Photoluminescent Oxygeneous-Graphitic Carbon Nitride Nanodot-Incorporated Bioderived Hyperbranched Polyurethane Nanocomposite with Anticounterfeiting Attribute

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ABSTRACT: Anticounterfeiting materials are neo-advanced materials with utility in covert and security strategies. In this context, a photoluminescent, mechanically robust, and thermally stable hyperbranched polyurethane (PU) nanocomposite was fabricated with oxygeneous-graphitic carbon nitride nanodots. The nanocomposite was characterized using infrared, ultraviolet–visible, and photoluminescence spectroscopy, X-ray diffractometry, transmission electron microscopy, and thermogravimetric analysis. The processed nanocomposite demonstrated improved physico-mechanical stability as well as enhanced thermal stability than the pristine PU. The nanocomposite displayed remarkable photoluminescence under long ultraviolet light (365 nm), courtesy of dispersion of oxygeneous-carbon nitride nanodots in the polymer matrix, without any solid-state quenching. The nanocomposite was consequently employed as an ultraviolet light-detectable anticounterfeiting ink material having reinforcing ability.

INTRODUCTION

Polyurethanes (PUs) have come a long way since their initial development by Bayer and co-workers in the 1930s.1 PUs display the hallmarks of an ideal polymer matrix, owing to their lightweight nature, better mechanical strength, and chemical resistance than most of their polymeric counterparts.2 This has led to a diversity of PUs being developed for common applications such as coatings, paints, adhesives, and foams. However, in the last few decades, the focus of PU synthesis has welcomingly shifted from petrochemical-based precursors to biobased precursors, making them more economically feasible and environmentally benign.3 Further, new innovations in the field of PUs have been ushered by the development of hyperbranched PUs (HPUs). In recent times, HPUs have received significant attention because of their unique attributes such as three-dimensional architecture, low solution and melt viscosity, high solubility, high reactivity, good compatibility with others, and so forth,4 which gives them distinct edge over the linear PUs in terms of structural versatility, processability, and material properties. Also, the fact that HPUs can be designed using biobased precursors makes them an inexpensive and ecofriendly commodity.5,6 However, insufficiencies in achieving the desired material properties have restricted their exploitation in advanced applications. There have been various concepts such as blending7–9 and interpenetrating networks10–12 with aromatic or similar polymers to improve the material properties of HPUs, although with complicated procedures and processing difficulties. Therefore, improving the material properties of HPUs by simple and inexpensive techniques is a lucrative challenge before their utilization for advanced applications.

Recent studies have confirmed that the material properties of pristine polymers can be drastically improved by the formation of polymer nanocomposites with suitable nanomaterials.13–16 In addition, these nanomaterials can also impart special properties to the polymers, which may not be otherwise achieved by the pure polymeric material alone.16–18 Especially, carbon-based nanomaterials with their myriad properties have carved out a niche for themselves that can be exploited to build polymeric nanocomposites for various applications.19–21 In

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this context, graphitic carbon nitride is a new emerging nanomaterial that has attracted considerable interest in recent years because of its similarity to graphene.22 Graphitic carbon nitride consists of a prebonded C−N core motif that imparts unique features, viz., thermal stability, chemical stability, optical property, electrochemical property, surface property, etc.23 Variants of graphitic carbon nitride in the form of nanosheets and nanodots have found widespread applications as photocatalysts, electrochemical sensors, energy storage devices, environmental remediators, and so forth.22,23 From this perspective, graphitic carbon nitride due to its uncanny structural similarity to graphene can be thereby utilized as a nanoreinforcing agent for improving the properties of polymers. However, until date, there have been very few reports on their use in polymer nanocomposites. For instance, Zhu et al. reported the development of graphitic carbon nitride nanosheet-reinforced polyimide nanocomposites with enhanced mechanical and tribological properties.24 Xu et al. demonstrated graphitic carbon nitride nanosheet-reinforced poly(urea-urethane) nanocomposites with self-healing and anticorrosive properties.25 Thus, there is plenty of scope for graphitic carbon nitride with its unique structural features and attractive set of properties to be applied as reinforcing materials for polymer nanocomposites.

