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SUPPORTING INFORMATION

CARDANOL BASED BENZOXAZINE BLENDS AND BIO-SILICA REINFORCED COMPOSITES: THERMAL AND DIELECTRIC PROPERTIES

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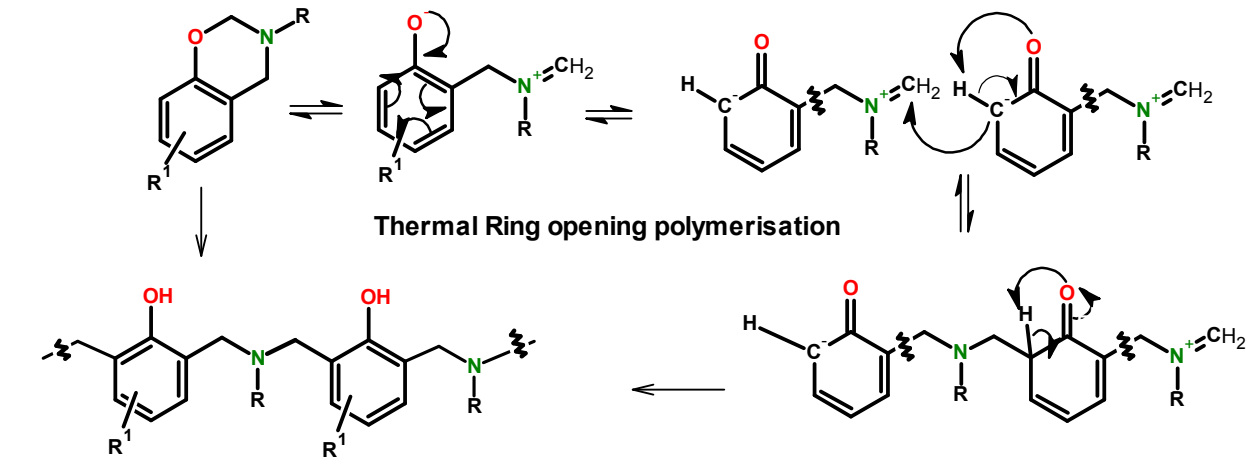
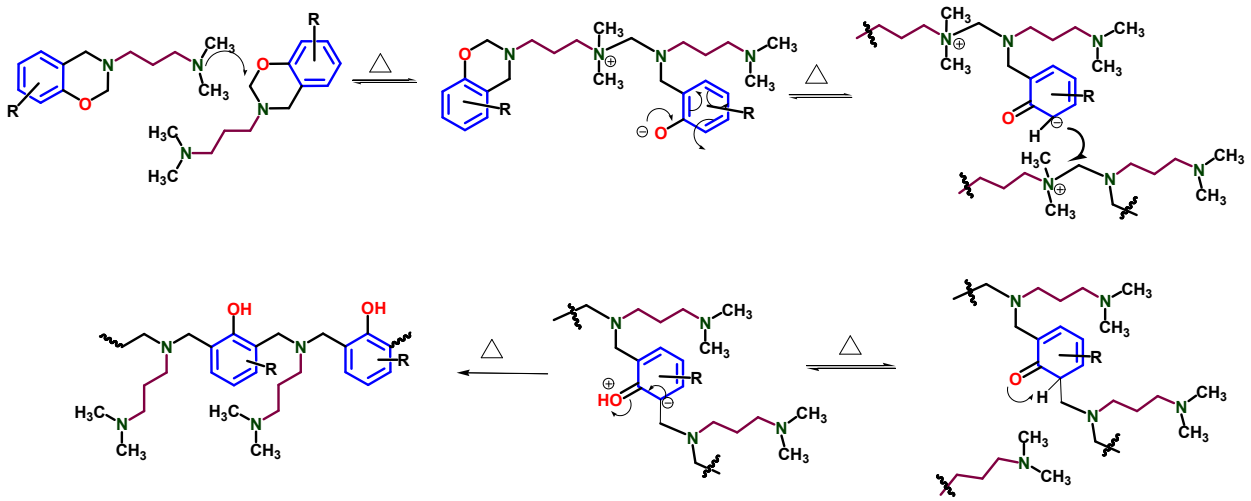
Table S1- Nomenclature of Monomer, Polymer, Cross linker and Catalysts used

