

Low-Surface-Free-Energy Materials Based on Polybenzoxazines

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Hydrophobicity and oleophobicity are highly desirable properties for materials that are used in a wide range of applications.^[1–11] In this context, poly(tetrafluoroethylene) (teflon) is considered to be the “benchmark” low-surface-free-energy material as it combines water repellence^[12] with other desirable properties.^[13] Unfortunately, the use of teflon comes with certain disadvantages, such as those resulting from its low oil repellence, high cost, and poor processability. Considerable research efforts have therefore been directed towards the development of nonwetable, low-surface-free-energy polymeric materials that exhibit good film-forming characteristics.^[14,15]

Intra- and intermolecular interactions are important for the surface properties of polymers. Jiang et al.^[16] have reported that at temperatures above the lower critical solution temperature (LCST), the compact, collapsed conformation of poly(*N*-isopropylacrylamide) (PNIPAAm) chains induced by intramolecular hydrogen bonding between the C=O and N–H groups in the main PNIPAAm chains leads to a low surface free energy and high contact angle for water. When the temperature is below the LCST, however, the predominantly intermolecular hydrogen bonding between the main PNIPAAm chains and water molecules leads to a higher surface free energy and lower water contact angle. In addition, Chung et al.^[17] have reported that the presence of amide groups in a fluorinated-main-chain liquid-crystalline polymer system tends to induce strong intermolecular hydrogen bonding, which results in higher surface free energies and higher degrees of hydrophilicity. According to these previous studies, it appears that intramolecular hydrogen bonding tends to lower the surface free energy more than intermolecular hydrogen bonding between main polymer chains.

Polybenzoxazines have many unique properties, such as low water absorption, high moduli,^[18] and high glass-transition temperatures.^[19] It is generally believed that hydrogen

bonding between polybenzoxazine polymer chains plays an important role in promoting these attractive properties.^[18] We report here that these readily available polybenzoxazines display extremely low surface free energies, even lower than that of pure teflon.

We used two bifunctional benzoxazine monomers, namely 2,2-bis(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)propane (BA-a) and 2,2-bis(3-methyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)propane (BA-m). By spin-coating, we produced films that were subsequently cured in an oven to obtain ultrathin films with a thickness of about 150 nm. Table 1 lists the surface

Table 1: Root-mean-square (rms) surface roughness and advancing contact angles for water, ethylene glycol (EG), and diiodomethane (DIM) on BA-a and BA-m polybenzoxazine film structures (standard deviations in the range 0.3–2.0). The corresponding surface-free-energies (γ) are also given.

T [°C]	t [h]	Roughness (rms) [nm]	Contact angle [°]			γ [mJ m ⁻²]	
			H ₂ O	EG	DIM		
BA-a polybenzoxazines							
60	1	2.1	97.9	73.2	17.6	48.45	
180	1	1.4	99.5	74.8	40.6	39.31	
	2	1.1	98.6	78.5	49.2	34.72	
	4	1.0	98.7	82.1	61.0	27.99	
	8	1.5	103.0	83.5	69.8	22.98	
240	22	1.0	104.3	83.1	70.8	22.43	
	0.5	1.7	108.5	84.1	63.2	26.73	
	1	1.0	111.5	88.6	76.8	19.21	
	2	1.2	110.7	88.1	76.5	19.38	
	4	1.8	92.3	71.4	63.8	27.11	
	8	1.3	79.4	61.3	55.7	32.03	
	BA-m polybenzoxazines						
	60	1	0.8	75.3	67.6	12.6	49.58
180	1	1.0	101.8	77.5	52.4	32.93	
	2	0.4	109.3	83.2	59.2	29.04	
	4	0.5	113.7	89.7	72.5	21.49	
	8	0.3	113.6	92.1	81.0	17.02	
	22	0.6	112.9	92.4	80.8	17.10	
210	0.5	0.4	105.2	80.4	76.4	19.37	
	1	0.2	114.0	93.3	82.1	16.43	
	2	0.5	112.5	90.3	81.7	16.63	
	4	0.7	103.0	75.5	72.2	21.65	
	8	0.2	80.4	56.8	59.3	28.98	

roughness and advancing contact angles of BA-a and BA-m polybenzoxazines after various curing times. The advancing contact angle is relatively less sensitive to surface roughness and heterogeneity than the receding angle, therefore the advancing angle data are commonly used to calculate the components of surface and interfacial tension.^[20,21] In the BA-a polybenzoxazine system at a curing temperature of 180°C, the advancing contact angle of diiodomethane increases with increasing curing time (from 41° after 1 h to 71° after 22 h). In contrast, the advancing contact angles of both water and ethylene glycol increased only slightly. In the case of samples kept at a higher curing temperature (240°C),