Again, in the current times, counterfeiting has become a rising issue worldwide for industries, governments, and customers. With the recent development and generalization of high-end equipment, counterfeited items have become more common, creating problem for the society.26 For example, the circulation of counterfeited paper currency leads to serious socioeconomic problems as well as undervalued authentic currency;27,28 production and distribution of counterfeited drugs pose severe health hazard, as they may contain unknown or incorrect amount of chemicals.29,30 In this context, anticounterfeiting has become a vital innovation for protecting important and valuable items that should not be replicated such as currency, documents, certificates, brands, luxury items, and tickets.31 During the past decade, an array of anticounterfeiting technologies have been developed to tackle counterfeiting. However, the counterfeiters have been successful in adapting to the current methods, which makes it imperative to develop new materials and innovative tools to detect and prevent counterfeiting. In this perspective, functional materials having distinct physical, chemical, or optical properties can be expected to provide anticounterfeiting measures because of difficulties associated with reproduction of their unique functions.32 Especially, photoluminescent materials with specific excitation and specific mode emission properties are considered to be good strategy for anti-counterfeiting applications. Photoluminescent anticounterfeiting appliances based on optical materials such as semiconductor quantum dots,33 carbon quantum dots,34 lanthanide-doped materials,35 and so forth have been developed recently. In this context, graphitic carbon nitride nanodots, with their excellent optical and photoluminescent properties, can serve as an ideal material for constructing anticounterfeiting materials that show specific excitation/emission properties. These photoluminescent nanodots combined with the unique attributes of biobased HPUs can forge a suitable material that is not only robust and ecofriendly but also intricate in its design. The design of such high-performance photoluminescent nanocomposites can be a prototype for coatings, labelings, and ink-jet printing with anticounterfeiting measures.

Thus, the current work describes the development of nanocomposites of bioderived HPU with oxygeneous-graphitic carbon nitride nanodots acting as a nano-reinforcing material. To the best of our knowledge, this is the first report on the fabrication of HPU nanocomposite with graphitic carbon nitride nanodots. The influence of the oxygeneous-graphitic carbon nitride nanodots as a reinforcing agent on the mechanical and thermal properties of the nanocomposite was studied. In addition, the performance of the nanocomposite as an anticounterfeiting tool was demonstrated.

## RESULTS AND DISCUSSION

Preparation and Characterization of Oxygeneous-Graphic Carbon Nitride Nanodots (Oxy-gCNDs). Oxy-gCNDs were prepared by microwave pyrolysis of guanidine hydrochloride and sodium citrate in basic aqueous medium as illustrated in Scheme 1. In recent times, guanidine hydrochloride has emerged as a popular choice for the synthesis of graphitic carbon nitride because of its low cost, nitrogen-rich, and highly reactive nature.31 Consequently, guanidine hydrochloride was chosen as the principal precursor. Sodium citrate played the role of surface passivating and stabilizing agent, as it contains ample carboxylic groups and hydroxyl group that helps in controlling the size and morphology of carbon nitride nanodots. Further, microwave pyrolysis offers the benefit of simultaneous, homogeneous, and expeditious heating, leading to uniform size distribution of the nanodots.32 As reported in the earlier work, the mechanism of formation of carbon nitride nanodots is presumed to follow a rapid pathway of cyclization and polymerization involving the precursors to give the graphitic carbon nitride core made up of tri-s-triazine motif.20,21
Preliminary investigations revealed that oxy-gCNDs possess a yellow amorphous appearance and hygroscopic nature. These oxy-gCNDs were found to have high dispersibility (nano-level) in water but very poor dispersibility in most of the organic solvents. The hygroscopic nature and high aqueous dispersibility indicated proper surface passivation or functionalization.
of graphitic carbon nitride core by oxygenous functional groups. Remarkably, these oxy-gCNDs exhibited high stability and good dispersibility in water even after exposure to ambient conditions for several months, without any signs of agglomeration. Similar to most carbon quantum nanodots, these highly water dispersible oxy-gCNDs displayed bright cyan photoluminescence under long UV light (365 nm wavelength) with good photostability even after several months on benchtop. UV−visible spectral analysis of oxy-gCNDs showed an intense absorption band centered at 235 nm, corresponding to π→π* electronic transition of the tri-s-triazine motif of graphitic carbon nitride. Additionally, a broad continuous absorption was observed in the range of 280−490 nm, which can be attributed to n→π* electronic transitions originating from surface passivating functional groups of oxy-gCNDs. Photoluminescence (PL) study of oxy-gCNDs showed a narrow and symmetrical maximum PL emission peak centered at 445 nm upon excitation at 360 nm, which can be held responsible for the bright cyan PL emission. Notably, the quantum yield of oxy-gCNDs (λex = 360 nm) was measured to be 19% using quinine sulfate as a standard. The PL emission peak was observed to be red-shifted relative to the maximum absorbance band of oxy-gCNDs (Figure 1a). Furthermore, oxy-gCNDs revealed notable variations in PL emission, as the PL emission peak was red-shifted from 435 to 475 nm, while its intensity increased and then decreased gradually upon varying the excitation wavelength from 320 to 420 nm (Figure 1b). These results suggested that oxy-gCNDs exhibited excitation wavelength-dependent PL behavior, owing to the effects of optical selection of differently sized nanoparticles (quantum confinement effect) and considerable distribution of emissive trap sites on the oxy-gCND surface, similar to most of carbon quantum dots. Transmission electron microscopy (TEM) analysis showed that the as-prepared oxy-gCNDs were monodispersed and possessed spherical morphology. Statistical analysis showed that these nanodots were distributed in the range of 1−3 nm with an average diameter of 2.2 nm (Figure 1c). Attenuated total reflection Fourier transform infrared (ATR−FTIR) spectral analysis showed the characteristic band at 815 cm−1 corresponding to the tri-s-triazine motif of graphitic carbon nitride and prominent bands around 1535, 1451, and 1390 cm−1 attributed to typical stretching modes of CN heterocycles. Additionally, occurrence of an intense sharp band at 1627 cm−1, corresponding to asymmetric stretching vibration of carboxylate anions, and two nearby bands at 3277 and 3150 cm−1, corresponding to N−H stretching of the primary amine group, coupled with O−H stretching of hydroxyl groups, further suggested the passivation of carboxylic and hydroxyl groups on the surface of oxy-gCNDs (Figure 1d).

