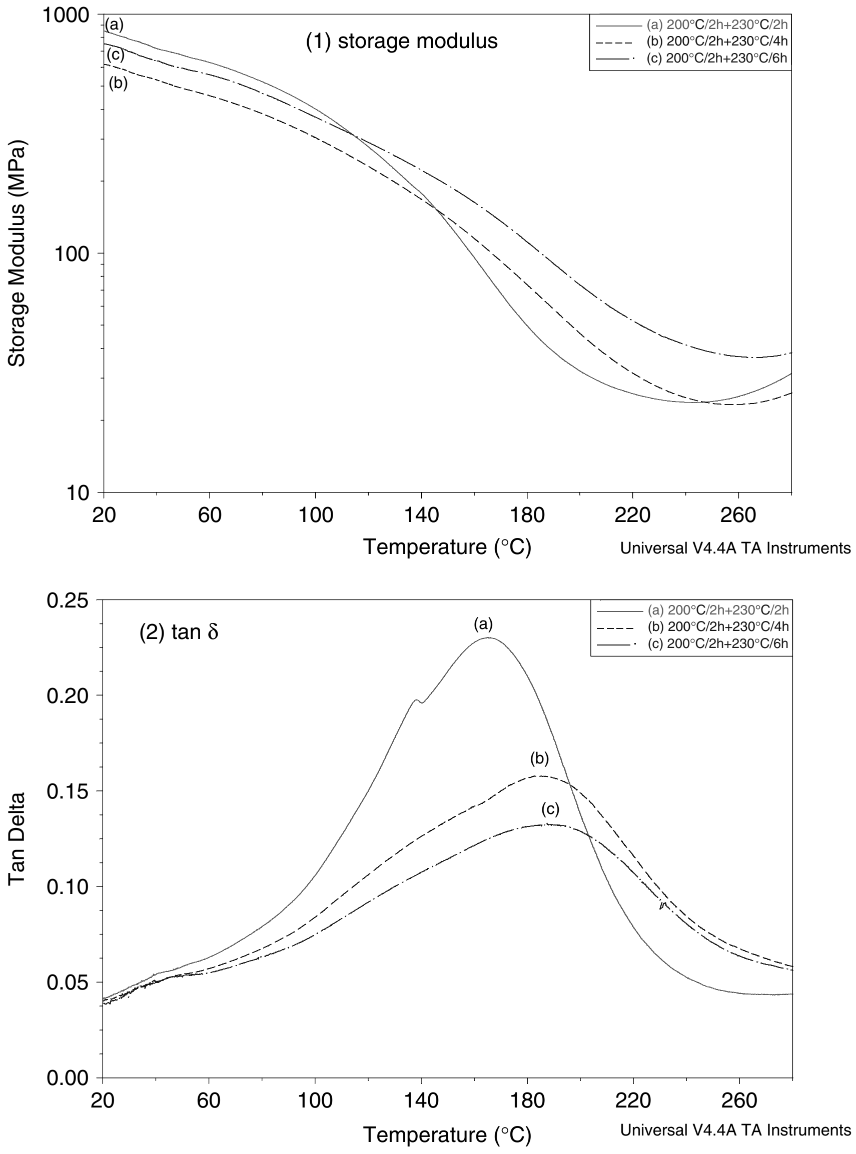


Figure 6. DMA thermograms of PBZ-A6.

Table 3. Thermal mechanical analysis for PBZ-A6

	Curing time (h)		Storage modulus (MPa)				
Sample	First step at 200 °C	Second step at 230 °C	25 °C	180 °C	200 °C	220 °C	T_g from tan δ peak (°C)
(a)	2	2	816.2	47.0	32.1	25.8	166.2
(b)	2	4	595.8	73.6	46.0	31.4	184.0
(c)	2	6	729.5	111.3	73.7	52.0	186.4

to be *ca* 3.2 GPa at room temperature and T_g (derived from tan δ) of 174 °C.

Generally, it is difficult to obtain free-standing PBZ films without adding plasticizers. Since PBZ-A6 exhibits superior flexibility and toughness, PBZ-A6 readily forms a free-standing, bendable film after polymerization with a thickness of *ca* 200 µm (Fig. 7). Notably, the PBZ-A6 film exhibits not only excellent flexibility but also high T_g due to the presence of the rigid imide-norborane rings in the PBZ. DMA results reveal that the presence of siloxane and imide moieties can significantly improve the flexibility and toughness of PBZs without sacrificing their high T_g.

