Mechanistic insights into ortho-blocked and ortho-free vitrimeric polybenzoxazines incorporating dynamic Schiff linkages for closed-loop recyclability

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Supporting Information

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Figure S4. Contact angle analysis performed on PVBI and PHBI

Figure S5. FTIR of Pristine and Recycled PVBI

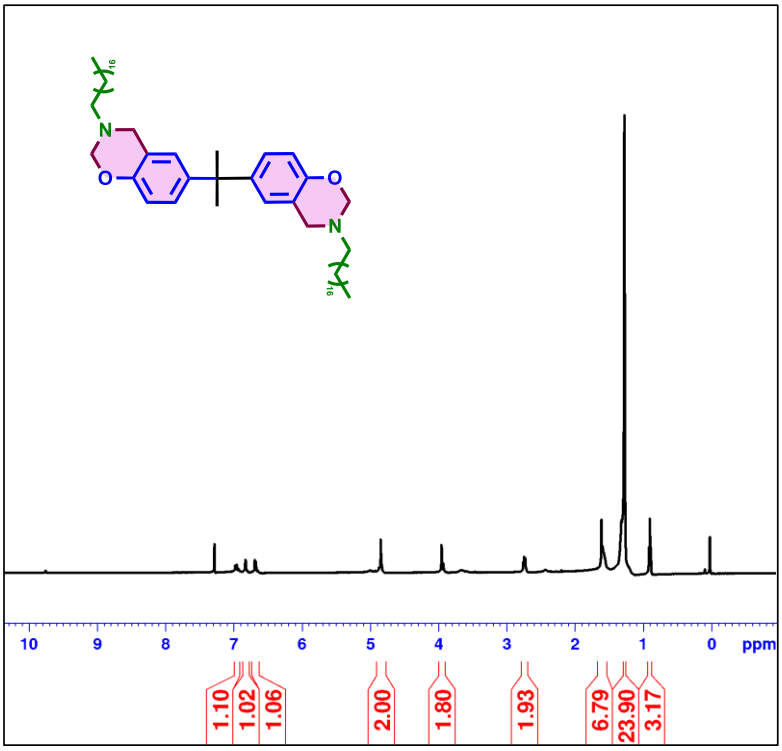

Figure S1. ^{1}H NMR spectra of control Sample – BASA.

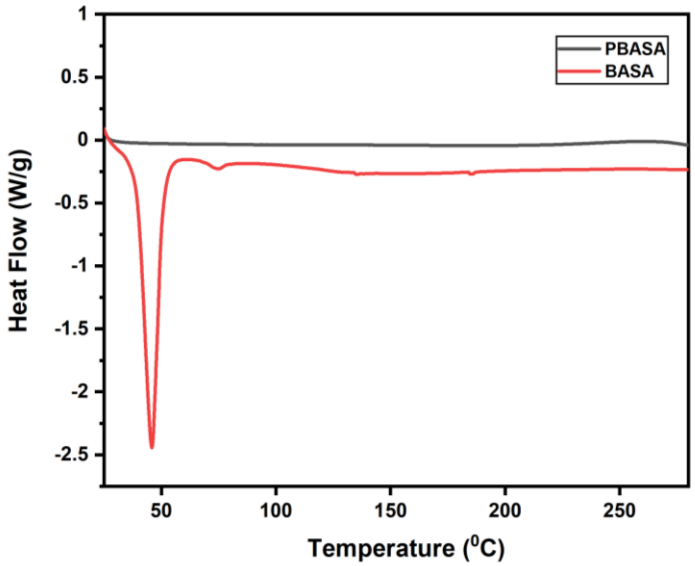

Figure S2. DSC comparison of BASA and PBASA.

