# Modification of Polymer Substrates with Low Surface Free Energy Material by Low-Temperature Cured Polybenzoxazine[a]

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The B-ala/AIBN PBZ system has a high extent of ring-opening of oxazine because phenol-containing oligomers are formed at the early stage of the curing process. As a result, the B-ala/AIBN PBZ system possesses a relatively stronger intramolecular hydrogen bonding and lower surface energy than the pure B-ala system at low temperature curing. In this context, poly(4-vinyl pyridine), poly(4-vinyl phenol) thin films and polycarbonate substrates, which lack liquid resistance, possess low surface free energy after modification with B-ala/AIBN = 5/1 PBZ.
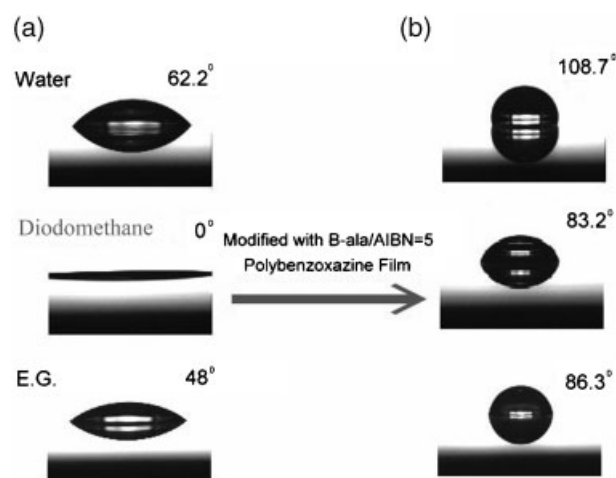
Introduction

Low surface energy polymeric materials with good film-forming characteristics have attracted great interest because of their practical applications.[1] Consequently great attention has been placed on precise strategies modifying these solid surfaces.[2] Most of the low surface energy polymeric materials that have been developed

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were based on flurorine- or silicon-containing polymers. Polybenzoxazine (PBZ), a new class of low surface energy material, has recently been developed displaying a strong intramolecular hydrogen bonding but extremely low surface free energy, even lower than pure Teflon.[3] However, the requirement of high-temperature curing (ca. 180–210 °C) of PBZ limits its broader applications, especially for most polymer substrates. A method of lower temperature curing for benzoxazine is thus urgently needed to broaden the application of PBZ in temperature-sensitive substrates such as most polymeric materials. In this context, we discovered that bis(3-allyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane (B-ala) can be cured at a relatively low temperature (120 °C) with the aid of 2,2′-azoisobutyronitrile (AIBN), resulting in even lower surface energy than that from the conventional method. Many polymer substrates such as polycarbonate, poly(4-vinyl pyridine), poly(4-vinyl phenol) and similar polymers can be coated by the modified polybenzoxazine in order to possess low surface energy.

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Experimental Part

Materials

All chemicals were used as received. Bisphenol A, paraformaldehyde (95%) and AIBN were supplied by Showa Chemical Company (Japan). 2,2′-Bis(3-methyl-3,4-dihydro-2H-1,3-benzoxazinyl)propane (BA-m) was supplied by Shikoku Corporation. Poly(4-vinylpyridine) ($\overline{M}_w = 60\,000$ g mol^{-1}) was obtained from Aldrich (USA). The synthesis of B-ala was based on the reaction of bisphenol A with allylamine and paraformaldehyde according to the previously reported procedure.[4] Poly(4-vinyl phenol) ($\overline{M}_w = 10\,000$ g mol^{-1}; PDI = 1.4) was synthesized according to the previously reported method.[5]

Contact Angle Measurement

The surface free energy of the polymer sample was determined by contact angle goniometry at 25 °C using a Krüss GH-100 goniometer interfaced with image-capture software by injecting a 5 μL drop of the test liquid. Deionized water, ethylene glycol (≥99%; Aldrich), and diiodomethane (99%; Aldrich) were used as standards for measuring the surface free energies.

