Unprecedented Influence of Carbon Dot@TiO₂ Nanohybrid on Multifaceted Attributes of Waterborne Hyperbranched Polyester Nanocomposite

Deepshikha Hazarika and Niranjan Karak*

Department of Chemical Sciences, Advanced Polymer and Nanomaterial Laboratory, Center for Polymer Science and Technology, Tezpur University, Napaam, Tezpur 784028, Assam, India

ABSTRACT: Herein, we wish to report fabrication of multifaceted environmentally friendly benign renewable resource-based waterborne hyperbranched polyester nanocomposites using three different doses of carbon dot@TiO₂ nanohybrid through a facile in situ polymerization technique in the absence of solvent or additional catalyst. Carbon dot@TiO₂ nanohybrid was prepared through a greener one-pot hydrothermal process from bio-based raw materials. The nanocomposites were characterized by different instrumental techniques. The thermosets of these nanocomposites are obtained by curing them with glycerol-based hyperbranched epoxy and fatty acid-based poly(amido amine). Enhancements of 6.67 folds tensile strength, 3.8 folds toughness, 1.7 folds Young’s modulus, >2.5 units gloss, and 46 °C thermal stability were observed for the thermosets by the formation of nanocomposites. The nanocomposites also showed antifogging and anti-icing properties. More interestingly, they can also be used for efficient separation of crude oil and water from their mixture. Thus, these environmentally benign polymeric materials could find applications in different fields.

1. INTRODUCTION

Advanced materials with unique multifunctional activities are the ultimate choice of the material community, which may be achieved through the unison of molecular engineering and nanotechnology. These materials not only assist the economy of a country, but also help to conserve exhaustible resources.¹ In this milieu, polymer nanocomposites enjoy synergistic advantages of both polymers and nanomaterials and hence received tremendous interest over the last two decades or so.¹,² Again, polymers among different polymers deserve special attention due to their inherent advantages like excellent processability and good compatibility with others, low density, good chemical resistance (except alkali), high flexibility, and overall low cost.³,⁴ However, as they suffer from poor mechanical strength, alkali resistance, and thermal stability, their advanced applications are limited.⁵ In this context, to address the above drawbacks and to impart new interesting properties, suitable nanomaterials may be incorporated into them.⁶,⁷ Several studies on the incorporation of various inorganic nanomaterials, such as ZnS,⁸ graphene,⁹ clay,¹⁰ multiwalled carbon nanotubes (MWCNTs),¹¹ TiO₂,¹² etc., into the polyester matrices to obtain nanocomposites with desirable properties have been cited in the literature. However, among them, TiO₂ is found to be very interesting as its polymer nanocomposites like epoxy,¹³ polyurethane,¹⁴ polyester,¹⁵ etc. offered not only improvement in mechanical, thermal, etc. properties but also impart some unique and useful attributes.¹⁴,¹⁵ Further, studies on polyester/TiO₂ nanocomposites are not comprehensive and systematic. Ghanem et al. reported fabrication of a hyperbranched polyester nanocomposite using TiO₂ by both in situ and ex situ methods but studied only its photocatalytic activity.¹² Zhang et al. studied only the thermal properties of copolyester/TiO₂ nanocomposites.¹³ Similarly, Santos et al. reported only the thermal properties and hardness of the nanocomposites of poly(ethylene terephthalate) (PET) and TiO₂.⁹ Therefore, all of the above-cited reports did not address the above-mentioned unique properties. In addition, they were obtained from petroleum resources and solvent-borne systems were used. Both of these are against the tenets of green chemistry as well as unable to maintain the concept of triple bottom line approach. As these are the central requirements for any kind of sustainable development, an environmentally benign facile approach involving waterborne system and renewable resources is the most desirable one to be adopted.³,⁴ Further, the use of bio-based renewable resources addresses the exhaustion of petroleum resources as well as refreshes the environment through achievement of carbon credit.⁶ It is not out of the scope to mention that incorporation of unique structural hyperbranched moiety in this system may also result in some

Received: December 29, 2017
Accepted: January 26, 2018
Published: February 9, 2018

DOI: 10.1021/acsomega.7b02079
ACS Omega 2018, 3, 1757−1769
unique attributes like high solubility, lower melt, and solution viscosity that make it interesting for many advanced applications.\(^3\),\(^5\) Thus, in the present investigation, an attempt was made to incorporate TiO\(_2\) in such waterborne hyperbranched polyester (WHP) systems to explore the above-mentioned unique attributes on the resultant system. TiO\(_2\) was selected as a nanomaterial to achieve high thermostability, delay heat conduction, and provide high free-energy barrier for ice nucleation along with improvement of mechanical and thermal properties. Furthermore, it influences optical and antibacterial activities. It can also provide roughness to the organic polymer surface due to inherent incompatibility as it is an inorganic material. All of these are the essential requirement for achieving properties like anti-icing, antifogging, oil–water separation, etc.\(^10\)–\(^12\) In this context, carbon quantum dot (CD) is found to be more attractive for its unique properties like low toxicity, chemical stability, high water solubility, easy functionalizability, good compatibility with other materials, etc. over inorganic quantum dots.\(^14\),\(^15\) Thus, to achieve the synergistic effect of CD and TiO\(_2\), a nanohybrid of them was prepared by a single-pot one-step facile protocol and proposed to use. Incorporation of similar nanomaterials other than TiO\(_2\) may also provide these properties; however, the use of this nanohybrid provides not only anti-icing and antifogging properties but also excellent enhancement in mechanical and thermal properties. The surface with good mechanical stability and durability is the necessary requirement for anti-icing and antifogging behavior. The fabrication and designing of such antifogging and anti-icing surfaces are very essential for using them in an array of applications.\(^16\)–\(^18\) It is pertinent to mention here that even though this nanohybrid has been reported in the literature,\(^19\),\(^20\)
no report has been found so far on the incorporation of such nanohybrid in waterborne hyperbranched polyester system and hence achieving these properties simultaneously in such polymer is a daunting challenge. Thus, these properties were studied using this polyester nanocomposite by following a similar method to that reported earlier in different polymers.21−24 Furthermore, the use of a fabrication process without involving a catalyst, organic solvent, and neutralizing agent not only reduces volatile organic compounds but also addresses environmental pollution and human health problems. Therefore, the present study reports the fabrication of an environmentally benign multifunctional nanocomposite of waterborne hyperbranched polyester and carbon dot@TiO2 (CD@TiO2) using bio-based raw materials for the first time through a solvent-free benign in situ polymerization method. Glycerol-based hyperbranched epoxy and fatty acid-based poly(amide amine)-modified above nanocomposite was evaluated as a tough polyester thermoset. The fabricated thermosetting nanocomposites with different weight percents of nanohybrid were examined as multipurpose advanced sustainable polymeric materials with special attributes like anti-icing, antifogging, etc. This material was also tried to be used as a membrane for separation of oil and water from their mixture.