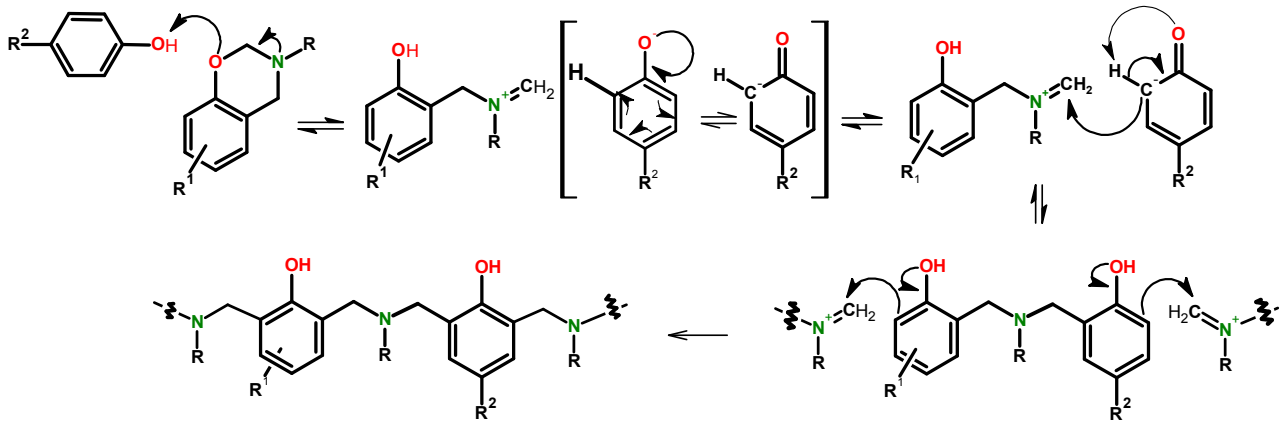
Sample name	Sample code
Bisphenol A aniline based benzoxazine (3,4-dihydro-6-(2-(3,4-dihydro-3-phenyl-2H-benze[1,3]oxazin-6-yl)propan-2-yl)-3-phenyl-2H-benzo[1,3]oxazine)	Bz A
Bisphenol F aniline based benzoxazine (bis(3,4-dihydro-3-phenyl-2H-benzo[1,3]oxazin-6-yl)methane)	Bz F
4, 4′-Bismaleimidodiphenyl methane	BMI-M
4, 4′-Bismaleimidodiphenyl sulfone	BMI-S
Cardanol aniline based benzoxazine	CrAb
Cardanol N,N-Dimetyl aminopropylamine based benzoxazine	CrDb
Cardanol CPL modified N,N-Dimetyl aminopropylamine based benzoxazine	CrCb
Cardanol aniline based benzoxazine/ Bisphenol A aniline based benzoxazine/Bismaleimide-M	CrAb/Bz-A/BMI-M 100 / 100 / 25 100 / 100 / 50 100 / 100 / 75
Cardanol aniline based benzoxazine/ Bisphenol A aniline based benzoxazine/Bismaleimide-S	CrAb/Bz-A/BMI-S 100 / 100 / 25 100 / 100 / 50 100 / 100 / 75
Cardanol aniline based benzoxazine/ Bisphenol F aniline based benzoxazine/Bismaleimide-M	CrAb/Bz-F/BMI-M 100 / 100 / 25 100 / 100 / 50 100 / 100 / 75
Cardanol aniline based benzoxazine/ Bisphenol F aniline based benzoxazine/Bismaleimide-S	CrAb/Bz-F/BMI-S 100 / 100 / 25 100 / 100 / 50 100 / 100 / 75



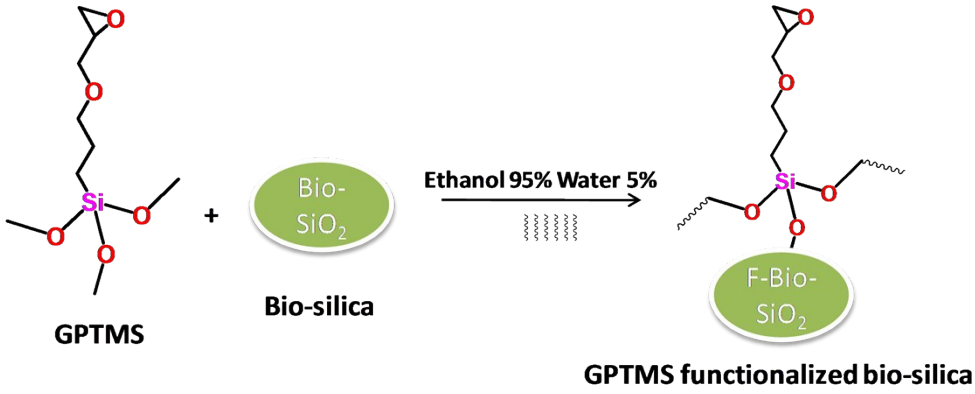
Scheme S1. Mechanism of Thermal Curing Behaviour of Benzoxazine.



Scheme S2. Mechanism of Tertiary (Dimethyl) Amine Based Polybenzoxazine Derivative.



Scheme S3. Mechanism of Phenolic Catalyst on Curing Behavior of Benzoxazine.



Scheme S4 GPTMS surface Functionalization on Biosilica.

MECHANISM

The cationic ring-opening polymerization mechanism proposed in Scheme S1 has been widely accepted by most researchers. A recent report has demonstrated a competitive pathway through phenoxy structures that finally converted into the phenolic polymers upon heating. Self-catalyzing N, N-dimethyl amino substituted group inbuilt benzoxazine based ring opening mechanism is explained in Scheme S2. The mechanism involves a quaternary ammonium intermediate i.e zwitterionic intermediate, which further produces another intermediate and the product was formed through proton transfer.

