High-Performing Biodegradable Waterborne Polyester/Functionalized Graphene Oxide Nanocomposites as an Eco-Friendly Material

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Supporting Information

ABSTRACT: The development of high-performing nanocomposites of homogeneously dispersed graphene oxide in a waterborne polyester matrix with controlled interfacial interactions is a daunting challenge owing to the presence of strong cohesive energy in both. Thus, in this study, graphene oxide was functionalized with toluene diisocyanate and butane diol through a simple method and incorporated into the waterborne polyester matrix through a facile in situ bulk polymerization technique without using any compatibilizing agent or organic solvent for the first time. The thermoset of the nanocomposite was formed by curing it with hyperbranched epoxy of glycerol and poly(amide amine). The resultant thermosetting nanocomposites with 0.1−1 wt % functionalized graphene oxide exhibited significant enhancement in mechanical properties such as elongation at break (245−360%), tensile strength (7.8−39.4 MPa), scratch hardness (4 to >10 kg), toughness (17.18−86.35 MJ/m²), Young’s modulus (243−358 MPa), impact resistance (8.3 to >9.3 kJ/m), and thermostability. Further, the Halpin−Tsai model was used to predict the alignment of graphene oxide. The nanocomposite was also biodegradable against the Pseudomonas aeruginosa bacterial strain. Furthermore, this nanocomposite exhibited strong catalytic activity for the aza-Michael addition reaction. Thus, the nanocomposite can be utilized as a high-performing sustainable material in different potential applications including as heterogeneous catalysts.

1. INTRODUCTION

Nanotechnology is a multidisciplinary field which involves design, engineering, and fabrication of devices at the nanoscale with significantly alternative and enhanced material properties.1 In this context, polymer nanocomposites have attracted considerable attention over the last two and a half decades.2 The combined effect of nanoreinforcing materials and the polymer matrix leads to the development of high-performing polymeric materials for various industrial applications through the enhancement of properties such as mechanical, thermal, optical, electronic, magnetic, and so forth.3 The incorporation of different nanoreinforcing agents such as clay, carbon nanotubes, metal oxide nanoparticles, graphene and its derivatives, and so forth, into a polymer matrix significantly improved the material properties.2,3,4 Graphene is gaining greater attention among them owing to its excellent mechanical properties, high aspect ratio, outstanding electrical and thermal conductivity, high surface area, and so forth. Further, its unique structure opens up a new avenue to fabricate more efficient devices for various applications.3,4 However, graphene oxide (GO) contains a variety of reactive oxygenous functional groups like hydroxyl, epoxy, and carboxylic acid compared to graphene and thereby facilitates the fabrication process. It readily forms aqueous dispersion, it is dispersible in various organic solvents and even in polymers, and its functional groups may interact with the polyester matrix.9 However, as the number of such polar functional groups in GO which interact among themselves so strongly is very large, the interaction with the polymer matrix is a genuine question. Therefore, to improve such interactions, some of the polar functional groups of GO may be functionalized with appropriate reactants to facilitate better interactions with the polyester matrix, which results in uniform dispersion in the polymer matrix.10,11 This functionalized GO (f-GO) is thought to be an ideal nanoreinforcing agent for waterborne polymers because the oxygenous groups of GO such as hydroxyl and epoxide spreading across the basal planes and carbonyl groups existing at edge sites facilitate the dispersion and interactions with the matrix, thereby helping in exfoliation of GO. In addition, fabrication and employment of such waterborne polymers are gaining significant interest because of their advantages such as no volatile organic compounds, low cost, nontoxicity, environ-
Among different types of waterborne polymers, polyesters are found to be more interesting, as they also possess similar functional groups such as carboxylic, hydroxyl, and so forth, which can interact with the similar functional groups of GO to form strong interfacial interactions. In addition, the functional groups of GO can also participate in the curing reaction of the polyester, especially in the presence of the epoxy and poly(amido amine) hardener system to form covalent and noncovalent linkages. Further, the fabrication of nanocomposites of waterborne hyperbranched polyester (WHP) with GO can also address the shortcomings of the pristine.
polyester system from low mechanical, thermal properties, and so forth, thereby facilitating their applications in various advanced fields. Further, apart from enhancement in these properties, incorporation of GO also retained biodegradability of the material. The design of such polyester from renewable feedstocks has achieved remarkable importance, as it provides assurance of sustainability for the development of economically attractive technologies. To date, a relatively restricted number of studies was reported on polyester/GO nanocomposites, and no report was available in the literature on the incorporation of GO in the biobased WHP system, so far. In the literature, Bastiurea et al. studied mechanical and thermal properties of polyester nanocomposites with GO and graphene, but the reported properties were not up to the mark. Further, Bora et al. reported the fabrication of unsaturated polyester and GO nanocomposites and studied mechanical and thermal properties of this nanocomposite; however, elongation at break was found to be very low. He et al. reported the thermal properties and fracture toughness of an unsaturated polyester/GO nanocomposite. However, mechanical properties of all the reported polyester/GO nanocomposites are found to be poor for their advanced applications. Further, all of the reported literature used large amounts of organic solvents for the fabrication of nanocomposites which are not attractive for industrial production. Furthermore, on the basis of the literature report on theaza-Michael addition reaction using GO, herein, we report the fabrication of the novel waterborne polyester-supported f-GO catalyst and its application for azamichael reaction in water as a greener solvent to achieve a complete environment-friendly process. The utilization of environmentally benign solvents and materials signifies an ideal green chemical technology process from both economic and environmental viewpoint.

