Supplementary information

BIODEGRADABLE TOUGH WATERBORNE HYPERBRANCHED POLYESTER/ CARBON DOT NANOCOMPOSITE: AN APPROACH TOWARDS ECO-FRIENDLY MATERIAL

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A. Chemical structure of HBE

The proposed chemical structure of HBE is shown in Fig. S1.

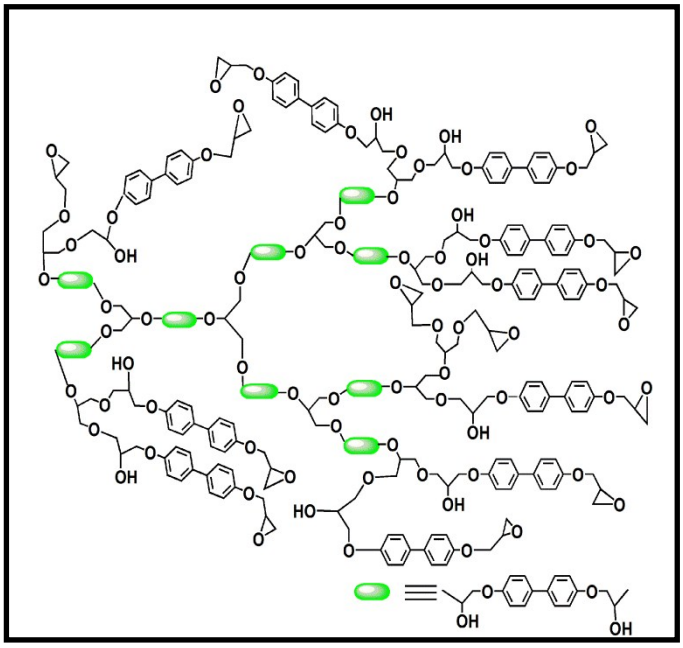

Fig. S1 Proposed chemical structure of HBE

B. ^{1}H and ^{13}C NMR of HBE

The above proposed structure is confirmed from FTIR, ^{1}H and ^{13} C NMR spectral analyses. The FTIR study confirmed the presence of bands (cm^{-1}) at 918–830 for oxirane ring, at 1037 for alkyl–aryl ether groups, at 2962–2874 for aliphatic, 3053 for aromatic –C–H stretching, at 1606 for–C=C– stretching vibrations and at 3445 for–O–H stretching vibration.[7,8] The ^{1}H and ^{13} C NMR spectra of HBE are shown in Fig. S2. In ^{1}H spectrum (Fig. S2a) of HBE ($CDCl_3$, Me_4Si) at δ_H (ppm): 2.69, 2.71 and 3.11 (oxirane proton); 3.31–3.87 (CH_2 of glycerol moiety); 6.82 and 7.21 (phenyl proton of BPA moieties) and 2.12 (-OH of glycerol moiety). [7,8] In ^{13}C NMR spectrum (Fig. S2b) of HBE (δC, ppm) peaks observed at 61 (methyl protons of the BPA moieties); 62 (CH_2 attached with OH); 71 (CH attached with OH); (113.94, 127.69 and 156.3 (different carbons of the BPA moiety); 30.94 and 41.62 (methyl carbon and the quarternary carbon of the BPA moiety); 44.64 and 50.40 (oxirane ring carbon); 143 (BPA carbons attached directly to the –O–linkage) [7,8] and are found to be according to the proposed structure. The dendritic (D) (68.9 ppm), linear(L) (68.6 ppm) and terminal (T) (69.5 ppm) units are the trisubstituted, disubstituted and monosubstituted glycerol units, shown in Fig. S2. The degree of branching (sum of intensity of dendritic and terminal to sum of intensity of dendritic, terminal and linear units) of HBE was found to be 0.89.