Fabrication and Characterization of Bioderived HPU/Oxy-gCND Nanocomposite (HPUNC). HPUNCs were fabricated by an Ax + Bx (x,y ≥ 2) polymerization technique using castor oil-modified polyol (COMP) as the branching moiety and varying loadings of oxy-gCNDs as the nano-reinforcing agent as shown in Scheme 2. Formation of the HPU nanocomposite depends on several factors, most notably the concentration of reactants and dispersion of the nanomaterial in the polymer matrix. The concentration of the reactants, especially the branching moiety, was maintained by dilution with solvent during the polymerization reaction. This strategy allowed the smooth completion of the reaction without any gel formation, which is a usually encountered problem during the formation of a hyperbranched polymer. Further, uniform dispersion of the nanomaterial in the polymer matrix is an important condition for the formation of a polymeric nanocomposite. The nano-reinforcing agent was properly dispersed in solvent by dispersion of the reactants, primarily the branching moiety, was maintained by dilution with solvent during the polymerization reaction. This strategy allowed the smooth completion of the reaction without any gel formation, which is a usually encountered problem during the formation of a hyperbranched polymer. Further, uniform dispersion of the nanomaterial in the polymer matrix is an important condition for the formation of a polymeric nanocomposite. The nano-reinforcing agent was properly dispersed in solvent by...
ultrasonication prior to its addition in the polymerization reaction. Oxy-gCNDs, by virtue of their surface passivating functional groups, formed a stable dispersion in dimethylformamide (DMF) for a short time, allowing timely addition in the reaction. Moreover, the nano-reinforcing agent was judiciously added to the prepolymer in the beginning of the second step with vigorous mechanical shearing force. This tactic aided the formation of a uniformly dispersed nanocomposite.