Benzoxazine monomer was cured with catalysts such as phenolic compounds, and its mechanism is described as a ring-opening addition reaction mechanism and is presented in

Scheme S3. The reactivity of CrAb/Bzs/BMIs with the different phenolic compounds such as 4-hydroxyacetophenone, 4-aminophenol, 4-hydoxyphenylmaleimide were studied and these catalysts stabilize the conjugate base of the benzoxazine during curing. The phenolic catalyst has possesses an electron withdrawing group and this group increases the acidity and thus induces the ring opening of benzoxazine at a lower temperature.

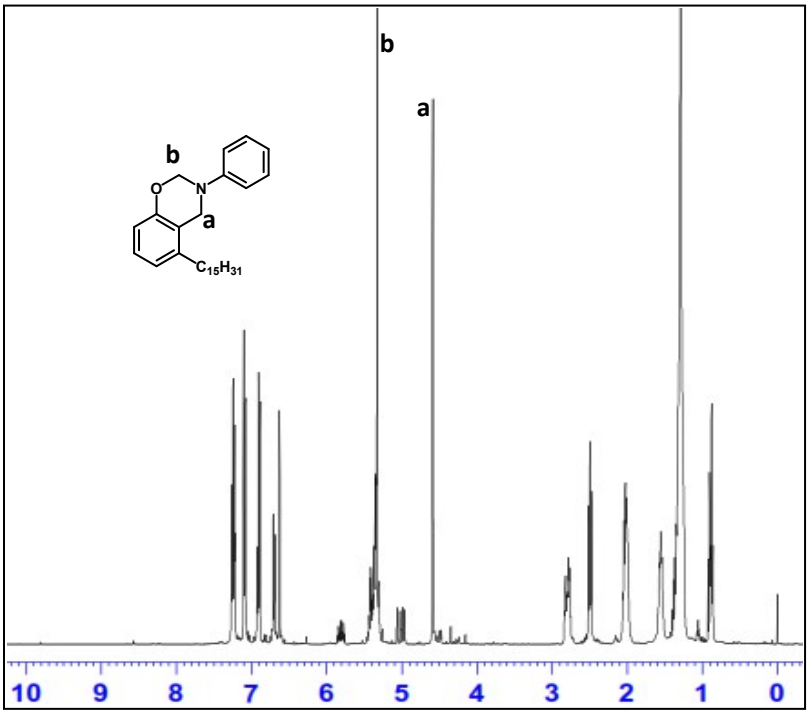


Figure –S1. ^{1}H NMR Spectra of CrAb Benzoxazine

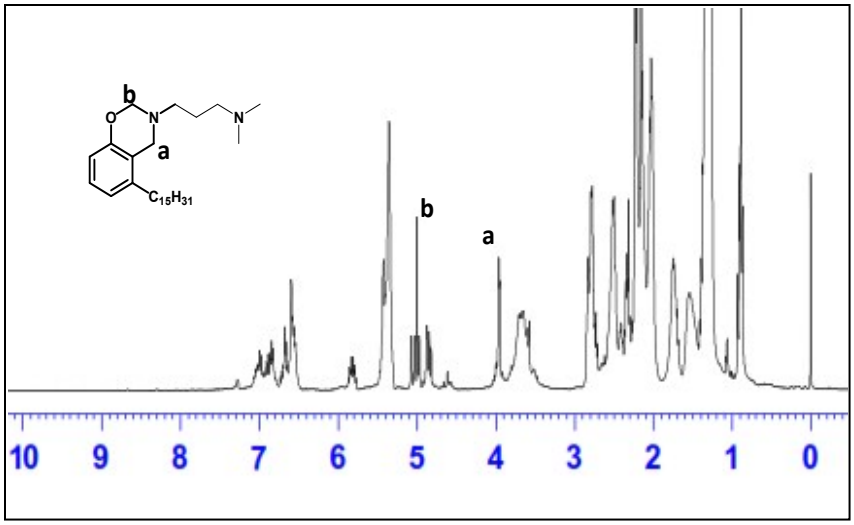


Figure –S2. ^{1}H NMR Spectra of CrDb Benzoxazine

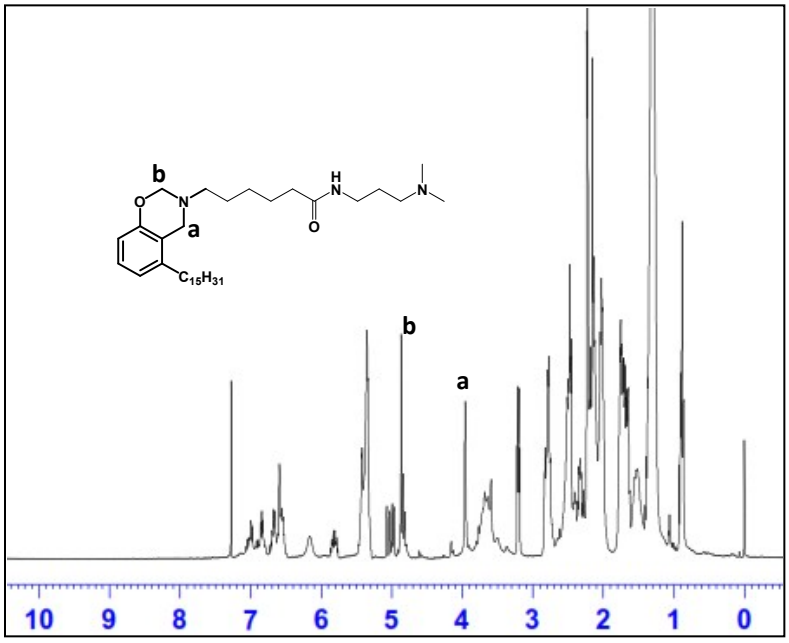


Figure –S3. ^{1}H NMR Spectra of CrCb Benzoxazine.

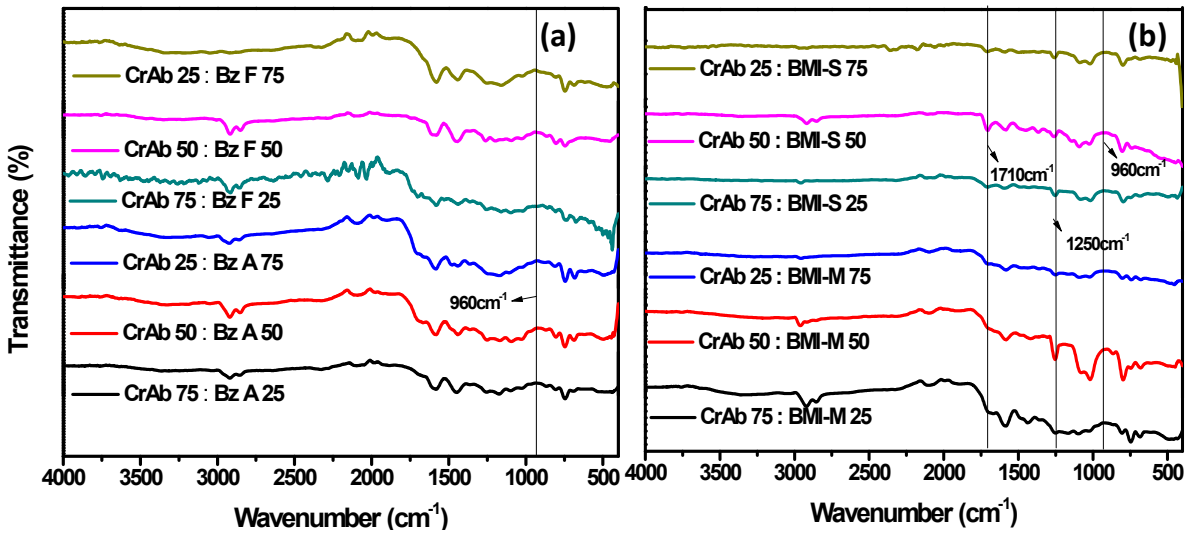


Figure S4. FT-IR spectrum of polybenzoxazine of (a) CrAb/Bzs and (b)CrAb/BMIs .