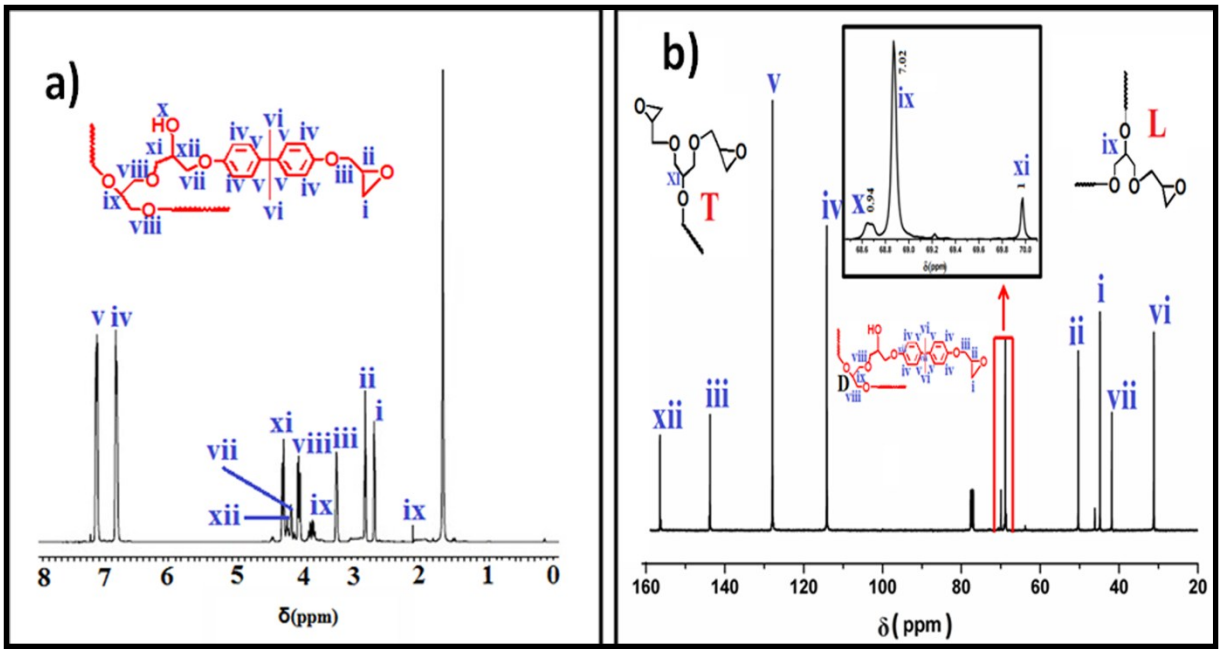

Fig. S2 a) ^{1}H NMR and b) ^{13}C NMR spectra of HBE

C. Physical properties of HBE

The different physical properties (epoxy equivalent, hydroxyl value, molecular weight and density) of HBE were determined and the results are given in Table S1.

Table S1. Physical properties of HBE

Properties	HBE
Epoxy equivalent (g/eq)	289
Hydroxyl value (mg KOH/g	157
Density (g/cc)	0.89
M_w	6403
M_n	5305
PDI	1.206

D. Mechanical properties of HBE

The different mechanical properties (tensile strength, elongation, toughness, scratch hardness and impact resistance) of HBE thermoset, obtained by curing with 50 wt% poly(amidoamine)

at 100 °C for 60 min and post cured at 120 °C for 10 min, were evaluated and results are given in Table S2. The stress-strain profile of HBE is shown in Fig. S3. The toughness of this HBE is calculated from area under stress-strain curve.