Table S1. Estimation of activation energy (E_a) for the benzoxazine curing using the Ozawa method

VBI	HBI
Y= -15.45x – 32.11 (R^2 = 0.99)	Y= -12.52x – 27.509 (R^2 = 0.99)
$Ln(\beta) = -1.052E_a/RT_P + C$	$Ln(\beta) = -1.052E_a/RT_P + C$
$-15.45x = -1.052E_a/RT_P$ (R= 8.314 J mol^{-1} K^{-1})	$-12.52x = -1.052E_a/RT_P$ (R= 8.314 J mol^{-1} K^{-1})
E_a/R = 15.45/1.052	E_a/R = 12.52/1.052
E_a = 15.45*8.314/1.052 = **122.1 kJ/mol**	Ea = 12.52*8.314/1.052 = **98.9 kJ/mol**

Table S2. Calculation of activation energy (E_a) using stress relaxation studies

PVBI	PHBI
Y= 6.23x – 14.79 (R^2 = 0.992)	Y= 8.284x – 15.66(R^2 = 0.999)
Ln(T*)= 6.18 *1000/T – 14.7	Ln(T*)= 8.28 *1000/T – 15.66
$\tau^* = \tau_0 \exp(E_a/RT)$ (R = 8.314 J mol^{-1} K^{-1})	$\tau^* = \tau_0 \exp(E_a/RT)$ (R = 8.314 J mol^{-1} K^{-1})
$\ln(\tau^*) = \ln(\tau_0) + E_a/RT$	$\ln(\tau^*) = \ln(\tau_0) + E_a/RT$
E_a/R = 6.18*1000	E_a/R = 8.284*1000
E_a = 6.18*1000*8.314 = 51.38 kJ/mol	E_a = 8.284*1000*8.314 = 68.873 kJ/mol

S3. Calculation of crosslink density

PHBI

$$\nu = \frac{E'}{3RT} = \frac{46.29 \times 10^6}{3 \times 8.314 \times 383.23} = 4842.2\ mol/m^3$$

PVBI

$$\nu = \frac{E'}{3RT} = \frac{3.960 \times 10^6}{3 \times 8.314 \times 383.23} = 414.2\ mol/m^3$$

Where v is crosslink density, E’ is storage modulus determined from the rubbery plateau, R is universal gas constant and T is the temperature at which the modulus is taken.

4. Swelling studies

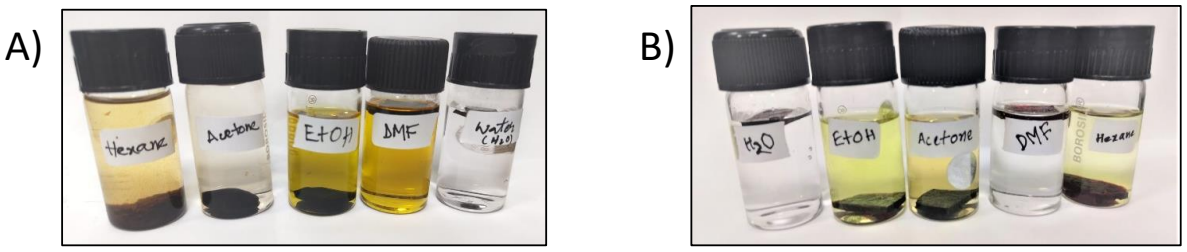

Figure S3. Photographs of cured polybenzoxazine in different solvents kept for one-week (A) PVBI, and (B) PHBI.

Table S3. Swelling ratio for cured polybenzoxazine in different solvents kept for one-week.

Solvent	PVBI	PHBI
Hexane	35.63	4.07
Acetone	34.64	14.97
Ethanol	13.51	3.94
DMF	15.23	2.85
Water	0.57	0.36