2. RESULTS AND DISCUSSION

2.1. Fabrication of Thermosetting Nanocomposite. The nanocomposite was obtained using a waterborne polyester and a water-dispersible CD@TiO2 nanohybrid through a simple in situ polymerization technique. Both the polyester and the nanohybrid are environmentally friendly, as well as the fabrication process of nanocomposite is nontoxic, odorless, nonflammable, environmentally friendly, and easy to clean up. In addition, most of the precursors used for fabrication of polyester and nanohybrid are naturally renewable, i.e., bio-based, where the amount of bio-based raw materials is 56.27% in polyester and 44% in the nanohybrid. Furthermore, the nanocomposite was obtained through a greener approach in the absence of solvent and catalyst, as well as a facile environmentally benign hydrothermal method was used for the preparation of nanohybrid. Some raw materials of hyperbranched epoxy and poly(amide amine) are also bio-based. Thus, the approach is in accordance with some of the principles of green chemistry.25 In addition, the pristine waterborne polyester is a biodegradable material.4 Thus, from the material as well as processing viewpoints, the nanocomposite has considerable greener contribution.

During the fabrication process, different oxygen functional groups of the nanohybrid interact covalently or noncovalently with the functional groups of polyester matrix, as shown in Scheme 1. These types of interactions not only favor uniform dispersion of the nanohybrid in the polyester matrix but also generate significant amount of interfacial area. This is responsible for the improvement in performance of the resultant material. Further, the presence of large numbers of polar functionalities in the nanocomposites helps in the formation of stable dispersion in most organic solvents like dimethylformamide, dimethyl sulfoxide, dimethylacetamide, ethanol, acetone, tetrahydrofuran, methanol, etc.

2.2. Characterization of the Nanocomposite. The fabricated nanocomposites were characterized by different spectroscopic techniques. The presence of functional groups
in the nanocomposites was confirmed by Fourier transform infrared (FTIR) (Figure 1a,b) studies. From the FTIR spectrum of bare TiO$_2$ (Figure 1a), $-\text{O}H$ stretching and bending bands were observed at 3434 and 1632 cm$^{-1}$, respectively. The broad band observed at around 681 cm$^{-1}$ is assigned to the stretching mode of Ti$-\text{O}$ bond, whereas the band at 1400 cm$^{-1}$ arises from TiO$_2$ lattice vibrations. Further, additional absorption bands at 2922 and 2852 cm$^{-1}$ are assigned to $-\text{C}H$ asymmetric and symmetric stretching vibrations in the nanohybrid, respectively. However, the band at 681 cm$^{-1}$ gets shifted to around 606 cm$^{-1}$ after incorporation of nanohybrid and bare TiO$_2$ into the polyester matrix. The incorporation of nanohybrid in the nanocomposites also leads to small shifts of some other FTIR absorption bands of polyester. The shifting of the bands indicates the interactions of carboxylic and hydroxyl groups of polyester matrix with the nanohybrid through hydrogen-bonding or other polar–polar interactions. Further, the observed broad band at 3500 cm$^{-1}$ is

Figure 2. (a–c) TEM images of PCTN2.5 at different magnifications, (d, e) lattice fringes, and (f) SAED pattern.
attributed to the interaction of hydroxyl groups of nanohybrid and polyester matrix.

The XRD pattern of pristine polyester (Figure 1c) showed a single broad peak in the range of 10°–30°, indicating its amorphous nature. In the XRD patterns of the nanocomposites (Figure 1d), it is seen that the intensity of original peaks of the nanohybrid as well as pristine system decreased and the peaks were broadened. Further, some of the peaks for the nanohybrid in the nanocomposite were diminished due to the presence of low amount of nanohybrid in the nanocomposite as well as interactions between polyester matrix and nanohybrid. These results indicate the structural modification of both the nanomaterial and polyester by the formation of nanocomposite.10,11

The surface morphology of the nanocomposite and the state of dispersion of the nanohybrid in the polyester matrix were studied from transmission electron microscopy (TEM) analyses. A good dispersion of the nanohybrid in the matrix is crucial to achieve the desired nanoreinforcing effect and thus obtain a high-performing material. The representative TEM images of PCTN2.5 displayed a homogeneous distribution of the nanohybrid in the polyester matrix, as shown in Figure 2a–c. The crystal lattice fringes with a d-spacing of 0.36 nm correspond to the (001) plane of anatase TiO2,19 and the lattice spacing of 0.32 nm corresponding to the (002) plane of CD19,20 was also observed in high-resolution TEM images (Figure 2d,e). Further, the selected area electron diffraction (SAED) pattern (Figure 2f) of the nanocomposite reveals the semicrystalline nature of the nanocomposite, which may arise due to the crystallinity of TiO2 nanoparticles. Further, surface plot of the nanohybrid (Figure S1) obtained from SEM image of it using Fizi ImageJ software confirmed the roughness of its surface.