Thin-Film Formation and Polymerization

0.5 g of the B-ala monomer was pre-mixed with a certain mole ratio of AIBN in 10 mL tetrahydrofuran (THF) at room temperature. The solution was then filtered through a 0.2 μm syringe filter before spin coated onto a glass slide (100 × 100 × 1 mm^3).

Polymer Thin Film Formation

Polymer solutions were prepared by dissolving the polymer in ethanol at a concentration of 10 wt.-%. 1 mL of the appropriate polymer solution was spin-coated onto a glass slide using a photoresistant spinner operating at 1 500 rpm for 45 s. The sample was then left to dry at 60 °C for 1 h to remove residual solvent. The B-ala monomer (0.5 g) was pre-mixed with AIBN in 10 mL toluene to produce a mole ratio of 5 (i.e. B-ala monomer/AIBN = 5) at room
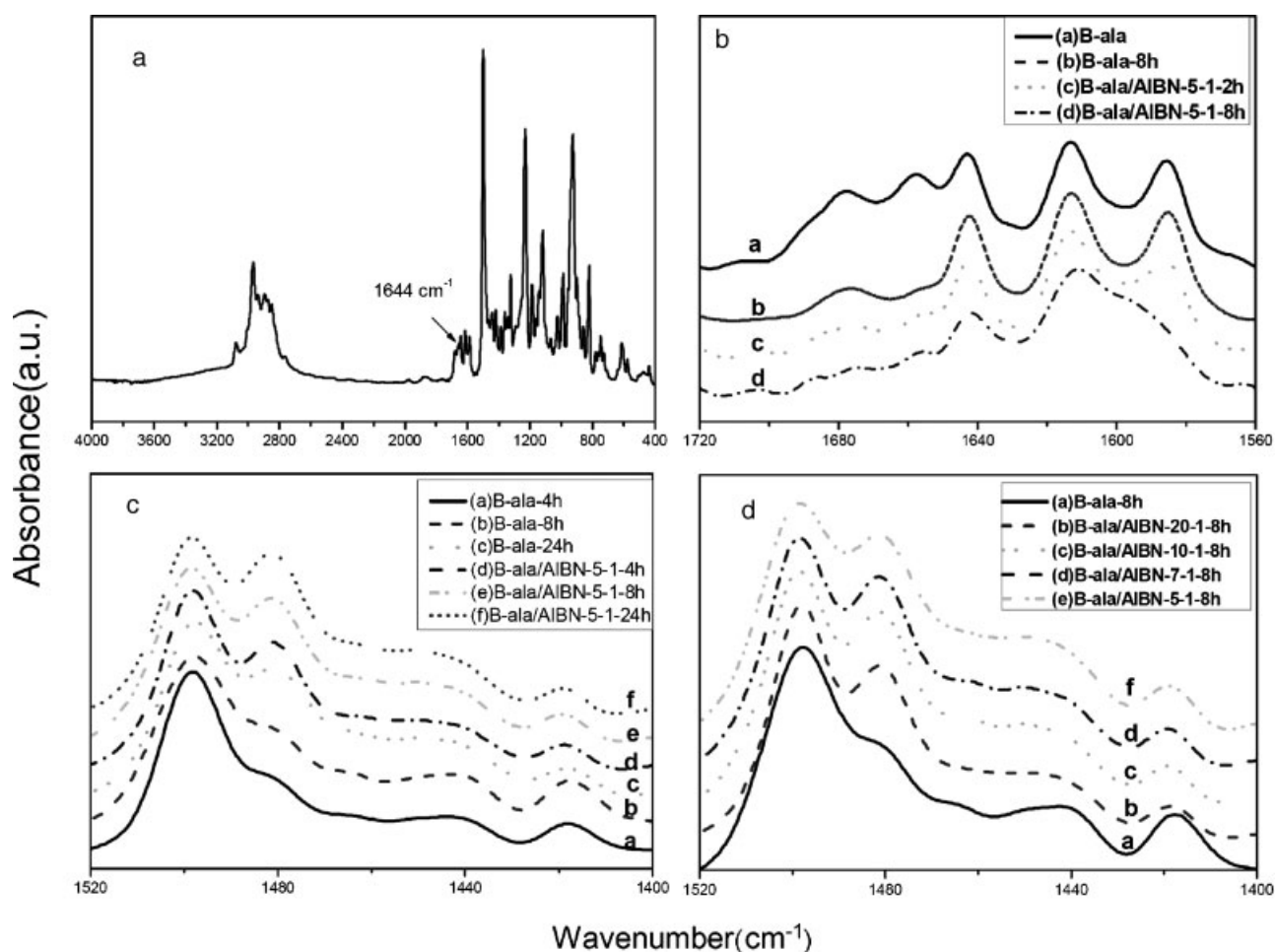