A comparison of the ATR–FTIR spectra of the initial prepolymer, HPU, and HPUNC revealed key changes in chemical functionalities, which suggested the formation of the PU linkages, as illustrated in Figure 2a. The FTIR of the prepolymer revealed the appearance of bands of –NH stretching at 3421 cm$$^{-1}$$ and free –C$$\equiv$$O band at 1736 cm$$^{-1}$$ prominently, along with free isocyanate (–NCO) band at 2260 cm$$^{-1}$$, indicating the formation of the isocyanate-terminated PU prepolymer as depicted in the first step of the fabrication process in Scheme 2. The bands of PU further became more conclusive and prominent in the FTIR of HPU and HPUNC after the second step of the fabrication process in Scheme 2. The broad band centered at 3362 cm$$^{-1}$$ was attributed to N–H stretching vibration of the urethane linkage, coupled with O–H stretching vibration. The sharp band at 1724 cm$$^{-1}$$ juxtaposed with the weak band at 1640 cm$$^{-1}$$ was alluded to free C$$\equiv$$O and H-bonded C$$\equiv$$O stretching vibration of urethane linkage, respectively. Further, the medium band at 1530 cm$$^{-1}$$ was attributed to the coupled vibrations of N–H bending and C–N stretching of the urethane linkage, whereas the medium intensity band at 1240 cm$$^{-1}$$ was ascribed to the C–O–C stretching vibrations of the urethane linkage. At the same time, the medium intensity band at 1045 cm$$^{-1}$$ was attributed to the C–O stretching vibration of the urethane linkage. Additional bands were observed prominently at 2938 and 2865 cm$$^{-1}$$ corresponding to the asymmetric and symmetric C–H stretching vibrations of –CH$$\_2$$ and –CH$$\_3$$ groups of the PU chain segments. Other C–H modes of vibrations, resulting from the chain segments of HPUNC, were also observed distinctly in the spectra at 1465 cm$$^{-1}$$ (–CH$$\_2$$ scissoring coupled with –CH$$\_3$$ asymmetric deformation), 1366 cm$$^{-1}$$ (–CH$$\_3$$ symmetric deformation), 1295 cm$$^{-1}$$ (–CH$$\_2$$ wagging), and 730 cm$$^{-1}$$ (–CH$$\_2$$ rocking in long aliphatic chains). Most notably, the band observed for free –NCO group at 2260 cm$$^{-1}$$ disappeared completely, suggesting complete and quantitative formation of HPUNC.

X-ray diffractograms of HPUNCs as shown in Figure 2b clearly indicated the presence of crystallinity. Two strong diffractions peaks were observed at 2$$\theta$$ = 21.5$$^\circ$$ (calculated d-spacing of 4.12 Å) and 2$$\theta$$ = 23.8$$^\circ$$ (calculated d-spacing of 3.73 Å) because of (110) and (200) planes of the crystalline poly($$\varepsilon$$-caprolactone)/diol (PCL) moiety, respectively. In addition, enhancement in the peak intensity of the PCL moiety with incorporation of a nano-reinforcing agent was observed. This enhancement can be attributed to the good nano-reinforcing effect of the oxy-gCNDs. This nano-reinforcing ability was reflective of the strong physico–chemical interactions between the near-graphitic nanomaterial and the crystalline segments of the polymer chains. Further, the nanocomposites displayed slight enhancement of peak intensity upon increasing the loading capacity of the nano-reinforcing agent. Calculation of % crystallinity of HPUNCs using peak integration function in Origin 8.5 affirmed this observation with corresponding values of 22.1% (0.5 wt %), 22.6% (1.0 wt %), and 23.5% (2.0 wt %) compared to that of 21.95% of only pure HPU. Hence, it can be stated that as the loading of oxy-gCNDs increased in the polymer matrix, the extent of these physico–chemical interactions also increased, imparting better reinforcement of HPUNC. TEM images of HPUNC in Figure 2c revealed the consistent dispersion of oxy-gCNDs (red circles) in the HPU matrix.

**Mechanical Properties of HPUNCs.** The mechanical properties of HPUNCs were evaluated and demonstrated in Table 1. Mechanical properties such as tensile strength, elongation at break, toughness, scratch hardness, and impact strength were significantly improved even at very low nanomaterial loading. Further, the nanocomposites displayed loading-dependent improvement of mechanical properties. The stress–strain profile of HPUNCs and HPU shown in Figure 3a, as well as the effect of nanomaterial loading on tensile strength, elongation at break, and toughness, shown in Figure 3b–d, highlighted the reinforcing effect of oxy-gCNDs.

The tensile strength of the nanocomposite improved gradually on increasing the nano-reinforcing agent loading from 0.5 to 2.0 wt %, showing maximum enhancement up to 1.9-fold. At the same time, elongation at break of the nanocomposite also improved slightly on gradual increase of nano-reinforcing agent loading, displaying maximum enhancement up to 1.2-fold. The values of toughness, calculated by integrating the area under curve from the stress–strain profile of HPUNCs, also showed improvement up to 2.5-fold with increasing nano-reinforcing agent loading. Further, the nanocomposite displayed improved values of scratch hardness and impact resistance, which could not be precisely quantified as they exceeded the maximum limit of the instruments. This improvement in the mechanical properties of the nanocomposites can be solely attributed to the presence of the oxy-gCNDs in the HPU matrix and strong interfacial interactions existing between them. At this juncture, it is pertinent to know that carbon nanostructures can act as a very good reinforcing material for polymers because of their structural stability and compatibility. In this context, oxy-gCNDs served the role of a suitable nano-reinforcing agent, as they possess a formidable semi-carbonized structural motif as well as various surface passivating functional groups which provided rigidity and flexibility to the polymer matrix by participating in various physico–chemical interactions within the polymer matrix. These oxy-gCNDs reinforcing the HPU matrix hence contributed to its high performance.