### 2.3. Rheological Study of the Nanocomposites

Rheological study of the nanocomposite was carried out using a rheometer to obtain some information about the interactions between the nanohybrid and the polyester matrix. Variations of shear viscosity with time and temperature under controlled stress and a single shear value were examined for all of the nanocomposites before curing. The results are shown in Figure 3a,b. It is noted that the viscosity remained almost constant with time. The nanocomposites exhibited higher viscosity than the pristine polyester due to the presence of interfacial interactions between the rigid nanomaterials with the flexible polyester matrix. Furthermore, dose-dependent viscosity was also obtained for the nanocomposites. However, the shear viscosity of all of the nanocomposites decreased with the increase of temperature. This is due to the increase in kinetic energy of the different components present in the nanocomposites, which decreases the structure-forming tendency of the polymer molecules and thus decreases viscosity. Further, viscoelasticity is a combination of elastic (solidlike) and viscous (liquidlike) behaviors, which are usually described by storage modulus (G′) and loss modulus (G″), respectively.28 These parameters were measured as a function of frequency (1–10 s⁻¹) under constant temperature (25°C) and constant stress (20 Pa). The dependence of the viscoelastic behavior of nanocomposite on the loadings of the nanohybrid was also studied. The results are shown in Figure 3c,d, and it is noted that both G′ and G″ increase with the increase of frequency (1–10 s⁻¹) at different rates as well as with the loadings of the nanohybrid. The trend of changes was in good agreement with the results demonstrated in the literature.28,29 This is due to the improvement of elastic behavior of the nanocomposites upon incorporation of the nanohybrid. This improvement arises from the strong interactions between the nanohybrid and the polymer matrix. The solidlike elastic behavior, i.e., G′ > G″, of the nanocomposites is due to the combination of polymer–nanohybrid and polymer–polymer interactions. This indicates the formation of a continuous network inside the polymer matrix. Furthermore, the variation of G′ and G″ with respect to temperature (25–75 °C) under constant frequency (1 Hz) and a controlled oscillatory stress of 20 Pa is shown Figure 3e,f. The decrease in G′ and G″ with the increase in temperature was observed for all of the nanocomposites. This is owing to the increase in kinetic energy and free volume of the polymer chains, which in turn decreases inter- and intramolecular interactions as well as entanglement density in the system. Thus, this result clearly demonstrated strong interactions between nanohybrid and the polyester matrix.5,28,29

### 2.4. Performance of the Thermosetting Nanocomposites

The improvement of the mechanical properties of the nanocomposites is the central interest of their fabrication. The nature of branching in the polymer chain plays a significant role in the contribution of mechanical properties, and increase in the amount of polar side chains in polymer backbone results in an enhanced tensile strength. Further, functional groups of nanocomposites play a vital role in increasing the interaction energy between the nanomaterial and the polymer matrix.28 The interaction between the nanohybrid and the polymer matrix is significant because uniformly dispersed nanoparticles in a polymeric matrix impart a high portion of interface owing to their high surface area. The weak interactions between them result in lower mechanical strength than the pristine system as the external applied load of the nanocomposite is unable to transfer to the nanomaterials.28–32 The mechanical properties, such as tensile strength, toughness, elongation at break, impact resistance, Young’s modulus, and scratch hardness of the

| Table 1. Performance Characteristics of the Nanocomposites |
|-----------------------------------------------|
| property            | WHP      | PTN1    | PCTN0.5 | PCTN1      | PCTN2.5    |
| swelling value      | 22 ± 2   | 23 ± 2  | 2 ± 1    | 22 ± 1     | 21 ± 1     |
| curing time (h)     | 5 ± 0.25 | 4 ± 0.25| 3 ± 0.25 | 2.5 ± 0.5  | 1.5 ± 0.5  |
| tensile strength (MPa) | 7.8 ± 2.3   | 15 ± 3  | 27 ± 2.8 | 33.5 ± 2   | 52 ± 3.5   |
| elongation (%)      | 245 ± 8  | 142 ± 10| 221 ± 5  | 215 ± 4    | 182 ± 5    |
| scratch hardness (kg)| 4 ± 1    | 7 ± 0.5 | 9 ± 1    | >10        | >10        |
| impact resistance (kJ/m²) | >8.3  | >8.3 | >8.3 | >8.3 | >8.3 |
| toughness (MJ/m³)   | 17.18 ± 3.5 | 18.1 ± 2.8 | 30.03 ± 3.2 | 56.20 ± 4 | 65.53 ± 3.5 |
| gloss               | 80 ± 2   | 85 ± 3  | 90 ± 4   | 98 ± 4     | 105 ± 2    |
| Young’s modulus (MPa)| 243 ± 3  | 270 ± 2 | 309 ± 2  | 350 ± 3    | 420 ± 2    |

*Maximum limit of the instrument.*
Scheme 2. Plausible Cross-Linking Reactions Occurred during the Modification of Nanocomposite