Table S2. Performance characteristics of HBE

Property	HBE
Curing time (min) 100 °C and 120 °C	60 and 10
Swelling value (%)	21
Tensile strength (MPa)	22
Elongation (%)	47
Impact strength (kJ/m)	>7.5
Scratch hardness (kg)	7
Toughness (MJm^{-3})	8.91
Gloss (°)	84

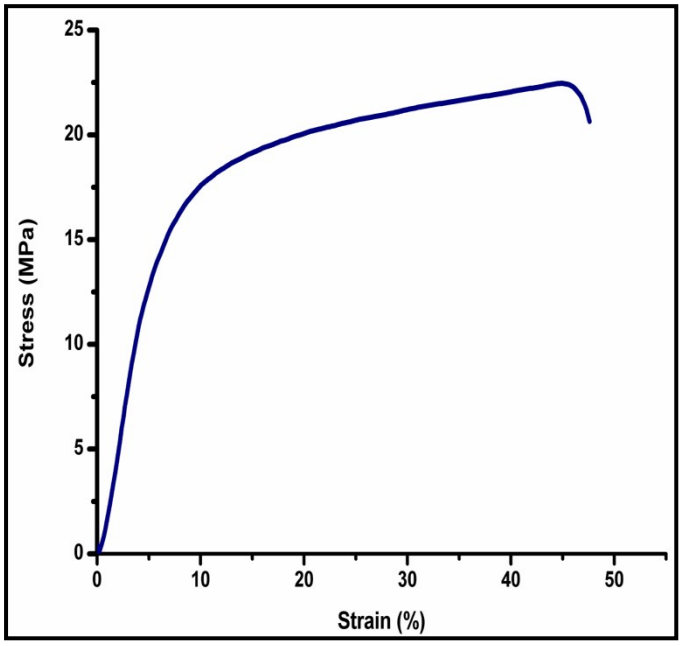

Fig. S3 Stress-strain profile of HBE thermoset

E. Characterization of carbon dot (CD)

1. XPS analysis

XPS was used to examine the elemental composition of CD. Fig. S4a shows XPS survey spectrum which reveals the presence of bands at around 285, 531, 398.5, and 164 eV correspond to C_{1s}, O_{1s}, N_{1s} and S_{1s} respectively. The atomic ratio of C/O/N/S is 63.64/ 33.22/1.54/ 0.59 as calculated from the survey spectrum. The C_{1s} core level band can be deconvoluted into five contributory peaks at 284.5, 285.6, 286.5 287.2and 288.2 eV, which are attributed to binding energy of C–C, C=C, C–N, C–O and C=O, respectively (Fig. S4b). N_{1s} band can be deconvoluted to three peaks at 398.3, 399.7 and 401.4 eV attributed to the pyridinic, pyrrolic and quaternary N, respectively. Similarly, the S_{2p} band consists of two peaks, centred at 162.7 eV and 167.5 eV corresponds to $S_{2P3/2}$ and $S_{2P1/2}$ respectively. On the other hand O_{1s} band is deconvoluted into three peaks centred at 530.5, 532.0 and 533.0 corresponds to lattice oxygen, C=O and C-O-C/C-OH respectively.[1-6]