Figure 1. FT-IR spectra of B-ala and B-ala/AIBN PBZ film. (a) B-ala, (b) B-ala and B-ala/AIBN = 5:1 cured at 120 °C, (c) B-ala and B-ala/AIBN = 5:1 cured at 120 °C, and (d) B-ala and different molar ratio of B-ala/AIBN cured for 8h at 120 °C.

temperature. Finally, the mixed solution was filtered through a 0.2 μm syringe filter before spin-coated onto the polymer thin film surface.

Fourier Transform Infrared Spectroscopy (FTIR)

All infrared spectra were recorded at using a Nicolet Avatar 320 FTIR spectrophotometer, 32 scans were collected with a spectral resolution of 1 cm^{-1}. Infrared spectrum of the polymer film was determined with the conventional potassium bromide (KBr) plates method. The sample was prepared by casting the THF solution directly onto a KBr plate and cured under conditions similar to those used in the bulk preparation.

Differential Scanning Calorimetry (DSC)

Thermal analyses were performed using a DuPont 910 DSC-9000 controller at a scan rate of 5 °C/min over the temperature range from 30 to 300 °C under a nitrogen atmosphere. All samples (ca. 5–10 mg) were weighed and sealed in a hermetic aluminum pan with lids.

Results and Discussion

The B-ala monomer contains a N-allyl group that can be polymerized through free radical polymerization with the aid of a free radical initiator. AIBN is known as an effective free radial initiator for addition polymerization of the N-allyl group.[4,6] Figure S5 shows the DSC thermograms of the bifunctional allyl-containing benzoxazine monomer B-ala, with and without AIBN as an initiator. Two exothermic peaks were observed for B-ala, which correspond to the crosslinking of the N-allyl group (260 °C) and the ring-opening polymerization (210 °C) of the benzoxazine.[4] When AIBN was added another exothermic peak appeared at 120 °C, which can be attributed to the breaking of its azo group. As shown in Figure 1a and 1b, the characteristic absorption band assigned to the allyl group appeared at 1 644 cm^{-1} (stretching of C=C). The intensity of this allyl peak (1 644 cm^{-1}) decreased in the presence of AIBN and increased with curing time (Figure 1b), implying that the polymerization of N-allyl groups took place by a free radical mechanism. However, the tetrasubstituted benzene mode at 1 484 cm^{-1}, corresponding to benzoxazine polymerization via ring opening, was somewhat unexpected to increase when AIBN was added (Figure 1c). Ishida et al.[7] studied the curing behavior of benzoxazine monomer and found that the benzoxazine precursor undergoes an autocatalytic type of curing mechanism catalyzed by the phenol group formed by ring opening of the oxazine ring. Based on a previous report,[8] the decomposition heat from the breaking of the azo group as observed for AIBN at 363 K was around 123 J g^{-1}.

Table 1. Advancing contact angles for water, ethylene glycol (EG), and diiodomethane (DIM) and their corresponding surface free energy of B-ala and B-ala/AIBN polybenzoxazine films. Curing temperature:120 °C, molar ratio of B-ala monomer/AIBN = 5/1, γ_s (HD): test liquids are deionized water and diiodomethane, γ_s (ED): test liquids are ethylene glycol and diiodomethane.