Therefore, in the present work, WHP nanocomposites were fabricated with different loadings of f-GO through an organic solvent and a compatibilizing agent-free in situ polymerization technique to obtain high-performing eco-friendly material. The properties of the thermosetting nanocomposite such as mechanical, thermal, biodegradation, and so forth, were also studied. The catalytic activity of the nanocomposite for the aza-Michael addition reaction was also evaluated along with its recyclability to judge the efficiency as a heterogeneous catalyst.

2. RESULTS AND DISCUSSION

2.1. Functionalization of GO. In the fabrication of the WHP/f-GO nanocomposite, key issues are dispersion of the nanomaterials and interfacial interactions of GO with the polyester matrix. The surface functionalization of GO enormously influences its state of dispersion in the polymer matrix. The oxygen-containing functional groups including carboxylic acid, hydroxyl, and epoxy groups can be used to change the surface functionality of GO. Thus, the functionalization of GO was achieved by the reaction of oxygenated functional groups of GO with isocyanate groups of toulene diisocyanate (TDI), followed by reaction with 1,4-butanediol (BD) and the resulted isocyanate-terminated GO. As isocyanate is highly reactive, covalent functionalization occurred by direct linkage of OH groups of GO with the isocyanate groups. A schematic preparation of f-GO is shown in Scheme 1. Stable dispersion of GO and f-GO was observed in different solvents such as tetrahydrofuran (THF), dimethylformamide, dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and so forth (Scheme 1).

2.2. Characterization. GO and f-GO were analyzed by different spectroscopic and diffraction techniques (Figure 1a–d). Fourier transform infrared (FTIR) is used to establish the presence of various oxygen-containing functional groups in them. In the FTIR spectrum of GO (Figure 1c), the occurrence of intense bands at 1720 cm\(^{-1}\) (C=O stretching), 1202 cm\(^{-1}\) (C–O–C stretching), and 1047 cm\(^{-1}\) (C–O stretching) and a broad band at 3402 cm\(^{-1}\) (O–H stretching) indicates the occurrence of oxygenous groups such as carboxyl, carboxylic, epoxy, and hydroxyl in it. The bands that appeared in the range of 3000–2700 cm\(^{-1}\) are owing to the stretching vibrations of \(\text{–CH}_2\) (symmetric and asymmetric). The FTIR spectrum (Figure 1c) of f-GO showed the presence of absorption frequencies at 1541, 1642, 1052, 1700, and 1217, cm\(^{-1}\), which are ascribed to the stretching vibration of bending of N–H of amide II, C=C, C–N, carbonyl of amide I, and C=O. Thus, this FTIR analysis confirmed the covalent bond formation with GO by TDI and BD. Further, X-ray diffraction (XRD) patterns (Figure 1a) of pristine GO showed two peaks at 10.1\(^\circ\) and 43.2\(^\circ\) for (002) and (001) graphitic planes, respectively. The peak at 10.1\(^\circ\) is due to the presence of abundant oxygenous groups which is similar to the reported

![Image](https://example.com/image.png)