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the contact angles of all three liquids increased initially during the first hour and then decreased steadily upon increasing the curing time. Curing at 240 °C for 1 h led to the highest contact angles for all three liquids (112° for water, 84° for ethylene glycol, and 77° for diiodomethane). For BA-m polybenzoxazine treated at a curing temperature of 180 °C, the advancing contact angles of all three liquids increased upon increasing the curing time, but tended to level off after 8 h. When cured at 210 °C, the contact angles of all three liquids followed similar trends to those observed for the BA-a polybenzoxazine cured at 240 °C, and curing at 210 °C for 1 h led to the highest contact angles (114° for water, 93° for ethylene glycol, and 82° for diiodomethane). The root-mean-square (rms) roughness of all polybenzoxazines is lower than 3 nm, therefore the influence of topography on the surface free energy is negligible.

We evaluated the surface free energies, γ , (Table 1) by using van Oss and Good's three-liquid method.^[22,23] For BA-a polybenzoxazine held at a curing temperature of 180 °C, the total surface free energy decreased substantially from 39.3 to 23 mJ m⁻² upon increasing the curing time from 1 to 8 h. Further increasing the curing time from 8 to 22 h did not result in any significant reduction in surface free energy. At a higher curing temperature (240 °C), however, the surface free energy decreased initially and then increased steadily upon increasing the curing time. The lowest value of the surface free energy was 19.2 mJ m⁻² after curing at 240 °C for 1 h. For the BA-m polybenzoxazine cured at a relatively low temperature (180 °C), the surface free energy decreased from 32.9 to 17 mJ m⁻² upon increasing the curing time from 1 h to 8 h and then remained nearly constant up to 22 h. After curing temperature at 210 °C, the surface free energy followed a similar trend to that of BA-a polybenzoxazine cured at 240 °C. In the BA-m polybenzoxazine system, curing at 210 °C for 1 h resulted in the lowest surface free energy (16.4 mJ m⁻²). For comparison, the surface free energy of teflon (21 mJ m⁻²) was also determined by using the same liquids.^[24] To our surprise, the surface free energies of these fluorine- and silicone-free polybenzoxazines are significantly lower than that of pure teflon.

According to previous studies,^[25,26] the surface free energy in an epoxy system increases upon increasing the curing time, whereas in this study we found that the surface free energies of the polybenzoxazine systems (at 180 °C) generally decrease upon increasing the curing time. We believe that these polybenzoxazines possess lower surface free energies than the epoxy systems due to the presence of strong intramolecular hydrogen bonding. Ishida et al. have reported that the network structure of polybenzoxazine is supported by strong hydrogen-bonding interactions between the polymer chains, which act as chemical cross-links.^[18] The hydrogen bond network structures of BA-a and BA-m polybenzoxazines have been discussed widely.^[27] To determine the degree of hydrogen bonding within these polybenzoxazines, we performed curve-resolving of their FTIR spectra with respect to the corresponding frequencies of each hydrogen-bonded species (Figure 1).

The distribution of hydrogen-bonded species in the polybenzoxazine is affected greatly by the amino groups in

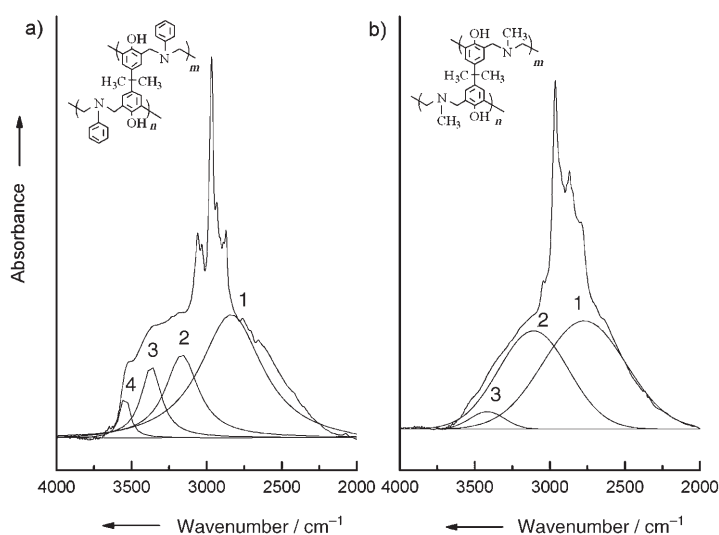


Figure 1. Curve fitting for the FTIR spectra of polybenzoxazines: a) BA-a polymer (curing temperature: 240 °C; curing time: 1 h) and b) BA-m polymer (210 °C, 1 h). 1) O⁻...H⁺N intramolecular hydrogen bonding; 2) OH...N intramolecular hydrogen bonding; 3) OH...O intermolecular hydrogen bonding; 4) OH... π intramolecular hydrogen bonding.