### Table 1. Mechanical Properties of HPUNCs

| parameter       | HPU   | HPUNC0.5 | HPUNC1.0 | HPUNC2.0 |
|-----------------|-------|----------|----------|----------|
| tensile strength (MPa) | 5.3 ± 0.2 | 6.4 ± 0.1 | 8.5 ± 0.2 | 12.0 ± 0.1 |
| elongation at break (%) | 610 ± 5 | 637 ± 10 | 676 ± 5 | 732 ± 2 |
| toughness$$^a$$ (MJ m$$^{-1}$$) | 28.34 | 35.56 | 58.24 | 72.20 |
| scratch hardness$$^b$$ (kg) | 10 | >10 | >10 | >10 |
| impact strength$$^c$$ (kJ m$$^{-2}$$) | 19.02 | 20.92 | 20.92 | 20.92 |

$$^a$$Calculated by integrating the stress–strain profiles of HPUNCs. $$^b$$Maximum limit of the instrument is 10 kg. $$^c$$Calculated by converting into energy unit as per thickness between 0.43 and 0.45 mm.

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Recent state-of-art literature endorses the reinforcing role of such carbon quantum nanodot-like materials with various polymeric materials. For example, Gobi and co-workers showed that incorporation of 2.5 wt % of graphene quantum dots in an epoxy resin led to a 2.25-fold increase in tensile strength, 1.18-fold increase in nominal strain at break, and 2.6-fold increase in toughness. In another instance, Zhang and co-workers reported that inclusion of 2 wt % carbon quantum dots in an epoxy resin polymer resulted in 1.39-fold increment in tensile modulus. Seminal works done by the author’s group toward the development of high-performance hyperbranched polymer nanocomposites with carbon quantum dot nanomaterials are also noteworthy. For instance, a hyperbranched epoxy resin nanocomposite with 1 wt % carbon dots showed improvement of 1.22-fold in tensile strength, 1.21-fold in elongation at break, and 1.17-fold in toughness; a hyperbranched waterborne polymer nanocomposite containing 1 wt % of carbon dots displayed enhancements of 1.8-fold in tensile strength and 1.4-fold in elongation at break; a hyperbranched waterborne polyester nanocomposite containing 1 wt % carbon dots demonstrated very high enhancements of 6.02-fold in tensile strength and 2.8-fold in toughness. In overall, these reports reiterated the role of carbon quantum nanodots as capable reinforcing agents for polymers and substantiated the results observed for HPUNCs.

Thermal Properties of HPUNCs. The thermal properties of HPUNCs were evaluated by thermogravimetric (TG) analysis. The TG curves of HPUNCs along with HPU and oxy-gCNDs are shown in Figure 4. The nanocomposites displayed slight and gradual improvement in thermal degradation temperature at a very low loading of nano-reinforcing agent. In addition, all the nanocomposites displayed enhancement of degradation temperatures corresponding to the loading of the nano-reinforcing agent (Table 2). This enhancement in thermal degradation temperatures can be mainly attributed to the presence of oxy-gCND nano-reinforcing agent in the HPU matrix and their reinforcing effect on the matrix. Here, it is pertinent to mention that graphitic carbon nitride possesses a host of unique properties including excellent thermal stability, owing to its near-graphitic core structure. Therefore, the dispersion of oxy-gCNDs in the polymer matrix imparted a stabilizing effect on the polymer matrix by absorbing the thermal energy in its core. In addition, reinforcement of the HPU matrix by oxy-gCNDs led to occupation of free volume available in the matrix, thereby restricting the arbitrary motion of the polymeric chains under thermal energy. This reinforcement ultimately imparted resistance to the degradation of the polymer matrix.