Surface behavior of PBZs

Since PBZs feature strong intramolecular hydrogen bonds, they exhibit extremely low surface free energies, even lower than that of pure Teflon®.[12] We compared the surface behavior during the curing process of the siloxane-imide-containing monomers

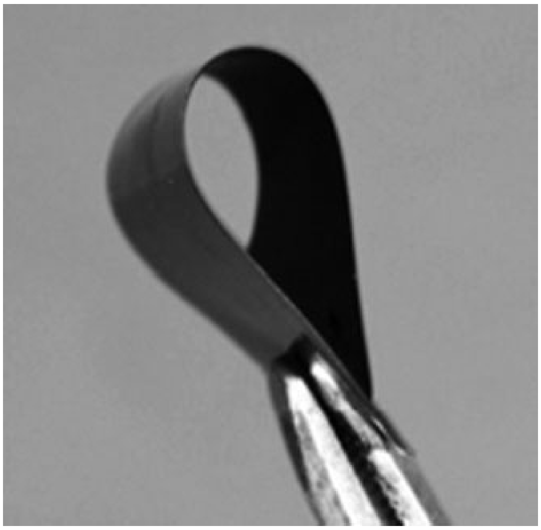


Figure 7. Photograph of a thin film of PBZ-A6.

Table 4. Advancing contact angles and corresponding surface free energies for PBZ films prepared from Ba, BZ-A1 and BZ-A6

	Curing conditions		Contact angle (°)			
Polymers	Temperature (°C)	Time (h)	Water	EG	DIM	Surface free energy, γ_s (mJ m^{-2})
PBa	230	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	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
PBZ-A6	230	1	113.7	93.9	92.3	12.4
		2	112.2	89.0	86.8	14.7
		4	111.9	88.7	86.8	14.7
		8	110.9	88.2	86.8	14.8
		24	108.3	82.3	84.3	16.2

BZ-A6 and BZ-A1 and the bisphenol-A-containing bifunctional benzoxazine monomer Ba after spin-coating to a thickness of *ca* 150 nm. Table 4 lists the advancing contact angles and standard deviations of three test liquids on the surface of the PBZ films after subjecting them to various curing and annealing times. Since the advancing contact angle is less sensitive to surface roughness and heterogeneity than the receding angle, advancing angle data are commonly used to calculate surface and interfacial tension components.[32,33] Under curing and annealing temperature of 230 °C, the water contact angles for the three PBZ films (PBa, PBZ-A1 and PBZ-A6) are all higher than 100° during the first hour, indicating hydrophobic properties. For all three systems, curing at 230 °C for 1 h provides the highest contact angles for the three test liquids. Notably, the contact angles for the PBZ-A6 system (113.7° for water, 93.9° for EG and 92.3° for DIM) are all higher than those for the PBa and PBZ-A1 systems.

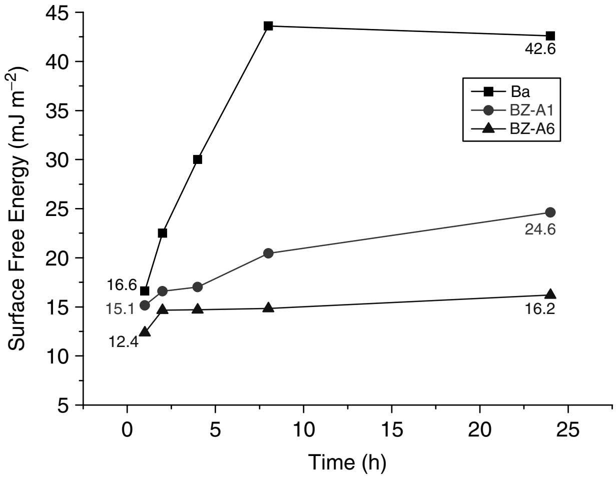


Figure 8. Surface free energies of PBZs after curing and annealing at 230 °C.

We employed the three-liquid method of van Oss *et al.*[34] to calculate the surface free energies (γ_s) of the systems. The results are summarized in Table 4. The two siloxane-imide-containing benzoxazine systems produced lower surface free energies. The lower surface free energy of PBZ-A6 (12.4 mJ m^{-2}) can be attributed to dual effects: forming intramolecular hydrogen bonds after ring opening of the benzoxazine and introducing a high content of low-surface-free-energy dimethylsiloxane chains. In a previous study[19] we found that the incorporation of a siloxane segment into a benzoxazine improves the thermal stability, while maintaining its low surface free energy after high-temperature thermal annealing for various periods of time. Figure 8 reveals that the surface free energy of PBa increases from 16.6 mJ m^{-2} after the first hour of curing to 42.6 mJ m^{-2} after thermal annealing for 24 h. The thermal stability in terms of surface free energy is significantly improved when siloxane segments are incorporated: the surface free energies of PBZ-A1 and PBZ-A6 increase to only 24.6 and 16.2 mJ m^{-2} after similar thermal annealing for 24 h. Such thermal stability improvement in surface free energy of PBZ-A6 stems from the combination of the benzoxazine groups and the presence of the longer siloxane-containing segments. The high char yield of PBZ-A6 (16–17 wt% in air at 850 °C) confirms its high content of siloxane-containing units. Thus, the incorporation of siloxane segments improves the thermal stability while maintaining low surface free energy after thermal annealing at high temperatures for lengthy periods of time.

