

Supporting Information

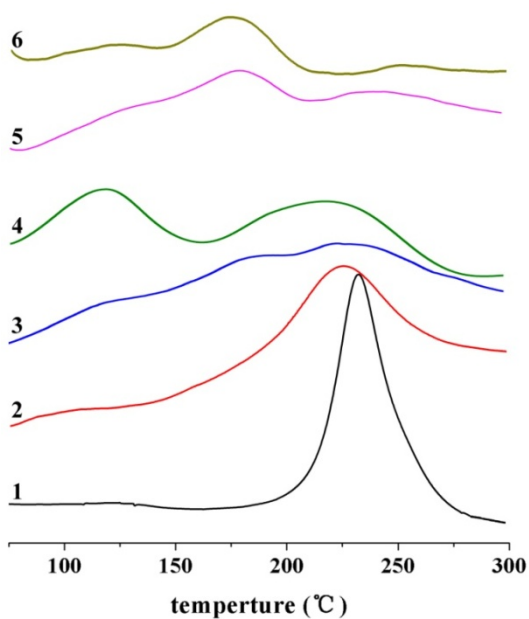


Fig.SI 1. DSC curves of the reactive BA-a/A1 mixtures of a variety of molar ratios: (1) without A1, (2) 1:0.25, (3) 1:0.5, (4) 1:1, (5) 1:2, and (6) 1:4.

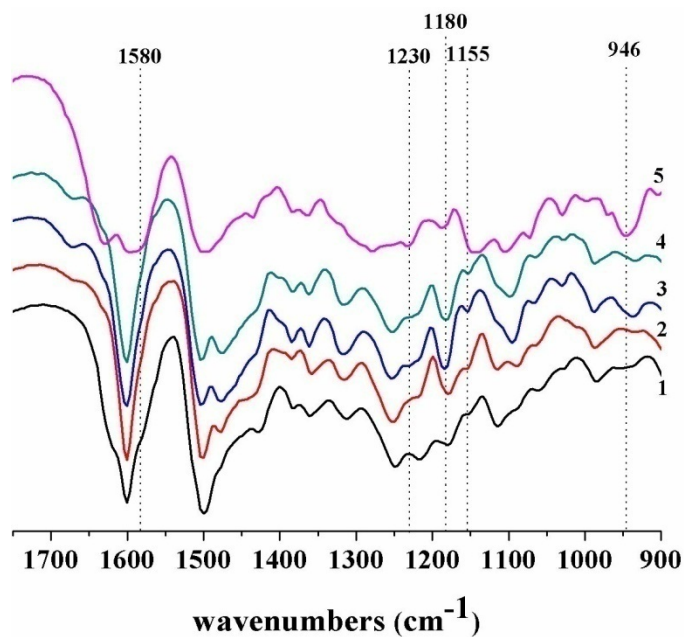


Fig.SI 2. FTIR spectra of the reactive BA-a mixtures with amines (1) A1, (2) A2, (3) A3, (4) A4, and (5) A5, heated at 100 °C for 60 minutes.

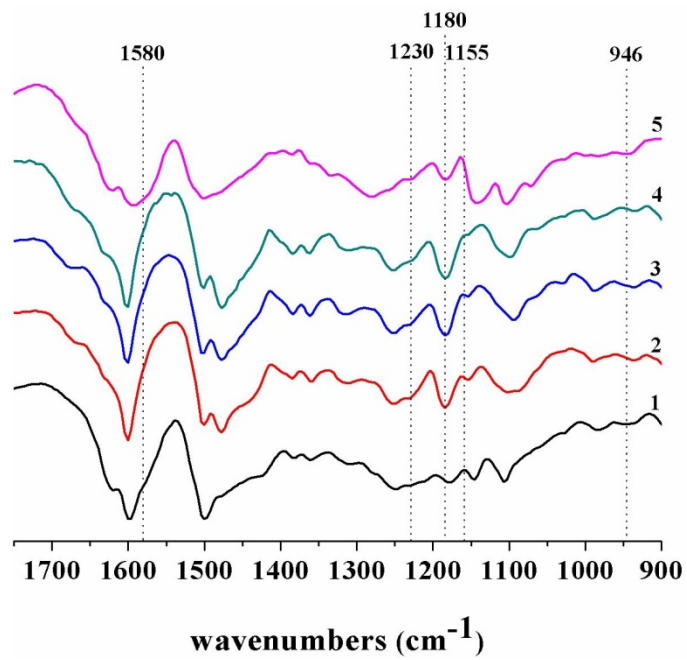


Fig.SI 3. FTIR spectra of the reactive BA-a mixtures with amines (1) A1, (2) A2, (3) A3, (4) A4, and (5) A5, heated at 120 °C and 150 °C for 2 h, respectively.