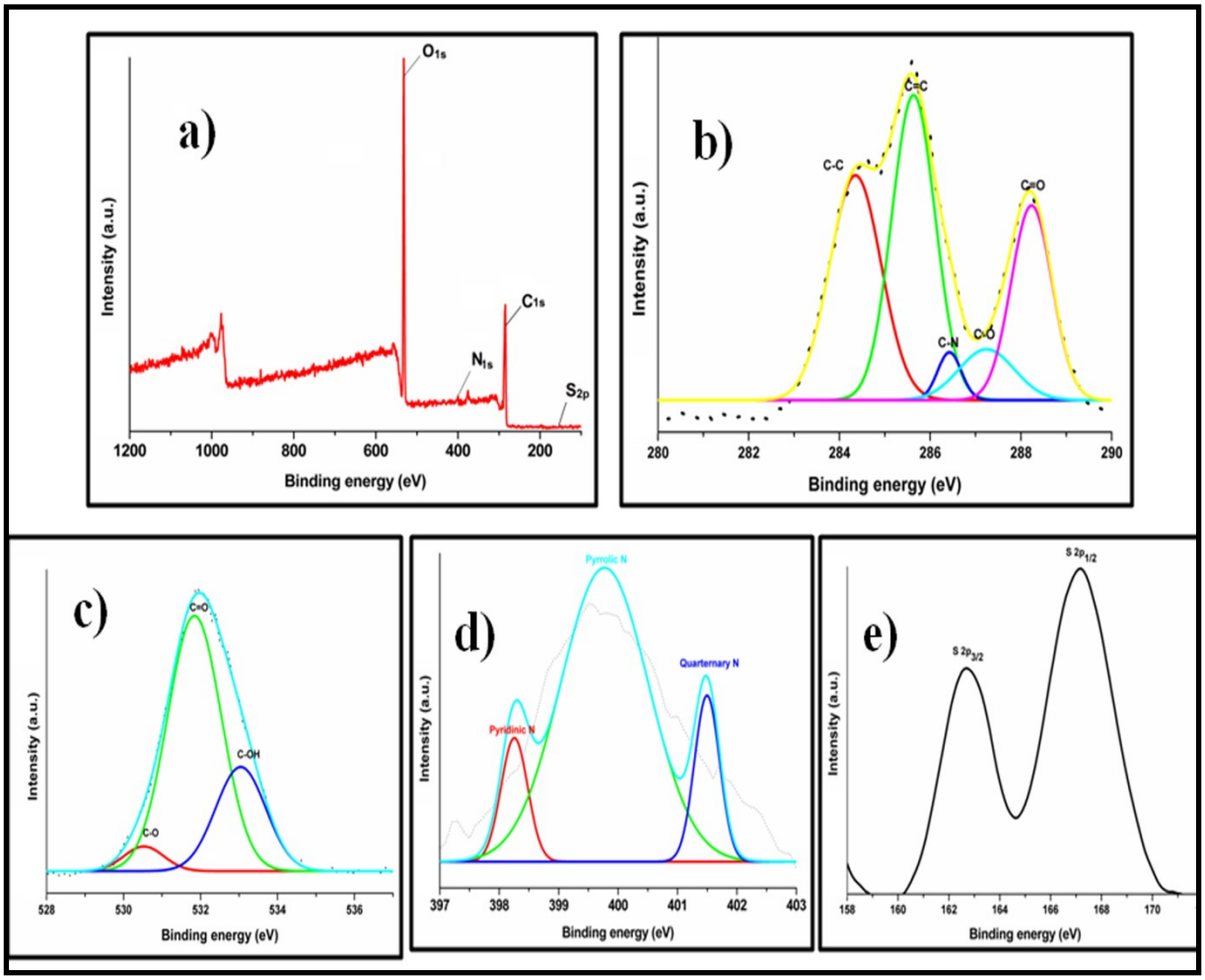

Fig. S4 XPS spectra of CD (a) Survey spectrum of CD with three major peaks of carbon, oxygen and nitrogen; XPS high resolution survey spectra of (b) C_{1s}, (c) O_{1s}, (d) N_{1s} and (e) S_{2p} regions of CD.

2. Raman analysis

Raman spectroscopy is also a powerful tool to identify the chemical state of carbon in CD. Fig. S5 shows the Raman spectrum of the CD. The peaks centred at 1372 and 1618 cm^{-1} are attributed to the D band corresponds to disordered structure and G bands corresponds to sp^2-bonded C atoms in CD, respectively.[3]