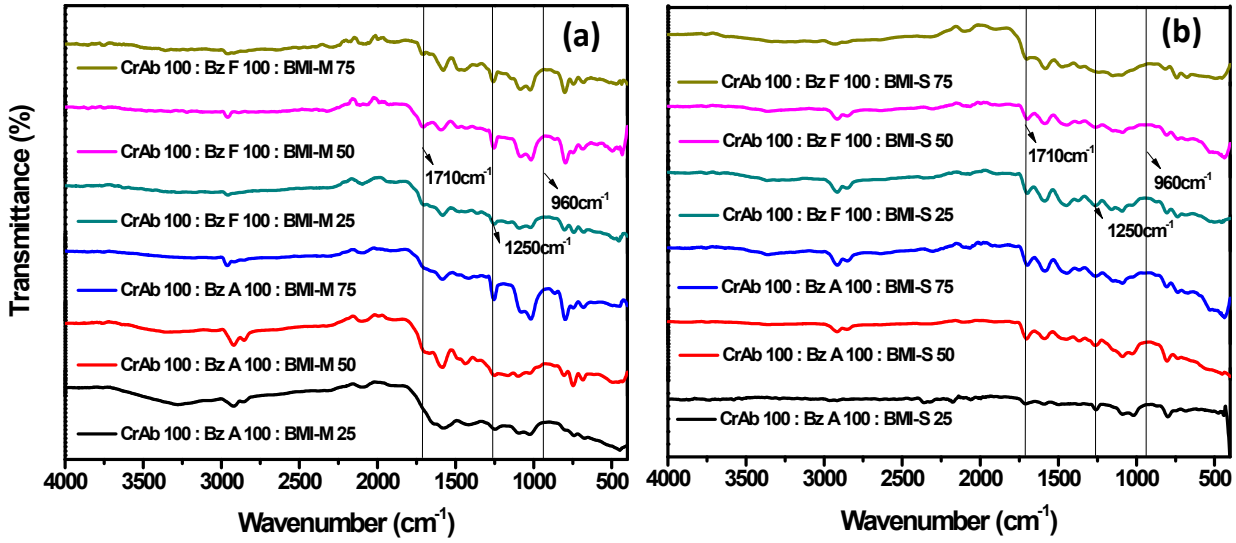


Figure S5. FT-IR spectrum of polybenzoxazine of (a) CrAb/Bzs/BMI-M and (b)CrAb/Bzs/BMI-S .

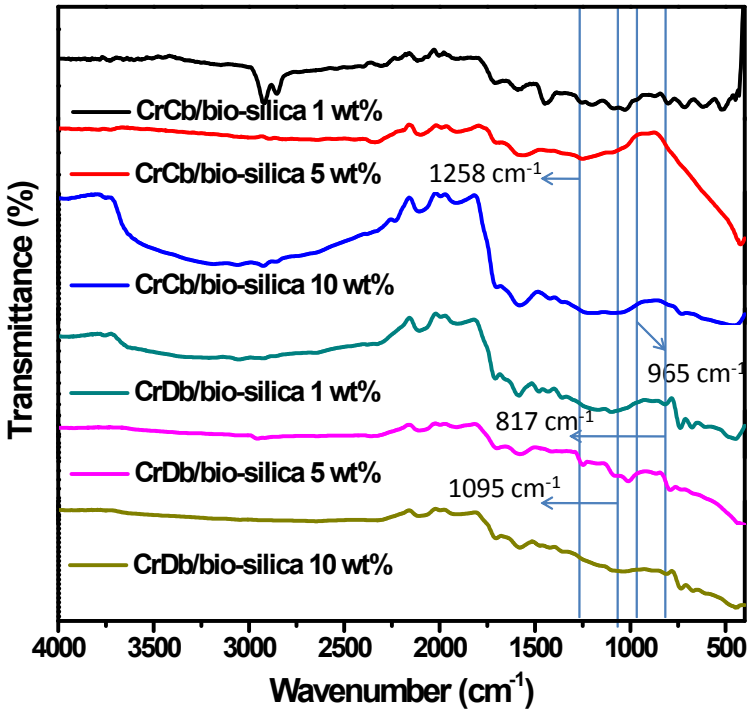


Figure S6. FT-IR spectrum of bio-silica reinforced cardanol based polybenzoxazine

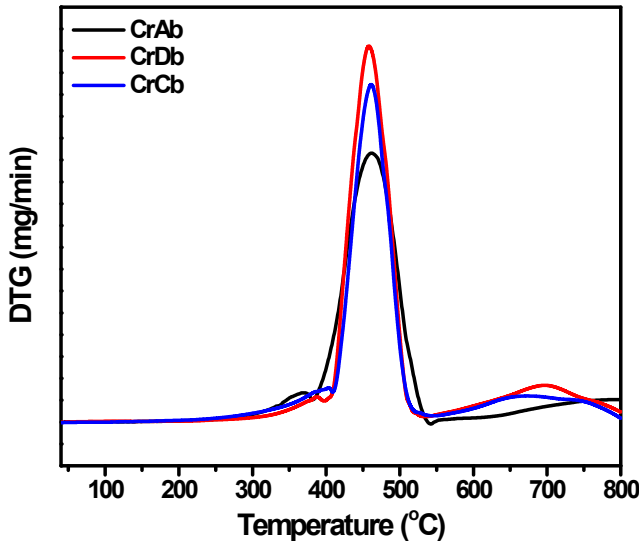


Figure S7. DTG Thermogram of Polybenzoxazine of CrAb, CrDb and CrCb.