Figure 2. (a) TEM images GO and (b–d) TEM images of f-GO at different magnifications for morphological observation, (e) HRTEM images at 2 nm for layer observation, and (f) SAED pattern of f-GO.
The positions of XRD peaks are slightly shifted after functionalization of GO which support the modification of GO. Furthermore, Raman spectroscopy is also an important technique to characterize the carbonaceous materials with ordered or disordered structures. Raman spectra of both GO and f-GO showed two fundamental vibration bands in the range of 1200–1700 cm\(^{-1}\) (Figure 1b). The vibration mode at 1580 cm\(^{-1}\) (G) is due to the scattering (first-order) of E\(_{2g}\) phonon vibration of sp\(^2\) carbon atoms, and the D vibration band (1351 cm\(^{-1}\)) is due to the A\(_{1g}\) breathing mode of carbon associated with structural defects and disorders. The UV–visible spectrum (Figure 1d), GO showed a peak at 233 nm owing to \(\pi\rightarrow\pi^*\) transitions, and a weak shoulder at 302 nm is due to n–\(\pi^*\) transitions of aromatic carbon–carbon bonds and C=O bonds. Further, transmission electron microscopy (TEM) analysis provides direct visualization of the morphology of GO and f-GO (Figure 2a–d). The exfoliated, transparent, and wrinkled GO nanosheets and f-GO were observed from its TEM images with micrometer lateral dimension. The occurrence of topological features, besides the overlapping area of GO nanosheets, revealed that they are extremely dispersed in water. According to the reported literature, the crumpled topology of GO is due to the presence of oxygenous functional groups as well as the extremely thin characteristic of the nanosheets. The high-resolution TEM (HRTEM) image of f-GO further confirmed the retaining of the layer structure of GO even after functionalization (Figure 2e). The selected area electron diffraction (SAED) pattern of f-GO is shown in Figure 2f.

### 2.3. Fabrication of WHP and f-GO Nanocomposites

As both the components polyester and GO are compatible because of the presence of an adequate number of polar functional groups, there are strong interactions among the components, which are shown in Scheme 2. This interaction also helps to stabilize the dispersed f-GO, and the stable dispersion was achieved by mechanical shearing force, followed by ultrasonication even in aqueous medium (Scheme 2). Ultrasonication generates a localized intensity with high pressure, temperature, and energy, which helps in the dispersion at the nanoscale level. To fabricate WHP/f-GO nanocomposites, an
in situ polymerization technique was employed under bulk conditions without using any solvent or compatibilizing agent. The −OH groups of f-GO interact covalently and non-covalently with the polyester matrix during the fabrication process. The nanocomposite was well-dispersed in water, ethanol, DMAc, DMSO, THF, and so forth.

The resultant nanocomposite was characterized by various spectroscopic techniques such as FTIR, XRD, and TEM. The characteristic absorbance bands for pristine polyester were found at 3451 cm$^{-1}$ (−O−H stretching), 2953−2805 cm$^{-1}$ (−C−H symmetric and asymmetric stretching), and 1739 cm$^{-1}$ (−C═O stretching). The characteristic carbonyl peak for ester was slightly shifted after the formation of the nanocomposite, as observed from the FTIR spectrum of PFGN1. Further, the band at 3000−3500 cm$^{-1}$ corresponding to the hydroxyl group of GO shifted to a lower wavenumber. The shifting of the bands as well as the decreased in intensities of carbonyl group usually considered as the evidence of hydrogen bond formation between the polyester matrix and f-GO. Therefore, the shifting of peak positions in the FTIR spectrum of the nanocomposite (Figure 3a) indicates the existence of strong interactions such as polar−polar, hydrogen bonding, and so forth, between the polyester matrix and f-GO. Further, in the XRD pattern of PFGN0.5 (Figure 3b), a broad peak was observed in the range of 15°−30° without the distinctive intense peak of f-GO. These peaks disappeared in nanocomposites because of the strong interaction of finely dispersed f-GO with the polar functional groups of pristine polyester, hyperbranched epoxy, and hardener, which reduces its crystallinity because of the masking effect since the quantity is very low. The SAED pattern of PFGN1 (Figure 4) further confirmed the amorphous nature of f-GO in the nanocomposites. TEM analysis was performed to further explore the morphology and dispersion of GO in the polyester matrix. The well dispersion of f-GO in the nanocomposite without any aggregation and the occurrence of thin layers of edge-folded f-GO sheets were visualized from the TEM micrograph of PFGN1 (Figures 4 and 5). Further, SEM images of the fractured surface of the nanocomposite are shown in Figure 5, which also provides dispersion characteristics of f-GO in the polyester matrix.

Figure 4. (a−d) Representative TEM images of PFGN1 at different magnifications, (e) layer observation of f-GO in the nanocomposite, and (f) SAED pattern.

Figure 5. (a,b) SEM images of the fractured surface of the nanocomposite and (c,d) TEM images of the nanocomposite under low magnification.