Curing time	Roughness	Contact angle			Surface free energy		
h	nm	°			mJ m^{-2}		
		Water	DIM	EG	γ_s(HD)	γ_s(ED)	γ_s
B-ala							
0.5	1.3	83.7	18.4	66.5	48.3	49.3	48.2
1	1.2	85.3	19.2	69.6	48.2	48.5	48.0
2	0.8	91.5	21.1	73.5	48.6	47.5	47.5
4	1.4	105.0	51.4	79.5	35.4	34.4	33.5
8	1.3	107.5	58.1	86.5	31.3	30.0	29.7
24	1.2	111.9	63.3	88.9	28.7	27.1	26.7
B-ala/AIBN = 5/1							
0.5	1.4	93.1	20.7	70.5	49.2	48.0	47.6
1	1.0	95.0	21.0	72.0	49.6	47.7	47.5
2	1.0	103.0	24.7	75.4	51.1	46.3	46.3
4	0.8	107.2	63.2	80.4	27.7	29.4	26.8
8	0.8	109.0	83.0	87.0	16.0	21.2	16.6
24	1	112.0	85.3	89.0	14.9	19.8	15.3

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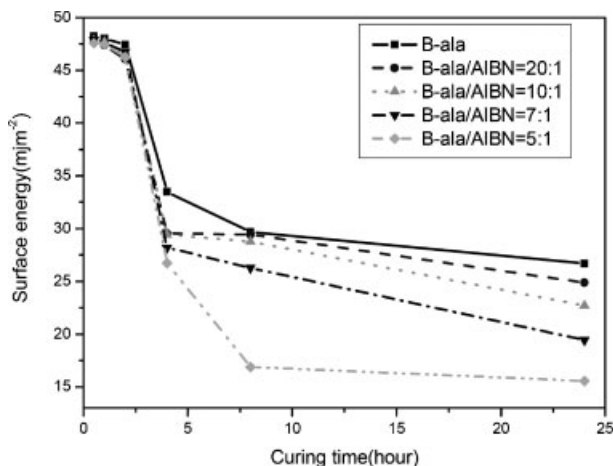
Figure 2. Surface free energy of B-ala and B-ala with different molar ratio of AIBN cured at 120 °C.
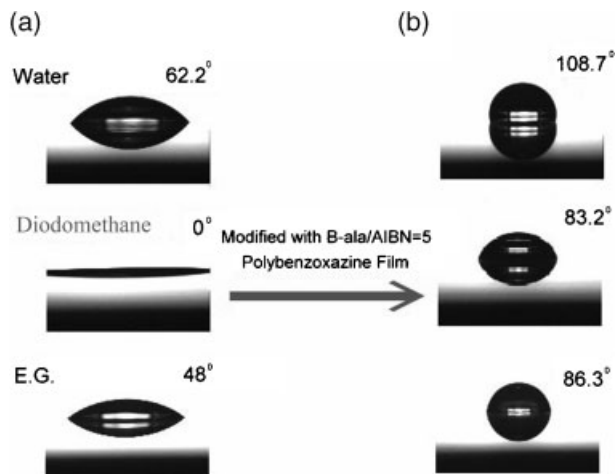

Figure 3. The advancing contact angle for water, ethylene glycol, and diiodomethane of (a) poly(4-vinyl pyridine) thin film (b) modified with B-ala/AIBN = 5 PBZ thin film.

Furthermore, phenolic-containing oligomers were formed due to the heat release from the breaking of the azo group of the AIBN. The phenol group of these oligomers provided a catalytic effect for the ring opening of the oxazine ring in the subsequent curing. More oligomers were formed during the earlier stages of the curing process resulting in the higher rate of ring-opening crosslinking of the oxazine ring. More AIBN was added to form more oligomers, thereby releasing more heat from the breaking of the additional azo groups and resulting in a higher rate of ring-opening crosslinking of the oxazine ring (Figure 1d). As a result, the radical initiator AIBN, not only initiated the free radical polymerization for the allyl group, but also catalyzed the ring-opening reaction of benzoxazine.