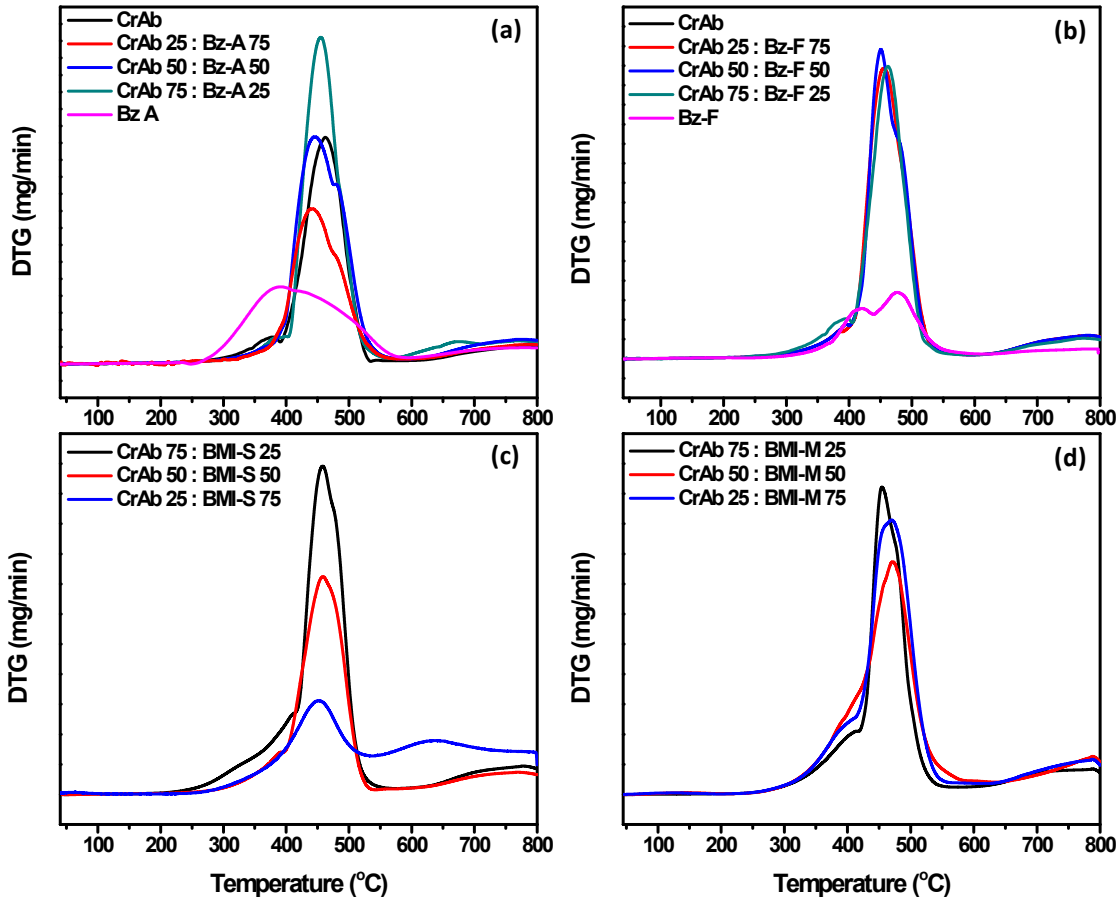


Figure S8. DTG thermogram of copolymer of (a) CrAb/Bz-A (b) CrAb/Bz-F; (c) CrAb/BMI-S; (d) CrAb/BMI-M.