5. Contact angle Analysis

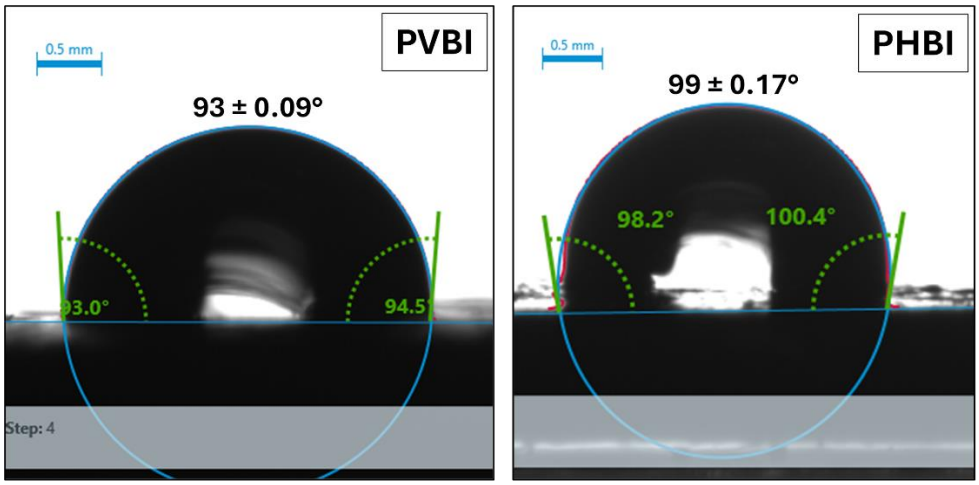

Figure S4. Contact angle analysis performed on PVBI and PHBI.

6. FTIR of Pristine and Recycled PVBI

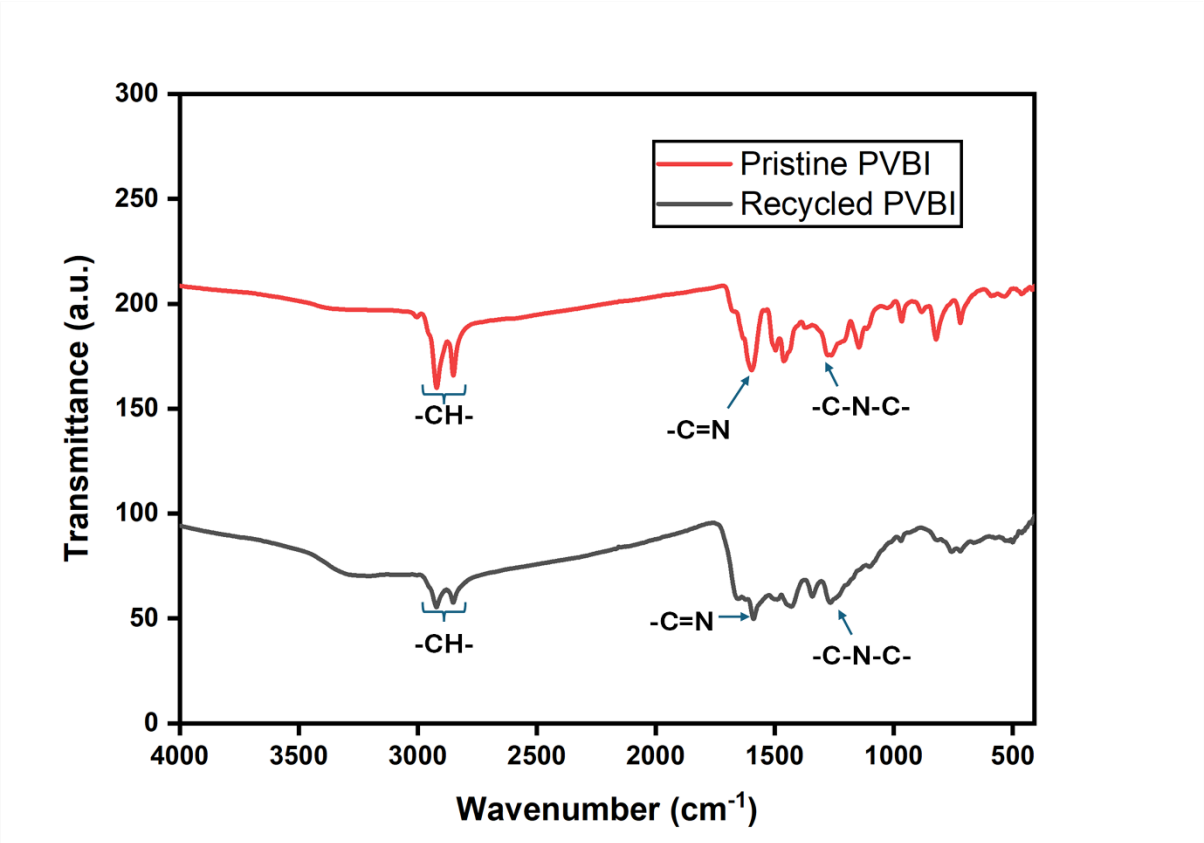

Figure S5. FTIR comparison of pristine sample and recycled sample.