**Supporting information**

# Unprecedented influence of carbon dot@$TiO_2$ nanohybrid on multi-faceted attributes of waterborne hyperbranched polyester nanocomposite

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## A. Characterization

Fourier transform infrared (FTIR) spectra of the nanocomposites were recorded by a Nicolet (Impact-410, USA) infrared spectroscopy using KBr pellets. UV spectra of the nanohybrid and the nanocomposites were recorded using an Evolution-300 UV-visible spectrophotometer (UV-300, ThermoFisher, USA). X-ray diffraction (XRD) (Bruker AXS, D8 FOCUS, Germany) study was also performed for both the nanohybrid and the nanocomposites. Further, the size and morphology of the nanohybrid in the fabricated nanocomposites were studied by TEM analysis (JEOL, JEMCXII, Japan, operating voltage of 200 kV). The rheological properties of the nanocomposites were evaluated using a rheometer (CVO100, Malvern, UK) with parallel plate geometry and oscillatory experiments were performed at an oscillatory stress of 20 Pa. Thermal properties of the thermosetting nanocomposites were evaluated by differential scanning calorimetry (DSC) studies and thermogravimetric analysis (TGA). TGA was carried out using a PerkinElmer TGA 4000 thermal instrument with nitrogen flow rate of 30 mL $min^{-1}$ at a scanning rate of 10 °C $min^{-1}$ in the temperature range of 25 - 700 °C. DSC was done by a PerkinElmer DSC 6000 (USA) instrument at a scanning rate

of 5 °C $min^{-1}$ for heating and 10 °C $min^{-1}$ for cooling in the temperature range of −70 - +160 °C under the atmosphere of nitrogen following a cycle of heating–cooling–heating. Mechanical properties were measured by a Universal Testing Machine (UTM, WDW10, Jinan, China) equipped with a 500 N load cell operated at a standard crosshead speed of 50 mm $min^{-1}$. The width, height and thickness of the thermosetting nanocomposite films used for mechanical test were 1 cm, 5 cm and 0.27 mm respectively. For each case, four samples were tested and the average value was taken. The impact strength of the nanocomposite were measured using an impact tester (S.C. Dey Co., Kolkata) with a maximum height of 1m, as per the standard falling weight (ball) method (ASTM D5628). Further, the scratch hardness of the nanocomposite was tested with the help of a scratch hardness tester, Model No. 705 (Sheen instrument limited, UK) using the standard method (ASTM G171).

The swelling value (%) of the thermosets was determined by measuring the weight of the dried film ($W_d$) and the equilibrated swelled film ($W_s$) using the following equation.

Swelling value= $(W_s-W_d)/W_d \times 100$ .....(1)

**B. Information of CD and CD@$TiO_2$**

The structure of CD and CD@$TiO_2$ was studied by XRD, SEM, TEM, etc.[1] The appearance of board peak (23°) in the XRD pattern of CD established its amorphous nature. TEM confirmed that it is uniformly dispersed spherical nanoparticles with size 1.5-7 nm and lattice spacing was 0.32 nm. It showed blue and green emission on exposure of UV light. CD showed strong fluorescence properties i.e wavelength dependent both down and up conversion flourscence properties in absence of any additional passivating agent due to the presence of nitrogen containing compounds. Further, the anatase structure of $TiO_2$ was established from its appearance of

characteristic peaks at 25.3, 48.0, 37.7, 55.6, 54.2, and 62.8° due to the (101), (200), (004), (211), (105), and (204) planes of anatase $TiO_2$. This anatase structure of $TiO_2$ was retained in CD@$TiO_2$ nanohybrid and thus established the crystalline nature of the prepared nanohybrid. $TiO_2$ nanoparticles are uniformly dispersed on the surface of CD and also nearly spherical in shape which was confirmed from TEM images of the nanohybrid. $TiO_2$ possess a high degree of crystallinity and a well-ordered structure as d-spacing calculated from crystal lattice fringes was 0.35 nm analogous to the (101) plane of anatase $TiO_2$. The presence of different elements like C, N and O in CD as well as C, N, O and Ti in CD@$TiO_2$ were confirmed from EDX analysis. Further, rough nanostructural surface was observed in case of nanohybrid (Figure S1). This was confirmed from surface plot of the nanohybrid by plotting with the help of Fizi ImageJ software.

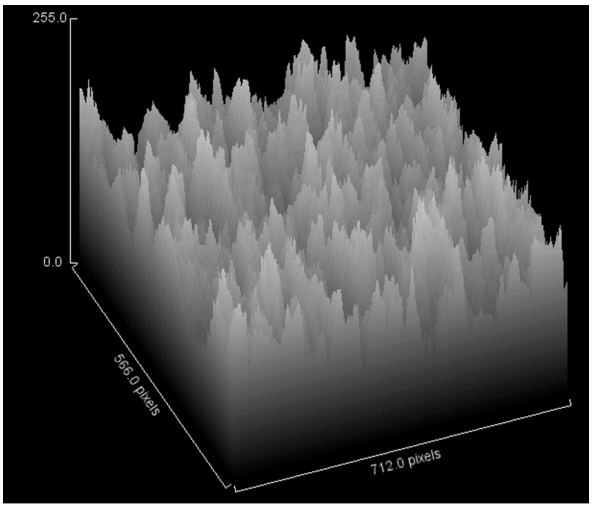


**Figure S1.** Surface plot of the nanohybrid

## C. Important characteristics glycerol based hyperbranched epoxy

This hyperbranched epoxy was prepared by polycondensation reaction of glycerol and bisphenol A with excess epichlorohydrin as reported earlier.[2] It showed characteristic bands in FTIR analysis (918-830 $cm^{-1}$ for oxirane ring), in $^1H$ NMR analysis, δ (ppm): 2,69-3.11

(oxirane) and 6.82, 7.21 (aromatic proton of bisphenol A) and in $^{13}C$ NMR analysis, δ (ppm): 44.6 and 55.4 (oxirane) and 113, 127, 156 (aromatic carbon).[2] This epoxy has 289 g/eq epoxy value, 157 g/eq hydroxyl value, 0.89 g/cc density, 6403 g/mol weight average molecular weight and 5305 g/mol number average molecular weight.[3]

## D. Measurement of contact angles

Contact angles of the nanocomposite were assessed directly by measuring the angle formed between the solid and the tangent to the drop surface using Imagej software as shown in Figure S2.