the Mannich bridges. For example, the network structure of the BA-m polybenzoxazine consists mainly of OH...N and O⁻...H⁺N intramolecular hydrogen bonds (proton-transfer equilibrium), whereas that of the BA-a polybenzoxazine possesses a relatively small number of such bonds. In the latter, however, some of the hydroxy groups form OH...O intermolecular hydrogen bonds. Consequently, the surface free energy of the BA-m polybenzoxazine is lower than that of the BA-a polybenzoxazine. This phenomenon can be explained by considering the fact that the strength of a hydrogen bond depends on the electronegativity of the group attached to the nitrogen atom: the electron density around the nitrogen atom attached to the benzene ring in the BA-a polybenzoxazine is lower than that in the BA-m polybenzoxazine because the electrons of the nitrogen atom of the former are more delocalized than those of the latter. Both BA-a and BA-m polybenzoxazines display strong intramolecular hydrogen bonding, which results in relatively low surface free energies. Higher curing temperatures tend to disrupt these hydrogen-bonding interactions and the resultant ratio of intra- and intermolecular hydrogen bonds may change after the sample is cooled to ambient temperature. Figure 2 displays the FTIR spectra of the BA-a and BA-m polybenzoxazine thin films as a function of the curing time (0 to 8 h) at 240 and 210 °C, respectively. The peak at 3417 cm⁻¹ corresponds to the OH...O intermolecular hydrogen bonds of the BA-a polybenzoxazine, and it is clear that the fraction of these intermolecular hydrogen bonds increases upon increasing the curing time. In the FTIR spectra of the BA-m polybenzoxazine, the peak at 3397 cm⁻¹ reflects the OH...O intermolecular hydrogen bonds.^[27] After curing the BA-m benzoxazine at 210 °C for 1 h, a minor portion of the hydrogen-bonding interactions have been converted into OH...O intermolecular hydrogen bonds. The intensity of the signals corresponding to

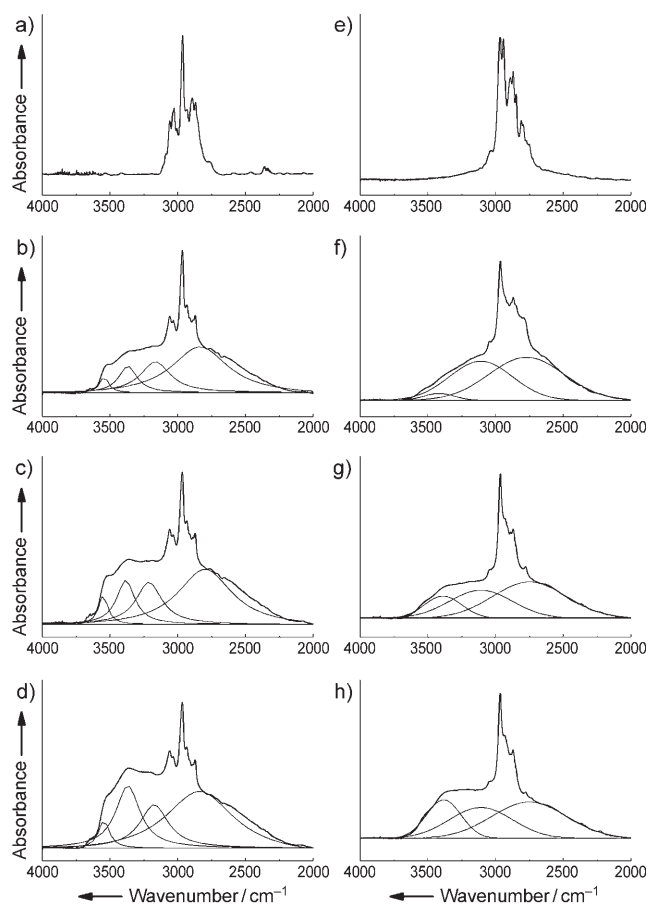


Figure 2. Curve fitting for the FTIR spectra of BA-a polybenzoxazines cured at 240°C for a) 0, b) 1, c) 4, and d) 8 h, and BA-m polybenzoxazines cured at 210°C for e) 0, f) 1, g) 4, and h) 8 h.

these hydrogen bonds increases upon increasing the curing time.