Figure 4. (a) Stress–strain profiles of the nanocomposites, (b) image of tensile test showing >200 strain, (c) thermogravimetric analysis curves, and (d) differential scanning calorimetry (DSC) curves of the nanocomposites.
nanocomposites, were evaluated and the results are given in Table 1. It is seen that the incorporation of even a small amount of the nanohybrid significantly improved the performance of the pristine polyester. This may be due to the combined effect of small size, large surface area, and quantum confinement of the nanohybrid as well as its strong interfacial interactions with the polyester matrix.29,30 The tensile strength of pristine polyester was improved after the formation of nanocomposite with both bare TiO2 and CD@TiO2 nanohybrids; however, the nanocomposite with 1 wt % bare TiO2 showed lower value of tensile strength than the nanohybrid (1 wt %). This is due to the incompatibility of TiO2 with the polyester matrix. The absence of suitable functionality in TiO2 to interact with the matrix is the probable cause of this result. Further, fine particle size of TiO2 leads to the formation of aggregate, as observed in the literature, making it poorly dispersed into the matrix. However, in case of nanohybrid, CD helps in its better dispersion and stabilization due to the presence of a large number of polar functional groups, which can interact with the polyester matrix. Further, the mechanical properties of the nanocomposites were found to be highly dependent on the loading of the nanohybrid. As the loading of the nanohybrid increases, the mechanical strength of the nanocomposite improved in the same manner. The tensile strength of PCTN2.5 increases 6.6 times compared to the pristine polyester. The nanoscale size effect of the nanohybrid can lead to a close association with the polyester matrix, which may be strengthened with the increase of nanohybrid loading. This tensile strength value is found to be superior to the reported polyester/MWCNT (28–35 MPa),31 vinyl ester/TiO2 (3.70–5.72 MPa),32 polyester/clay (2.42–6.28 MPa),3 PET/PECD0.5 (26.1 MPa),35 poly(ethylene terephthalate)/TiO2 (27.1–34.4 MPa),34 and other nanocomposites. However, elongation at break decreased after the formation of nanocomposite and also decreased with increase in the loading of nanohybrid. Even then the strain value (>200%) of the nanocomposites was significantly high. This is because of the presence of different flexible moieties like aliphatic moieties of polyester and hardener, ether linkages, etc., as well as plasticizing effect of the long hydrocarbon chain of hardener.30 Further, the interactions shown in Scheme 2 are associated with various secondary interactions, such as polar—polar, H-bonding, and other interactions of the polar functional groups, which may help in full molecular chain extension of the polyester. Furthermore, graphic structure of CD with polar functional groups may result in good flexibility due to slippage of layers during the application of high load. The polar functional groups of CD also provide strong physicochemical interactions with the polar groups of polyester, hyperbranched epoxy, and poly(amic di amine) hardener and help in full extension of chain molecules. Further, these values were found to be better than those of the already reported nanocomposites of epoxy/TiO2 (2–3.5%),30 polyester/clay (12.45)%7 PET/clay (2–3%),28 polyester/MWCNT (4–8%),31 PET/TiO2 (30.5–34.4%),34 and PECD0.5 (162%).33 Typical stress–strain curves and tensile process of the nanocomposites are shown in Figure 4ab, and areas under these curves were used to measure toughness of the material. The toughness of the nanocomposite was also found to be enhanced, and the values increased with the loading of nanohybrid. The values were superior to those reported for PECD0.5 (32.8 MJ/m3)33 and poly(phenyl sulfone)/TiO2 (15.5–20 MJ/m3)35 nanocomposite. Further, the toughness of the thermostet drastically enhanced the other mechanical properties, such as impact resistance and scratch hardness. Therefore, these properties were also improved after the formation of nanocomposites. The impact resistance was higher than 1–7 wt % TiO2-based unsaturated polyester nanocomposite (4.2–6 kJ/m).36 The enhancement of these properties is ascribed to the significant interfacial interactions and good compatibility between the polyester matrix and the nanohybrid. The small sizes of CD and TiO2 provide a large surface area for strong interactions with the matrix and thus all of the mechanical properties of the nanocomposites were improved without much affecting flexibility. The peripheral polar functional groups of the nanohybrid also provide strong physicochemical interactions with glycerol-based hyperbranched epoxy and poly(amic amine) hardener, which also help in the enhancement of the mechanical properties of the nanocomposites.30 Further, Young’s modulus of the nanocomposite also increased dramatically with the loading of nanohybrid and this may happen due to favorable size and
distribution of the nanohybrid that cause strong interactions between the nanohybrid and the polyester matrix.

2.5. Thermal Properties of the Nanocomposites. The thermal stability of the nanocomposites was studied from thermogravimetric analyses. The initial degradation temperature of polyester thermosets increased after the formation of nanocomposites with bare TiO$_2$ as well as CD@TiO$_2$ nanohybrid. The initial degradation temperature further increased with the increase of amount of nanohybrid loading (Figure 4c). The improvement in thermal stability is due to high cross-link density and strong covalent and noncovalent interactions along with some secondary interactions like polar−polar, hydrogen-bonding, and other interactions. The improvement in thermal stability is due to high cross-link density and strong covalent and noncovalent interactions along with some secondary interactions like polar−polar, hydrogen-bonding, and other interactions. The improvement in thermal stability is due to high cross-link density and strong covalent and noncovalent interactions along with some secondary interactions like polar−polar, hydrogen-bonding, and other interactions. The improvement in thermal stability is due to high cross-link density and strong covalent and noncovalent interactions along with some secondary interactions like polar−polar, hydrogen-bonding, and other interactions.

Both the pristine thermoset and the nanocomposites were degraded mainly through two-stage degradation patterns as observed in TGA curves, where the first step (250−270 °C) is related to the degradation of aliphatic moieties, whereas the second stage (330−350 °C) is due to degradation of aromatic moieties. However, DSC results (Figure 4d) clearly revealed no significant differences in $T_g$ values between the pristine polyester and nanocomposite due to contradictory effect of increasing intermolecular attractive forces as well as the occurrence of poly(ethylene glycol) (PEG) shell around the nanohybrid. This interaction of flexible PEG chain is due to favorable compatibility of the nanohybrid containing Ti−O bonds with the −O− linkages of PEG.