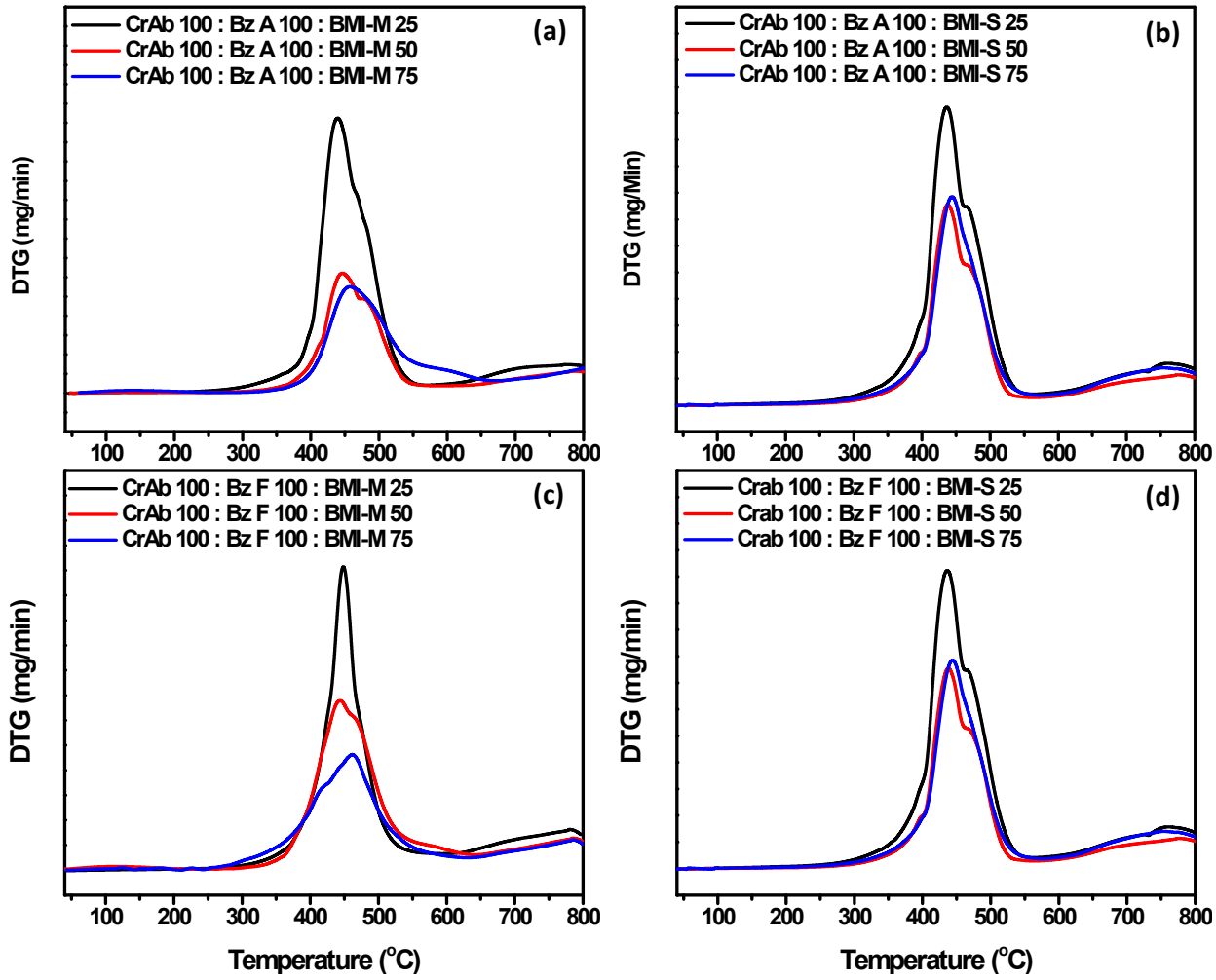


Figure S9. DTG thermogram of a copolymer of (a) CrAb/Bz-A/BMI-M; (b) CrAb/Bz-A/BMI-S. (c) CrAb/Bz-F/BMI-M; (d) CrAb/Bz-F/BMI-S.

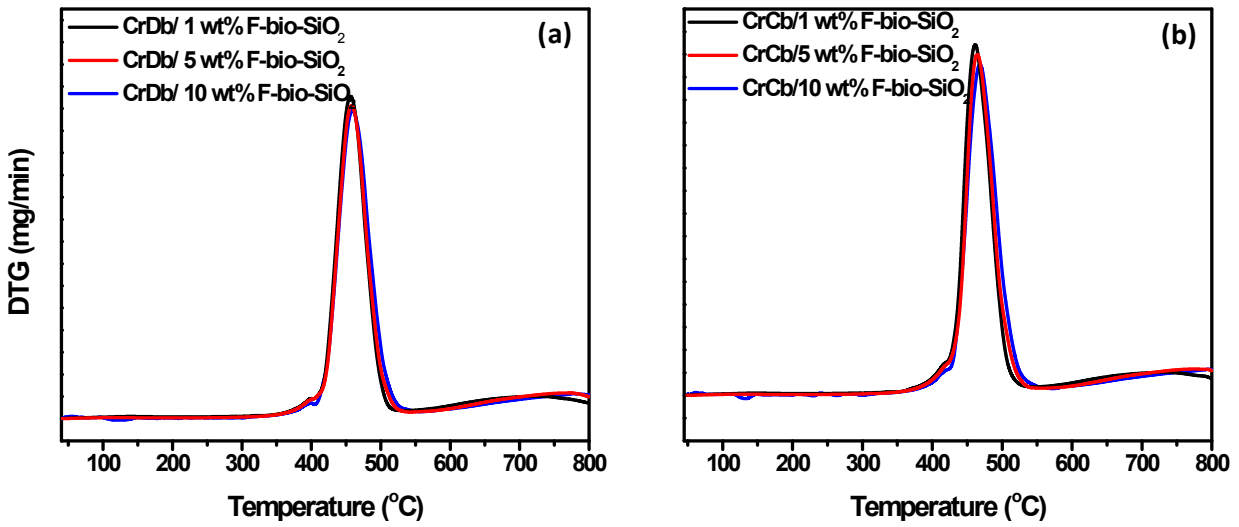


Figure S10. DTG thermogram of poly CrDb or CrCb/composites; (a) DTG thermogram of CrDb/F-bio-silica; (b) DTG thermogram of CrCb/F-bio-silica.