Anticounterfeiting Application. HPUNC was dispersible in polar aprotic solvents such as tetrahydrofuran (THF), dimethylformamide (DMF), dimethylsulfoxide, and so forth, displaying a light yellow transparent solution. This solution transparency can be attributed to both the aliphatic nature of the HPU matrix and quantum size effect of the oxy-gCNDs. In addition, the dispersed nanocomposite was found to exhibit bright cyan photoluminescence, owing to the presence of oxy-gCNDs in the polymer matrix. The transparency and

Figure 3. (a) Stress–strain profiles of HPU and HPUNCs; effect of nanomaterial loading on (b) tensile strength, (c) elongation at break, and (d) toughness.

Figure 4. TG curves of oxy-gCNDs, HPU, and HPUNCs.
photoluminescent property of HPUNC make the corresponding dispersion an attractive material for anticounterfeiting, as such materials are hard to replicate and process. As shown in Figure 5a, the HPUNC dispersion in xylene is light yellow in color in daylight but emits bright cyan emission under long UV light (365 nm). This dispersion can be loaded into a gel/sketch pen refill and used directly as ink. To demonstrate the performance of HPUNC as an anticounterfeiting ink, the characters “TU” and “APNL” were written on a commercially available filter paper and the characters “HPUNC” written on a sheet of ordinary plastic using a sketch pen filled with the HPUNC ink. The characters were not observed by the naked eye in the normal daylight but were clearly visible in PL mode (bright cyan color) under illumination of a 365 nm UV lamp, as visualized in Figure 5a (top and bottom). Most importantly, this ink was stable for several months in ambient conditions and applicable on different surfaces such as paper and plastic. Moreover, the HPUNC ink also exhibited reinforcing effect on the coated material. This reinforcing effect was confirmed by evaluating the mechanical property of the commercial filter paper coated with the HPUNC ink. As evident from the stress–strain profile in Figure 5b, the tensile strength of HPUNC-coated paper manifolded by 2.14 times, while the elongation at break drastically improved by 3.82 times, signifying excellent reinforcing ability of the HPUNC ink. This improved physico-mechanical property of the nanocomposite ensured stability of the nanocomposite and protection of the coated material and its content toward any external forces or any kind of wear or tear to some extent. Moreover, the bioderived nature of the nanocomposite and its intricate design and processing endowed eco-friendliness and exclusivity, respectively. These observations reiterated the potential utility of HPUNC dispersion as a high-performance anticounterfeiting ink that can be used for loading important information for secret communications and security features.

### EXPERIMENTAL SECTION

**Materials and Methods.** Guanidine hydrochloride (Alfa Aesar, USA), sodium citrate (SRL, India), PCL (number-average molecular weight = 2000 g/mol, Sigma–Aldrich, USA), and isophorone diisocyanate (IPDI, Sigma-Aldrich, USA) were used as received. Xylene (Merck, India) and THF (Merck, India) were vacuum-distilled and kept in 4A-type molecular sieves before use. Monoglyceride of sunflower oil (MGE) and COMP were prepared as reported elsewhere and were vacuum-dried at 50 °C prior to use. Other chemicals and solvents were of reagent grade and used without further purification.

**Preparation of Oxygeneous-Graphitic Carbon Nitride Nanodots (Oxy-gCNDs).** Oxy-gCNDs were prepared by microwave pyrolysis of guanidine hydrochloride and sodium citrate with slight modification of an earlier report. Briefly, guanidine hydrochloride and sodium citrate in the mol ratio of 9:1 were homogenized together in deionized water, and the pH of the mixture was adjusted to 12 using 25% aqueous NH3. Subsequently, the reactants were subjected to microwave irradiation for 8 min in a domestic microwave oven, operating at the power output of 600 W. After cooling, the as-obtained dark brown residue is dissolved in deionized water and filtered to separate the coarse residue. The filtrate is further centrifuged to separate any suspended particulates, and the light yellow supernatant is collected to give highly dispersible oxy-gCNDs (concentration of 22 mg mL⁻¹).

**Fabrication of Bioderived Aliphatic HPU/Oxy-gCND Nanocomposite (HPUNC).** HPUNC nanocomposite was fabricated by an in situ polymerization technique using oxy-gCNDs as the nanoreinforcing agent. In a typical prepolymerization process, PCL (0.0015 mol), IPDI (0.0025 mol), and MGE (0.001 mol) were reacted together at 130 ± 5 °C for 3 h in xylene as the solvent under N2 atmosphere in the first step. The highly viscous fluid obtained in the first step was
The manuscript was written through contributions of both the authors.

**Notes**

The authors declare no competing financial interest.

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