2.6. Antifogging and Anti-icing Attributes of the Nanocomposites. Prevention of fog is a daunting challenge for various optical applications of transparent materials. This is due to the reason that fog reduces the effectiveness of light transmission and therefore optical efficiency. The antifogging property of the nanocomposite was checked by placing the sample inside a refrigerator for minimum 30 min and then exposing it to a humid laboratory environment, and the results as well as visual transparency of both the bare glass and nanocomposite films are shown in Figure 5a−c. In this figure, it is seen that the bare glass slide after taking out from the refrigerator under ambient conditions fogged immediately and presented a large amount of tiny condensed droplets, causing a significant reduction of the optical transmittance, and the words below are blurred. Although the nanocomposite film (PCTN2.5) significantly prevented the formation of fog and exhibited excellent transparency, the words below are clearly visible. Thus, the nanocomposite film plays an active role in the antifogging property of glass. Further, the same test was performed in different samples and under different humid conditions (60−80%) as well as over boiled water, and the results of these experiments are given in Figure 6. It is seen that the nanocomposite exhibited antifogging behavior in high humidity (60−80%); thus, it is expected to achieve this property in low humidity too. Further, the uncoated glass over boiling water showed condensation of water droplets and it became hazy, whereas the coated glass slide remained clear after being removed from the refrigerator (Figure 6). The antifogging performance could be because of the fact that the more hydrophobic the material, the lower will be the rate of water cooling. Further, longer times were required to form the initial fog on the hydrophobic surface, especially on super-hydrophobic surface so that the nanocomposite was covered with least water droplets and thus remained transparent in all times. The superhydrophobicity behavior of the material was explained by measuring the contact angle of the surface (135−150°) using ImageJ software (Figures S2 and S3; Table S1). The antifogging property of polyester nanocomposite was not found in the literature and hence there is no scope for comparison. However, a few other materials are reported in the literature, which include 15 wt % PEG ($M_w = 1000−6000$ g/mol) and 30 wt % SiO$_2$-modified TiO$_2$ films.
Functionalized poly(vinyl alcohol) (PVA)/poly(acrylic acid), poly(vinyl alcohol)/Na films, etc. with antifogging property. Furthermore, in recent years, to solve the adhesion and accumulation of ice, researchers have been more focused on the design of superhydrophobic surfaces with nanoparticles, nanostructures, or anti-icing coatings as chemicals are extremely
expensive as well as procedures are complicated and cause environmental hazards. Although there are many reports on anti-icing behavior of superhydrophobic surface using nanostructures, the anti-icing property of waterborne polyester nanocomposite using CD@TiO$_2$ was not reported so far. Thus, the anti-icing property of polyester nanocomposite was studied here. It was observed that the water droplets formed ice on both the uncoated surface of aluminum and glass substrates, whereas no ice formation was observed on the coated surface of glass and aluminum plates (Figure 7a–g). It is seen from this figure that after 1 min water droplets on the uncoated surface start losing their transparency as ice formation has started, whereas the droplets on the coated surface remained transparent. Further, the freezing delay time of water droplets on the nanocomposite surfaces (PCTN2.5) was measured by placing 5 μL of water droplets at -15 °C (Figure 8) and the experiment was repeated several times to get the statistical data using analysis of variance. The delay time during the measuring process was defined as the time at which the water droplets began to transform from being transparent to being completely frozen. Initially, the water droplets were all transparent and the droplets slowly became dense with time such that the light spot vanished. The freezing delay time was found to be 940 ± 40 s. Furthermore, the anti-icing test was performed on different surfaces (PCTN0.5 and PCTN1) keeping the volume of the water droplet same (5 μL), but the shape of the water droplet was different in case of bare glass slide because of difference in the surface. It is seen from Figure 8 that all of the nanocomposites showed excellent anti-icing behavior. This is due to superhydrophobicity of the surfaces, which has excellent applicants for icephobicity due to their extraordinary water repellency. Icephobicity usually refers to an ability to delay or prevent ice nucleation and deposition on surfaces. This can be achieved using surface with high water contact angle and low surface energy. The formation of ice can be prevented via two approaches: one is by reducing the contact time to help quick shedding of water droplets before ice can nucleate on the surface and the other is by delaying heterogeneous nucleation through a combination of surface and therefore being able to prevent the fog formation. The ice formation could be delayed in superhydrophobic surface owing to the tardy heat conduction as well as high free-energy barrier of nucleation. The delayed freezing of water droplets on the superhydrophobic surfaces is explained as follows: rougher the surface is, lower will be the water−solid contact area and hence more entrapped air will be there in the water−solid interface. Therefore, the process of heat exchange between the water droplets and solid will slow down because of the presence of entrapped air in the water−solid interface acting as an insulator. This process leads to longer and delayed freezing time of water droplets. Thus, water droplets on coated superhydrophobic surface were frozen with a much longer delay time compared to their uncoated one. Studies on the anti-icing property of polyester-based nanocomposite are very limited in the literature. However, studies are available for the anti-icing property of fluorosilane-treated aluminum panel and polybenzoxazine nanocomposite containing 50 wt % SiO$_2$. In addition, the nanocomposite can also be used as security ink as it has unique properties like nonvisibility under visible

Figure 9. Separation of crude oil and water from their mixture by the nanocomposite. Images of (a) crude oil and water mixture and separation of the components at different times by (b, c) coated and (d) uncoated filter paper, (e) UV−vis spectra, (f, g) microscopic images of the feed and filtrate, and (h) separation efficiency of the nanocomposite membrane.
light but provides different colors at different wavelengths of UV light. In addition, it also exhibited excellent thermal stability and photostability, good compatibility with other materials, etc. For this purpose, a solution of nanocomposite at a concentration of 2 mg/mL was used to write the structure of phenol on a filter paper, which was not visible under visible light. However, the same can be clearly seen under the illumination of a 365 nm UV light (Figure 6h,i). This information can be seen repeatedly as and when required under exposure of such wavelength of light. Thus, this nanocomposite-based security ink can be used for preserving and secretly communicating important information particularly for defense systems.