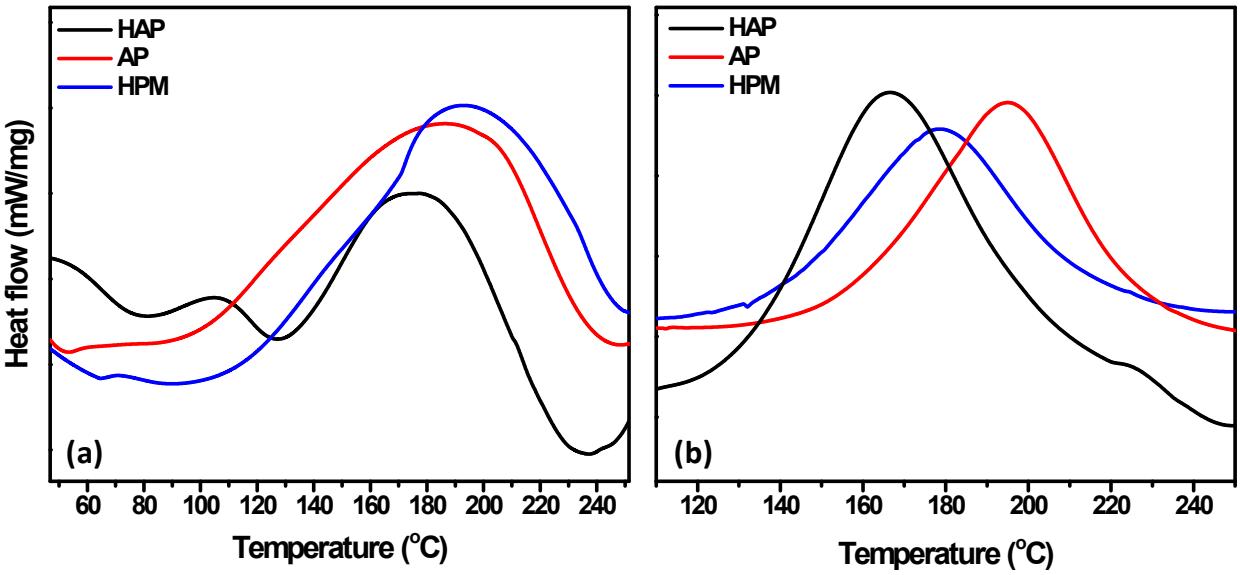


Figure S11. DSC thermogram of catalytic curing behavior of (a) CrAb/Bz-A/BMI-S, and (b)CrAb/Bz-F/BMI-S ternary blends.

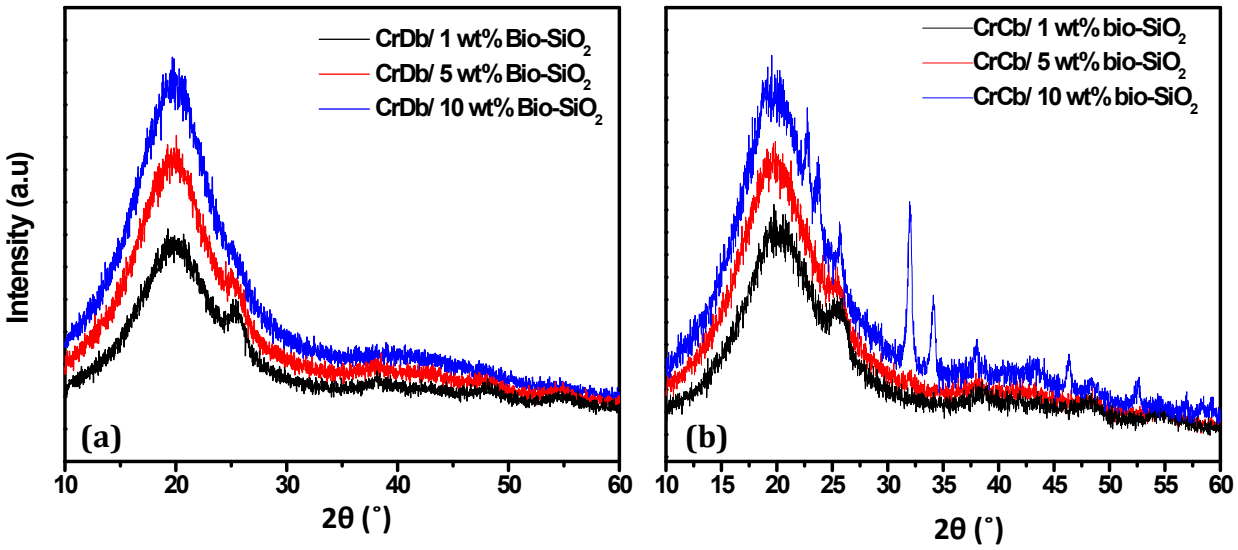


Figure S12. XRD spectrum of bio-silica reinforced cardanol based polybenzoxazine; (a) bio-silica incorporated CrDb polymer and (b) bio-silica incorporated CrCb polymer.

Table S2. Catalytic curing Behavior of CrAb/Bz-A/BMI-S and CrAb/Bz-F/BMI-S Ternary Blends.

10 wt% Catalyst with ternary blends	**Curing behaviour of CrAb/Bz-A/ BMI-S Ternary blend**				**Curing behaviour of CrAb/Bz-F/ BMI-S Ternary blend**			
	T_i (°C)	**T_p (°C)**	**T_f (°C)**	**ΔH (mJ/mg)**	**T_i (°C)**	**T_p (°C)**	**T_f (°C)**	**ΔH (mJ/mg)**
4-Hydroxy phenylmaleimide (HPM)	94	192	249	216	136	195	241	197
4-Aminophenol (AP)	89	187	245	183	125	178	233	179
4-Hydroxyacetophenon (HAP)	84	173	236	156	116	168	221	193