Combining our analyses of the FTIR spectra (Figure 3a), the variations in the water contact angles (Figure 3b), and the surface free energies (Figure 3c), it is clear that enhanced intramolecular hydrogen bonding leads to a decrease in the surface free energy and an increase in the water contact angle, whereas increasing the fraction of intermolecular hydrogen bonding leads to the opposite effect. These observations are in good agreement with the results of previous studies on surface-free-energy effects.^[16,17]

In conclusion, from analyses of FTIR spectra and surface free energies we have found that strong intramolecular hydrogen bonding between the hydroxy groups of polybenzoxazines decreases their surface free energies, whereas intermolecular hydrogen bonding between the hydroxy groups of polybenzoxazines increases them. The lowest surface free energies that we observed for the BA-a and BA-m polybenzoxazine systems were 19.2 and 16.4 mJm^{-2} , respectively. These values are lower than that of pure teflon (21 mJm^{-2}). While polybenzoxazines and fluoropolymers both possess low surface free energies, the former are cheaper to prepare and easier to process, and therefore polybenzoxazines might replace fluoropolymers in biotechnological applications^[28] and as low-surface-free-energy coatings.^[29]

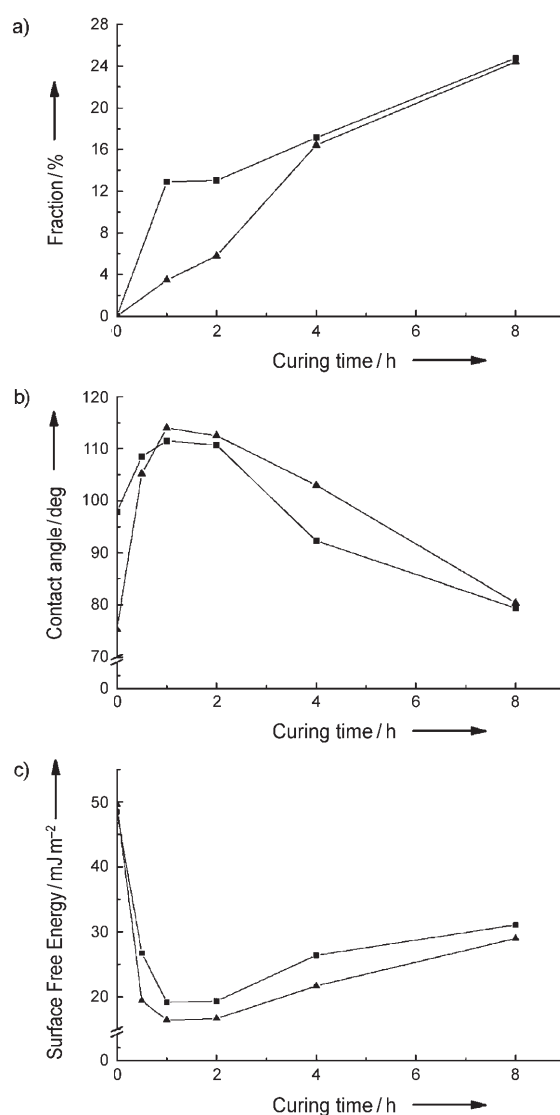


Figure 3. Variations of a) the fraction of intermolecular hydrogen bonding, b) the water contact angles, and c) the surface free energies of the BA-a (■, cured at 240°C) and BA-m polybenzoxazines (▲, cured at 210°C).

These BA-a and BA-m polybenzoxazines are examples of the first new class of low-surface-free-energy polymer materials since the discovery of the well-known fluoropolymers and silicones.

Experimental Section

A BA-a or BA-m benzoxazine (Shikoku Corp.) solution (30 mg mL^{-1} in tetrahydrofuran) was spin-coated onto a glass slide ($100 \times 100 \times 1 \text{ mm}^3$) at 1500 rpm for 45 s. The sample was left to dry at 60°C for 1 h before it was cured in an oven (Table 1). Infrared spectra were recorded with a Nicolet Avatar 320 FTIR spectrophotometer. The sample was prepared by casting the THF solution directly onto a potassium bromide plate and curing under conditions similar to those used in the bulk preparation. The advancing contact angle of the polymer sample was measured at 25°C with a Kruss GH-100 goniometer interfaced with image-capture software by injecting a 5- μL liquid drop. Deionized water, ethylene glycol ($\geq 99\%$; Aldrich),

and diiodomethane (99%; Aldrich) were used as standards to measure the surface free energies. Surface roughness profiles of film structures were acquired with a Digital Instruments DI5000 scanning probe microscope.

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