2.7. Separation of Oil and Water from Their Mixture. The separation of oil and water from their mixture is a daunting challenge because of the increasing industrial oil-contaminated water as well as the frequent oil spills accidents occurring across the globe. Thus, the nanocomposite with excellent mechanical properties and repellency to crude oil showed potential to further develop as an advanced oil/water separation membrane. The separation of oil and water from their mixture was performed as shown in Figure 9a–d. A thin membrane of the nanocomposite was used to separate the oil—water mixture using a sintered funnel with suction pumping system. The figure clearly revealed the efficient separation of the components using nanocomposite membrane, whereas no separation was observed under normal filtering system. The retention of hydrophobic oil in the sintered funnel is due to the superoleophobic nature of the nanocomposite. The permeability flux of the nanocomposite membrane was calculated using eq 3 by recording the time taken for collection of the measured volume of water from the oil—water mixture, and the value was found to be 660 mL m⁻² h⁻¹. Further, the separation efficiency or oil rejection coefficient calculated according to eq 1 was 99% (5 min). This efficiency value (99%) was found to be the same as calculated using eq 2 from UV—vis spectral analysis (Figure 9e). The value is higher than that of cellulose nanofiber aerogel (98.6%)⁴⁹ and comparable to that of chitosan-based aerogel membrane (99%).⁵⁰ Furthermore, microscopic images of the feed and the filtrate are shown in Figure 9fg which confirmed the complete separation. Most importantly, the recyclability of the nanocomposite membrane was examined for oil—water separation up to fourth cycle without further loss of separation efficiency (Figure 9h). Thus, the nanocomposite-based membrane possesses high potential to be used for the separation of industrial oil-polluted water.

3. CONCLUSIONS

In conclusion, multifunctional waterborne polyester/CD@TiO₂ nanocomposite was fabricated for the first time through a greener in situ method without using solvent and catalyst. The nanocomposite exhibited excellent mechanical and thermal properties. Most interestingly, multifaceted attributes like anticing and antifogging properties were observed in the same nanocomposite, which is rare to achieve. Further, this nanocomposite has the ability to be used as an anticounterfeiting material. It is also possible to separate crude oil from water efficiently, and this study also provides a facile and fast approach for the removal of oil from water. Therefore, this multifunctional nanocomposite has great potential for multifaceted advanced applications.

4. EXPERIMENTAL SECTION

4.1. Materials. Citric acid (Merck, Germany), glycerol (Merck, Germany), poly(ethylene glycol) (PEG-200, Mₙ = 200 g/mol, Merck, Mumbai), and 2,2-bis(hydroxymethyl)propionic acid (bis-MPA, Sigma-Aldrich, Germany) were used after drying in a vacuum oven. Titanium butoxide (Sigma-Aldrich, Germany) and poly(amido amine) hardener (HY840, Ciba Geigy, Mumbai; amine value, 5–7 equiv/kg) were used as received. All other chemicals used in this study were of reagent grade and used without further purification. CD@TiO₂ nanohybrid was prepared by the same hydrothermal method as reported earlier,⁵⁰ and the basic information about CD and CD@TiO₂ is provided in the Supporting Information (SI). The glycerol-based hyperbranched epoxy was obtained by the reported method, and its important characteristics are provided in the Supporting Information (SI).

4.2. Fabrication of Waterborne Hyperbranched Polyester (WHP)/CD@TiO₂ Nanocomposites. WHP nanocomposites were fabricated using nitrogen-containing CD@TiO₂ through a facile in situ method without using a catalyst, a neutralizing agent, and an organic solvent. The fabrication of the nanocomposites was carried out under nitrogen atmosphere at a specified temperature and constant mechanical stirring. The first step of the fabrication process was the prepolymer formation by the reaction of citric acid and PEG-200 at 140 °C. After cooling this reaction mixture to 60 °C, required amounts of bis-MPA and glycerol were added into it along with the desired amount of CD@TiO₂ nanohybrid and the reaction was carried out again at 140 °C. This nanocomposite was then mixed homogeneously with glycerol-based hyperbranched epoxy and poly(amido amine) in the ratio of 1:0.5:0.25 by weight at room temperature. The mixture was coated on glass plates and mild steel plates for mechanical testing after peeling out the cured films. The plates were cured at 150 °C for a specified time after being degassed under vacuum for 24 h at room temperature. Then, by following the same preparative protocol, three different nanocomposites were fabricated using 0.5, 1, and 2.5 wt % CD@TiO₂ and denoted as PCTN0.5, PCTN1, and PCTN2.5, respectively. The nanocomposites of polyester with bare TiO₂ (1 wt %) and CD (0.5 wt %) were also prepared for comparison purpose and coded as PTN1 and PECD0.5, respectively.

4.3. Characterization. The fabricated nanocomposites were characterized using different spectroscopic techniques like FTIR, XRD, UV, TEM, etc.

4.4. Antifogging Test. Antifogging ability of the coated films is tested by holding them at low temperature in a cold chamber (−20 °C) for 1 h, followed by returning to ambient conditions for the formation of moisture drops. Photographs were then taken in each case. The transparency of the coated surface under the fogging or frosting conditions was also evaluated to examine the antifogging behavior of the nanocomposite films.

4.5. Anti-icing Test. The anti-icing behavior of the nanocomposite films was tested by pouring cooled water droplets (−15 °C) onto the chilled surfaces of the coated and bare glass and aluminum plates using a syringe and kept under freezing condition for 5–15 min. Photographs of the water droplets were taken immediately.

4.6. Separation of Crude Oil and Water from Their Mixture. A thin film of PCTN2.5 was cast on the surface of a normal filter paper and heated at 100 °C for 4 h in an oven.
The thickness of the film was 0.16 mm. Then, it was used for separating crude oil and water from their mixture using suction filtering system. Here, it is pertinent to mention that the crude oil obtained directly from oil pool was heated with water at 70–75 °C for about 30 min and then this liquid mixture was filtered in a suction pump using the above coated membrane. The original filter paper was also used for the same purpose to find the difference.