UV resistance

We examined the UV resistance properties of the PBZs. Figure 9 presents the variation in water contact angles after exposure to UV-A radiation. The water contact angles of PBa, PBZ-A1 and PBZ-A6 films cured at 230 °C for 1 h are all greater than 100°, indicating that they all possess hydrophobic surfaces. The water contact angle of PBa markedly decreases to 12.1° from 106.1° after 24 h of UV-A exposure, and decreases to 5.1° after 100 h of exposure. In a previous study[15] we found that a fraction of the intramolecular hydrogen bonds of as-cured samples converted into intermolecular hydrogen bonds after UV exposure, thereby resulting in increased hydrophilicity. For the siloxane-imide-containing PBZ-A1, the water contact angle is maintained at 107.1° after 24 h of UV-A exposure, but it decreases to 42.5° after

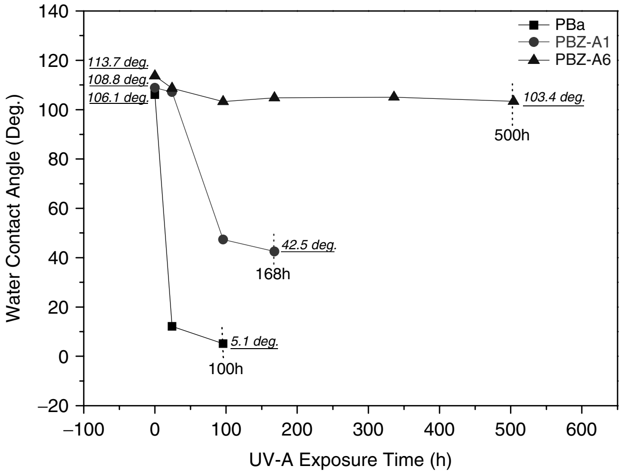


Figure 9. Water contact angles of PBZ films after UV-A exposure for various periods of time.

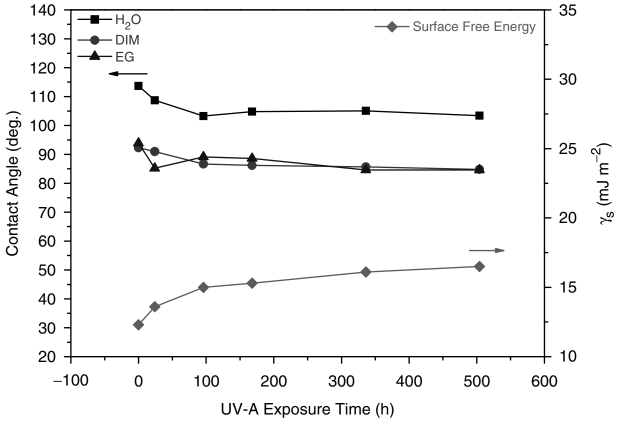


Figure 10. Contact angles and surface free energies of PBZ-A6 films after UV exposure for various periods of time.

168 h. Notably, PBZ-A6 maintains its hydrophobic properties; the water contact angle remains at 103.4° after UV-A exposure for 500 h.

Figure 10 shows the surface free energy (calculated using the three-liquid method[34]) of PBZ-A6 during UV-A exposure. We observe a similar trend in contact angle data when using EG and DIM as solvents, the contact angles of these two solvents decreasing only less than 10% after 500 h of UV-A exposure. The surface free energy of PBZ-A6 remains extremely low at 16.5 mJ m^{-2} after UV exposure for 500 h.

CONCLUSIONS

We have synthesized a new siloxane-imide-containing benzoxazine, BZ-A6. The cured product from PBZ-A6 possesses extremely low surface free energy, 12.4 mJ m^{-2}, and improved thermal and UV stabilities. PBZ-A6 can be prepared as a free-standing film after introducing a flexible siloxane segment into benzoxazine. PBZ-A6 shows high T_g (186.4 °C) and very good UV stability after 500 h of exposure time. Through the incorporation of a longer siloxane-imide moiety (BZ-A6) into the cured PBZ-A6, the toughness, flexibility, thermal properties, and thermal and UV stability in terms of low surface free energy are all significantly improved over the conventional bisphenol-A-type PBZ. PBZ-A6 has potential applications in UV- or weather-resistant, self-cleaning coating materials.

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