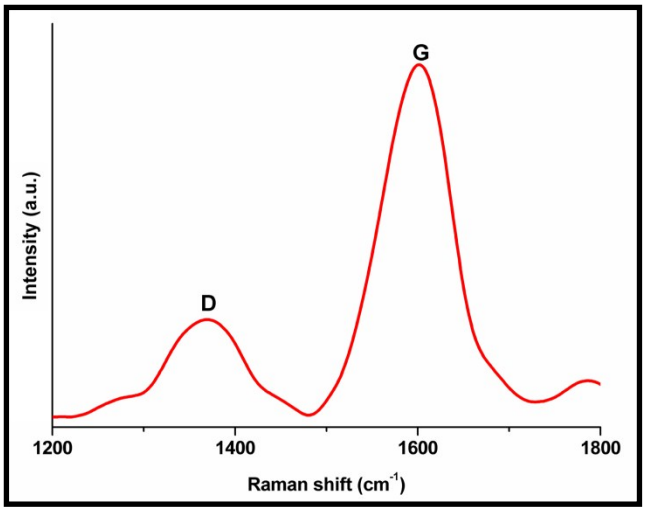

Fig. S5. Raman spectrum of CD

F. XRD of polyester/CD nanocomposite

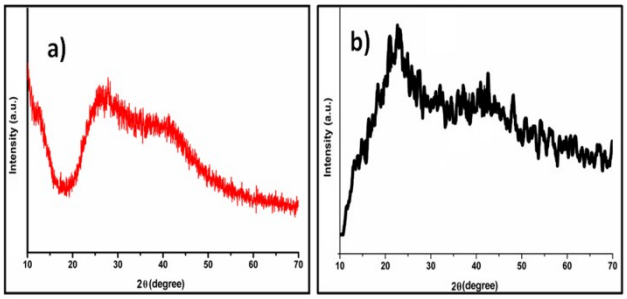

Fig. S6 XRD patterns of a) PCD1 and b) PCD 0.1

G. Self-cleaning activity of waterborne polyester/CD nanocomposites

The photographs for decolourization of model dirt, methylene blue under sunlight by CD and PCD 0.5 are shown in Fig. S7.

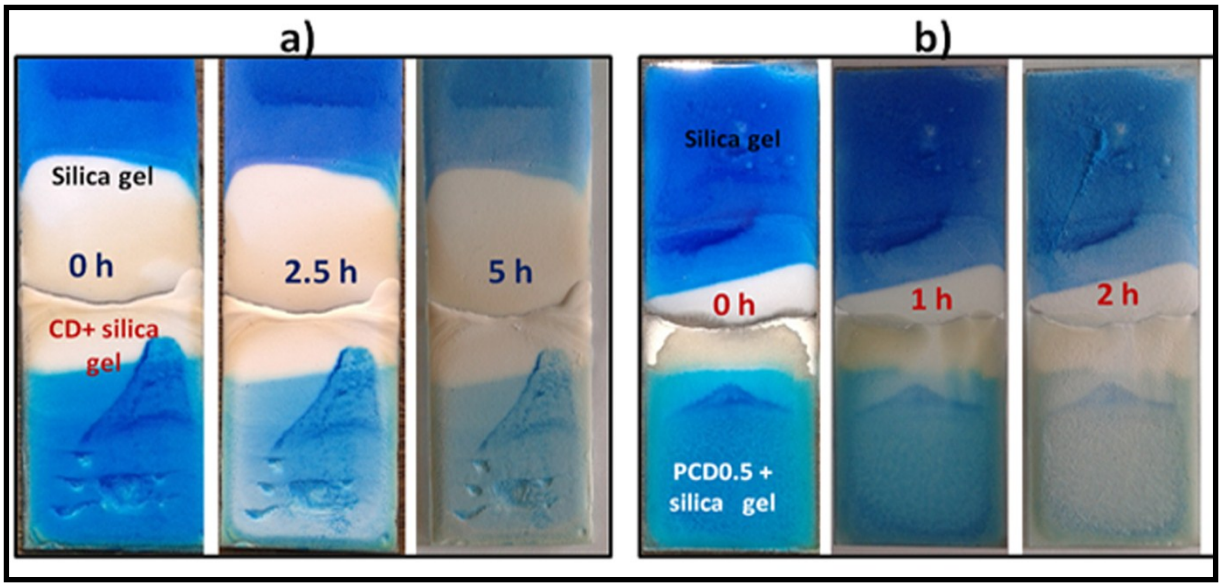

Fig. S7. Photographs showing decolorization of methylene blue under exposure of sunlight by a) CD and b) PCD0.5.

Reference

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