The efficiency of oil/water separation was defined as oil rejection coefficient \( R (%) \) and calculated according to the following equation:

\[
R (%) = \frac{M_t}{M_o} \tag{1}
\]

where \( M_t \) and \( M_o \) are masses of initial water and collected water, respectively.

UV-vis analysis was carried out to analyze the filtrate, from which oil rejection value can be calculated using the following equation:

\[
R (%) = \left( 1 - \frac{C_o}{C} \right) \tag{2}
\]

where \( C_o \) and \( C \) are the concentrations of the feed and filtrate, respectively.

Further, water flux of the separable membrane was calculated using the following equation:

\[
\text{flux} = \frac{V}{St} \tag{3}
\]

where \( V \) is the volume of water that permeates through the fabricated membrane, \( S \) is the effective area of the fabricated fabric, and \( t \) is the time for complete separation.

# ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b02079.

Characterization techniques; important information and charactersistics of glycerol-based hyperbranched epoxies, CD, and CD@TiO2 and contact angle measurement (PDF)

## AUTHOR INFORMATION

### Corresponding Author

E-mail: karakniranjan@gmail.com. Tel: +91-3712-267009. Fax: +91-3712-267006.

ORCID®

Niranjan Karak: 0000-0002-3402-9536

Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors acknowledge SAIF of NEHU, Shillong, for TEM analysis and SAIC, Tezpur University, for XRD analysis.

## REFERENCES

(1) Paul, D. R.; Robeson, L. M. Polymer nanotechnology: Nanocomposites. Polymer 2008, 49, 3187–3204.
(2) Zhang, L.; Zhang, H.; Guo, J. Synthesis and properties of UV-curable polyester-based waterborne polyurethane/functionalized silica composites and morphology of their nanostructured films. Ind. Eng. Chem. Res. 2012, 51, 8434–8441.
(3) Hazarika, D.; Karak, N. Waterborne sustainable tough hyperbranched aliphatic polyester thermostats. ACS Sustainable Chem. Eng. 2015, 3, 2458–2468.
(4) Dai, J.; Ma, S.; Wu, Y.; Han, L.; Zhang, L.; Zhu, J.; Liu, X. Polymesters derived from itaconic acid for the properties and bio-based content enhancement of soybean oil based thermostats. Green Chem. 2015, 17, 2383–2392.
(5) Zhao, Y.; Wang, F.; Fu, Q.; Shi, W. Synthesis and characterization of ZnS/hyperbranched polyester nanocomposite and its optical properties. Polymer 2007, 48, 2853–2859.
(6) Bora, C.; Bharali, P.; Baglari, S.; Dolui, S. K.; Konwar, K. Strong and conductive reduced graphene oxide/polyester resin composite films with improved mechanical strength, thermal stability and its antibacterial activity. Compos. Sci. Technol. 2013, 87, 1–7.
(7) Dalir, H.; Farahani, R. D.; Nhim, V.; Samson, B.; Levesque, M. L.; Therriault, D. Preparation of highly exfoliated polyester clay nanocomposites: process-property correlations. Langmuir 2012, 28, 791–803.
(8) Ureña-Benavides, E. E. U.; Kayatia, M. J.; Davis, V. A. Dispersion and rheology of multiwalled carbon nanotubes in unsaturated polyester resin. Macromolecules 2013, 46, 1642–1650.
(9) Santos, L. M.; Carone, C. L. P.; Einloft, S. M. O.; Ligabue, R. A. Preparation and properties of aromatic polyester/TiO2 nanocomposites from polyethylene terephthalate. Mater. Res. 2016, 19, 158–166.
(10) Kumar, K.; Ghosh, P. K.; Kumar, A. Improving mechanical and thermal properties of TiO2-epoxy nanocomposite. Composites, Part B 2016, 97, 353–360.
(11) Charpentier, P. A.; Burgess, K.; Wang, L.; Chowdhury, R. R.; Lotus, A. F.; Moula, G. Nano-TiO2/polyurethane composites for antibacterial and self-cleaning coatings. Nanotechnology 2012, 23, No. 425606.
(12) Ghanem, A. F.; Badawy, A. A.; Ismailb, N.; Tian, Z. R.; Rehim, M. H. A.; Rabia, A. Photocatalytic activity of hyperbranched polyester/TiO2 nanocomposites. Appl. Catal., A 2014, 472, 191–197.
(13) Zhang, G.; Ke, Y.; Song, Y.; Lu, S.; Wang, Z. Preparing copolyester-titanium dioxide nanocomposites with low melting point via in situ hydrolysis, catalysis and esterification process. High Perform. Polym. 2015, 28, 445–452.
(14) Fernando, K. A. S.; Sahu, S.; Liu, Y.; Lewis, W. K.; Guliants, E. A.; Jafariyani, A.; Wang, P.; Bunker, C. E.; Sun, Y.-P. Carbon quantum dots and applications in photocatalytic energy conversion. ACS Appl. Mater. Interfaces 2015, 7, 8363–8376.
(15) Zhou, L.; He, B.; Huang, J. Amphiphilic fluorescent carbon dots: one-step green synthesis and application for light-emitting polymer nanocomposites. Chem. Commun. 2013, 49, 8078–8080.
(16) Lu, X.; Wang, Z.; Yang, X.; Xu, X.; Zhang, L.; Zhao, N.; Xu, J. Antifogging and antireflective silica film and its application on solar modules. Surf. Coat. Technol. 2011, 206, 1490–1494.
(17) England, M. W.; Urata, C.; Dunderdale, G. J.; Hozum, A. Anti-Fogging/self-healing properties of clay-containing transparent nanocomposite thin films. ACS Appl. Mater. Interfaces 2016, 8, 4318–4322.
(18) Hu, X.; Wang, Y.; Yu, Y.; Wang, Y.; Zhou, J.; Song, L. Highly transparent superhydrophilic graphene oxide coating for antifogging. Mater. Lett. 2016, 182, 372–375.
(19) Kochuveedu, S. T.; Jang, Y. J.; Jang, Y. H.; Lee, W. J.; Cha, M. A.; Shin, H.; Yoon, S.; Lee, S. S.; Kim, S.; Shin, K.; Steinhardt, M.; Kim, D. Visible-light active nanohybrid TiO2/carbon photocatalysts with programmed morphology by direct carbonization of block copolymer templates. Green Chem. 2011, 13, 3397–3405.
(20) 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.
(21) Liu, B.; Zhang, K.; Tao, C.; Zhao, Y.; Li, X.; Zhu, Y.; Yuan, X. Strategies for anti-icing: Low surface energy or liquid infused? RSC Adv. 2016, 6, 70251–70260.
(22) Zhang, S.; Huang, J.; Cheng, Y.; Yang, H.; Chen, Z.; Lai, Y. Bioinspired surfaces with superwettability for anti-icing and ice-phobic application: Concept, mechanism, and design. Small 2017, No. 1701867.
polycondensation for orthopaedic implants.