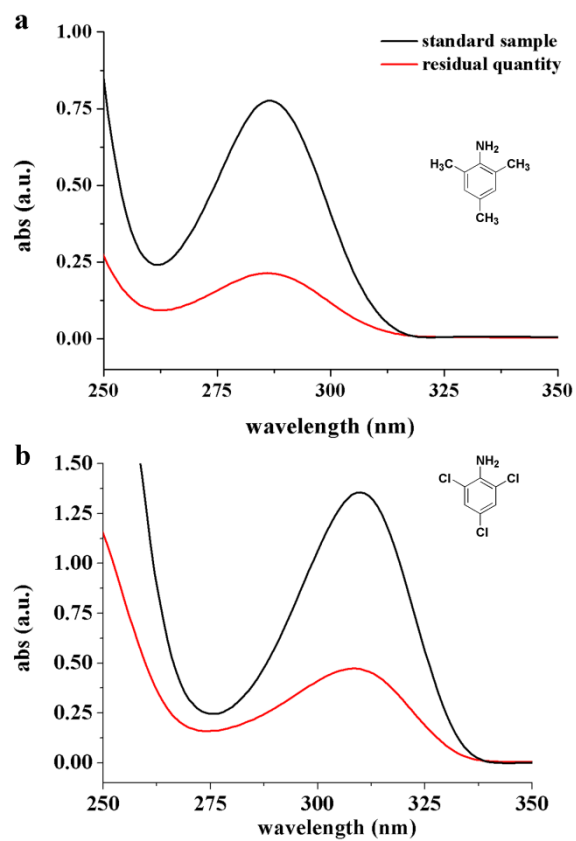


Fig.SI 4. UV-vis absorption spectra of the residual quantity of amines. (a) 2,4,6-Trimethylaniline, and (b) 2,4,6-Trichloroaniline. (the residual amines in the completely amine cured benzoxazine resins were extracted with methanol in a Soxhlet extractor.)

TableSI 1 Relative viscosity and reaction activity of benzoxazine/amine curing systems at different temperatures

| Curing system | 120 °C | | 150 °C | |
|---------------|-------------------|--|-------------------|--|
| | Gel time (min) | Reaction activity (min ⁻¹) ¹⁾ | Gel time (min) | Reaction activity (min ⁻¹) |
| pure BA-a | 364 | 2.75×10 ⁻³ | 189 | 5.29×10 ⁻³ |
| BA-a/A1 | 11 | 9.09×10 ⁻² | 3 | 3.33×10 ⁻² |
| BA-a/A2 | 36 | 2.78×10 ⁻² | 10 | 1.00×10 ⁻² |
| BA-a/A3 | 63 | 1.59×10 ⁻² | 15 | 6.67×10 ⁻² |
| BA-a/A4 | 33 | 3.03×10 ⁻² | 12 | 8.33×10 ⁻² |
| BA-a/A5 | 81 | 1.23×10 ⁻² | 33 | 3.03×10 ⁻² |

TableSI 2 Thermal properties of benzoxazine /amine curing systems.

| Curing system | T _{5%} (°C) ^a | T _{10%} (°C) ^b | T _{max} (°C) ^c | Y _c (%) ^d |
|---------------|-----------------------------------|------------------------------------|------------------------------------|---------------------------------|
| pure BA-a | 293 | 331 | 394 | 35 |
| BA-a/A1 | 278 | 335 | 377 | 43 |
| BA-a/A2 | 272 | 289 | 412 | 38 |
| BA-a/A3 | 251 | 266 | 407 | 19 |
| BA-a/A4 | 267 | 281 | 409 | 20 |
| BA-a/A5 | 318 | 351 | 438 | 35 |

^a T_{5%}: The temperature for which the weight loss is 5%;

^b T_{10%}: The temperature for which the weight loss is 10%;

^c T_{ma}: The temperature for maximum weight loss; ^d Y_c: Char yields at 800 °C under nitrogen atmosphere.

Table SI 3. The values of T_g , E' and ρ of benzoxazine /amine curing systems.

| Sample | T_g (°C) | E' (MPa) | | ρ (mol•m ⁻³) ^a |
|-----------|------------|------------|-----------|--|
| | | 50 °C | $T_g+ 50$ | |
| pure BF-a | 185 | 5182 | 1269 | 0.100 |
| BF-a/A1 | 160 | 4914 | 1735 | 0.144 |
| BF-a/A2 | 86 | 5400 | 1289 | 0.126 |
| BF-a/A3 | 105 | 4749 | 1081 | 0.101 |
| BF-a/A4 | 90 | 4066 | 1605 | 0.156 |
| BF-a/A5 | 169 | 2759 | 385 | 0.031 |

^a crosslinking density was calculated by the modified Nealsen equation (modification of the Flory's rubber elasticity theory).