Table 1 lists the surface roughness and the advancing contact angles of the three test liquids and the respective surface free energies (γ_s) of B-ala and B-ala/AIBN PBZs with various curing times. The lowest surface free energy obtained was 15.3 mJ m^{-2} from the B-ala/AIBN = 5:1 PBZ system after 24 h of curing at 120 °C. In both B-ala and B-ala/AIBN PBZ systems at the curing temperature of 120 °C, the advancing contact angles of all the three test liquids (water, ethylene glycol and diiodomethane) increased as curing time was increased. At the same curing time, all the advancing contact angles from B-ala/AIBN PBZ films were relatively higher than those from B-ala PBZ films, especially in the diiodomethane liquid system. The surface free energy, γ_s, was calculated by using van Oss and Good's three-liquid method[9] and two-liquid geometric method.[10] The extremely low surface free energy ($\gamma_s = 15.3$ mJ m^{-2}) from the B-ala/AIBN = 5:1 PBZ system after 24 h of curing was even lower than that of pure Teflon ($\gamma_s = 16.43$ mJ m^{-2}).[3] This phenomenon can be explained in terms of the more

intramolecular hydrogen bonding formed. To determine the extent of hydrogen bonding within B-ala and B-ala/AIBN PBZs, curve-fitting of FT-IR spectra of all hydrogen bonds were performed. Figure S7 displays the FT-IR spectra of the B-ala/AIBN PBZ thin films as a function of curing time (2, 4, 8, and 24 h) at 120 °C. The FT-IR spectrum of the pure B-ala system is similar to the B-ala/AIBN system. The fraction of the peak at 3 207 cm^{-1}, corresponding to the OH···N intramolecular hydrogen bond, increased when the curing time increased, while the OH···O intermolecular hydrogen bond at 3 417 cm^{-1} slightly decreased when the curing time increased. When AIBN was added,

Table 2. The advancing contact angle for water, ethylene glycol, and diiodomethane of poly(4-vinyl phenol), poly(4-vinyl pyridine) and polycarbonate substrates before and after modification with B-ala/AIBN = 5/1 PBZ thin film cured 8 h at 120 °C.

Polymer substrates	Contact angle			Surface energy
	°			mJ m^{-1}
	Water	DIM	EG	γ_s
Before modification				
Poly(4-vinyl phenol)	72.1	44.4	45.6	40.5
Poly(4-vinyl pyridine)	62.2	0	48.0	57.4
Polycarbonate	89.5	35.0	56.0	42.3
After modification				
Poly(4-vinyl phenol)	107.0	80.6	87.3	17.6
Poly(4-vinyl pyridine)	108.7	83.2	86.3	16.6
Polycarbonate	107.3	80.3	86.2	17.9

the rate of the ring-opening reaction and the fraction of the intramolecular hydrogen bonding both increased. The surface free energies versus the curing times at 120 °C of various molar ratios for B-ala monomer to AIBN are shown in Figure 2. The lowest surface free energy for the B-ala/AIBN = 5: 1 PBZ system was 15.3 mJ m^{-2} which was even lower than the BA-m PBZ system cured in 1h at 210 °C (16.4 mJ m^{-2}).[3]

The thermal curing process of this B-ala/AIBN PBZ system is performed at 120 °C, therefore, the spectra shown in Figure 1, it can be used to modify many polymer substrates. Figure 3 shows the advancing contact angles of water, ethylene glycol, and diiodomethane on the poly(4-vinyl pyridine) thin film before and after modification with B-ala/AIBN = 5/1 PBZ, the advancing contact angles of the three test liquids all increase substantially. Poly(4-vinyl phenol) film and polycarbonate substrates give the same trend as shown in Table 2.

Conclusion

The free radical initiator AIBN, induces polymerization of the *N*-allyl group of the B-ala monomer and produces phenol-containing oligomers. These oligomers are able to catalyze the ring opening of the oxazine ring at a relatively low curing temperature (120 °C) to produce polybenzoxazine with stronger intramolecular hydrogen bonding but lower surface energy. B-ala and B-ala/AIBN PBZ thin films both possess low surface free energy as strong intramolecular hydrogen bonds are formed during the curing process. The B-ala/AIBN PBZ system has a relatively lower surface free energy than the pure B-ala system because of the higher extent of the ring-opening of oxazine. Moreover, this system can modify many polymer substrates that are thermally stable at or above 120 °C.

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