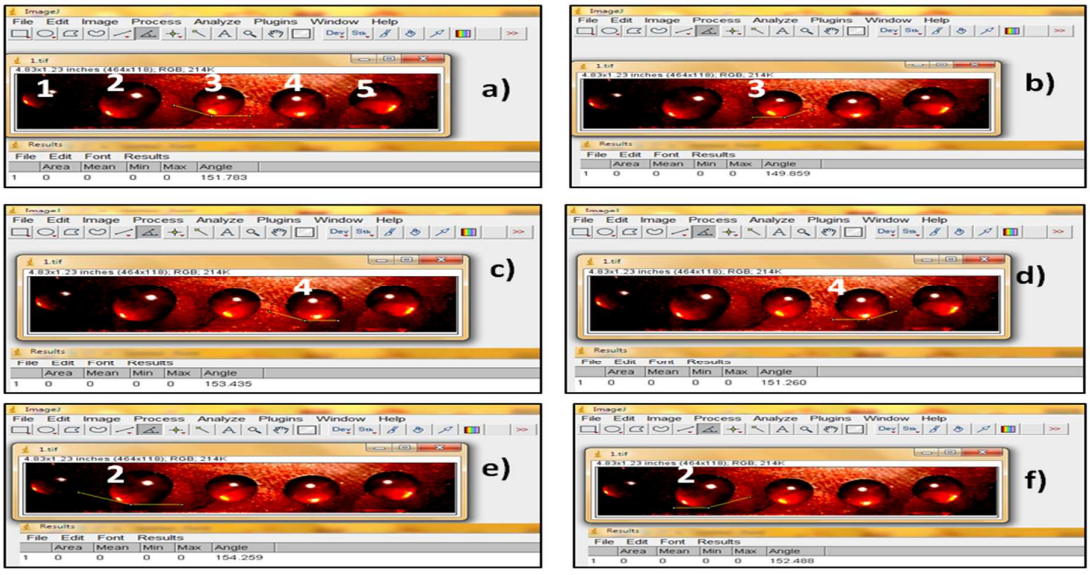


**Figure S2.** Direct measurement of contact angle using ImageJ software

**Table S1** Advancing angle, receding angle and angle of hysteresis of the nanocomposite

| **Water droplets number** | **Advancing angle (°)** | **Receding angle (°)** | **Angle of hysteresis (°)** |
|---|---|---|---|
| 2 | 154.2 | 152.4 | 1.8 |
| 3 | 151.7 | 149 | 2.7 |
| 4 | 153.4 | 151.2 | 2.1 |

Further, droplets of water placed on differnt surface display superhydrophobicity, with contact angle in the range of 135-152° as calculated using ImageJ software (Figure S3).

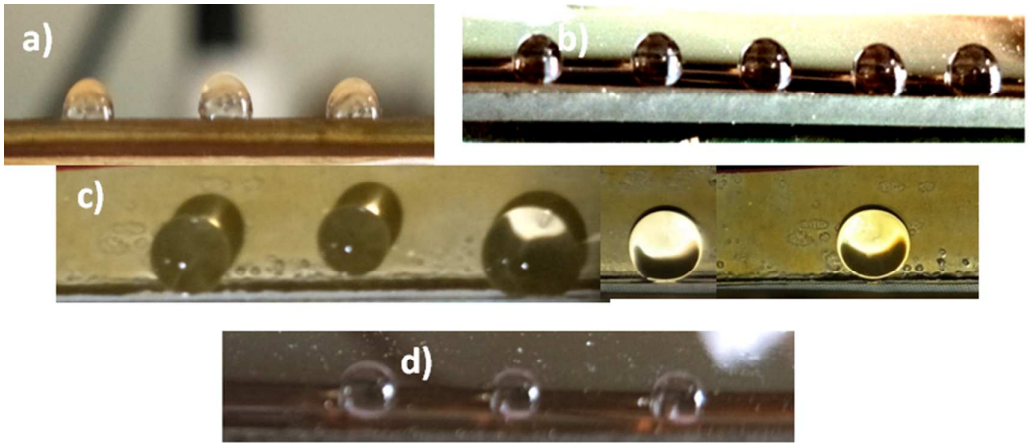


**Figure S3.** Water droplets on a) PCTN0.5, b) PCTN1 and (c, d) PCTN2.5 surface showed the superhydrophobicity behaviour.

**Reference**

1. Hazarika, D.; Karak, N. Photocatalytic degradation of organic contaminants under solar light using carbon dot/titanium dioxide nanohybrid, obtained through a facile approach. *Appl. Surf. Sci.* **2016**, *376,* 276–285.

2. Barua, S.; Dutta, G.; Karak, N. Glycerol based tough hyperbranched epoxy: synthesis, statistical optimization and property evaluation. *Chem. Eng. Sci.* **2013**, *95*, 138–147.
3. Hazarika, D.; Karak, N. Biodegradable tough waterborne hyperbranched polyester/carbon dot nanocomposite: An approach towards eco-friendly material. *Green Chem*. **2016**, *18*, 5200-5211.