(25) Anastas, P.; Eghbali, N. Green Chemistry: Principles and Practice. Chem. Soc. Rev. 2010, 39, 301–312.

(26) Chen, J.; Zhou, Y.; Nan, Q.; Sun, Y.; Ye, X.; Wang, Z. Synthesis, characterization and infrared emissivity study of polyurethane/TiO2 nanocomposites. Appl. Surf. Sci. 2007, 253, 9154–9158.

(27) Singh, R.; Sureshin, G.; Shrinkant, S. Thermal and mechanical properties of nano-titanium dioxide-doped polyvinyl alcohol. Polym. Bull. 2013, 70, 1251–1264.

(28) Tang, Y.; Hu, X.; Zhang, X.; Guo, D.; Zhang, J.; Kong, F. Chitosan/titanium dioxide nanocomposite coatings: Rheological behavior and surface application to cellulose paper. Carbohydr. Polym. 2016, 151, 752–759.

(29) Yang, J.; Han, C. R.; Duan, J. F.; Xu, F.; Sun, R. C. Mechanical and viscoelastic properties of cellulose nanocrystals reinforced poly(ethylene glycol) nanocomposite hydrogels. ACS Appl. Mater. Interfaces 2013, 5, 3199–3207.

(30) De, B.; Voit, B.; Karak, N. Transparent luminescent hyperbranched epoxy/carbon oxide dot nanocomposites with outstanding toughness and ductility. ACS Appl. Mater. Interfaces 2013, 5, 10027–10034.

(31) Beg, M. D. H.; Mohsiul Alam, A. K. M.; Yunus, R. M.; Mina, M. F. Improvement of interaction between pre-dispersed multi-walled carbon nanotubes and unsaturated polyester resin. J. Nanopart. Res. 2015, 17, No. 53.

(32) Salehian, H.; Jahromi, S. A. J. Effect of titanium dioxide nanoparticles on mechanical properties of vinyl ester-based nanocomposites. J. Compos. Mater. 2015, 49, 2365–2373.

(33) Hazarika, D.; Karak, N. Biodegradable tough waterborne hyperbranched polyester/carbon dot nanocomposite: An approach towards eco-friendly material. Green Chem. 2016, 18, S200–S211.

(34) Han, K.; Yu, M. Study of the preparation and properties of UV-blocking fabrics of a PET/TiO2 nanocomposite prepared by in situ polycondensation. J. Appl. Polym. Sci. 2006, 100, 1588–1593.

(35) Diez-Pascual, A. M.; Diez-Vicente, A. L. Effect of TiO2 nanoparticles on the performance of polyphenylsulphone biomaterial for orthopaedic implants. J. Mater. Chem. B 2014, 2, 7502–7514.

(36) Chakraddh, K. V. P.; Subbaiah, K. V.; Kumar, M. A.; Reddy, G. R. Blended epoxy/polyester polymer nanocomposites: Effect of "nano" on mechanical properties. Polym. −Plast. Technol. Eng. 2012, 51, 92–96.

(37) Polizos, G.; Tuncer, E.; Sauers, I.; More, K. L. Physical properties of epoxy resin/titanium dioxide nanocomposites. Polym. Eng. Sci. 2011, 51, 87–93.

(38) Howarter, J. A.; Youngblood, J. P. Self-cleaning and next generation anti-fog surfaces and coatings. Macromol. Rapid Commun. 2008, 29, 455–466.

(39) Shimada, T.; Matsubara, T.; Hasei, T. Japan Patent 2015063641 A, 2015.

(40) Lee, H.; Alcaraz, M. L.; Rubner, M. F.; Cohen, R. E. Zwitterwettability and anti-fogging coatings with frost-resisting capabilities. ACS Nano 2013, 7, 2172–2185.

(41) Li, Y.; Fang, X.; Wang, Y.; Ma, B.; Sun, J. Highly transparent and water-enabled healable anti-fogging and frost-resisting films based on poly(vinyl alcohol)-nafion complexes. Chem. Mater. 2016, 28, 6975–6984.

(42) Wang, Y.; Orol, D.; Owens, J.; Simpson, K.; Lee, H. J. Design and development of anti-icing aluminium surface. Mater. Sci. Appl. 2013, 4, 347–356.

(43) Subramaniam, S. B.; Kondrashov, V.; Rühe, J.; Varanasi, K. K. Low ice adhesion on nano-textured superhydrophobic surfaces under supersaturated conditions. ACS Appl. Mater. Interfaces 2016, 8, 12583–12587.