2.4. Curing of the Nanocomposite. The thermosets of the polyester nanocomposite were obtained by curing it with glycerol-based hyperbranched epoxy and hardener such as poly(amide amine) at elevated temperatures in a hot oven. The obtained films of the nanocomposite were dark brown in color. The presence of varieties of reactive polar functional groups such as hydroxyl, carboxylic, epoxy, and so forth, in the system made the mechanism of the curing process complex. As a result, different reactions occurred between them, and the plausible cross-linking interactions are shown in Scheme 3. The primary amine groups of the hardener opened the epoxy ring of hyperbranched epoxy of glycerol, leading to the generation of secondary amine and −OH groups. The free hydroxyl groups of the nanocomposite interacted with epoxide groups of hyperbranched epoxy. The hydrogen bonding was formed between −C═O of the polyester with the hydroxyl group of f-GO and hyperbranched epoxy. The transesterification reactions between ester and hydroxyl groups can also occur. Further, the free hydroxyl groups of f-GO and polyester interact with the
amino group of the hardener. Furthermore, the etherification reaction of hydroxyl and epoxy may also take place. The different reactions among epoxide groups of hyperbranched epoxy, carboxylic, and hydroxyl groups of the nanocomposite and f-GO and amino groups of the poly(amido amine) hardener could also occur.23,24

Table 1. Performance Characteristics of the Nanocomposites

| property             | WHP         | PGN0.1      | PFGN0.1     | PFGN0.5     | PFGN1       |
|----------------------|-------------|-------------|-------------|-------------|-------------|
| swelling value       | 22 ± 1      | 23 ± 1      | 22 ± 2      | 22 ± 2      | 21 ± 1      |
| curing time (h)      | 5 ± 0.025   | 4.8 ± 0.5   | 4.6 ± 0.05  | 4.5 ± 0.015 | 4.3 ± 0.01  |
| tensile strength (MPa)| 7.8 ± 1.5   | 11.7 ± 1    | 16.3 ± 1.6  | 29.1 ± 2    | 39.4 ± 2.5  |
| elongation (%)       | 245 ± 2     | 167 ± 3     | 273 ± 2     | 320 ± 2     | 360 ± 3     |
| scratch hardness (kg)| 4 ± 0.1     | 6 ± 0.1     | 8 ± 0.2     | >10         | >10         |
| impact resistance (kJ/m^2) | >8.3       | >8.3        | >8.7        | >8.8        | >9.3        |
| toughness (MJ/m^3)   | 17.18 ± 1.5 | 18.5 ± 2    | 36.24 ± 2.2 | 61.41 ± 2.4 | 86.35 ± 3  |
| gloss (%)            | 80 ± 2      | 85 ± 1      | 90 ± 3      | 94 ± 2      | 100 ± 2     |
| Young’s modulus (MPa)| 243 ± 3     | 259 ± 2     | 266 ± 4     | 312 ± 3     | 358 ± 5     |

*aThe highest limit of the instrument. bCalculated area under stress-strain curves.

Figure 6. (a) Stress-strain profiles of the thermosets and (b) comparison between fitting results of the Halpin-Tsai model and the experimental data.
2.5. Performance Characteristics. The main aim of incorporating GO into the WHP matrix is to address its poor mechanical properties. The factors such as particle–particle interactions and nanoparticle–matrix interactions play a key role in the performance of the nanocomposite. The attraction forces between particles influence the particle–particle interaction and weaken the performance of the nanocomposite. The attraction and repulsion forces can be controlled by the particle size, particle volume fraction, particle surface modification, particle weight fraction, and so forth. The enhanced mechanical properties can be achieved through stronger interfacial interactions between nanomaterials and the polymer matrix. The different mechanical properties such as scratch hardness, tensile strength, elongation at break, impact resistance, toughness, and so forth, of WHP and WHP/f-GO nanocomposites with different loadings of f-GO were evaluated, and the values are summarized in Table 1. The stress–strain profiles of the nanocomposite (Figure 6a) showed the relationship between f-GO loading and tensile strength of the nanocomposite. The mechanical behavior of the nanocomposites apparently exhibited an enhancing trend upon loading f-GO. From Table 1, it is seen that the nanocomposite showed significant enhancement in tensile strength compared to the pristine polyester. The enhancement can be ascribed to the well dispersion of f-GO in the polyester matrix and the existence of covalent bonding among the polyester matrix and f-GO along with various secondary interactions. These help to construct sturdy interfacial interactions between the polyester matrix and homogeneously dispersed f-GO. The presence of such interactions resulted in the partially restricted polymer phase, and the orientation of the polymer chain and f-GO along the route of the tensile flow greatly contributes to the observed enrichment of the tensile strength. Further, these properties were found to be dose-dependent, and the values increased with the increase in the loading of f-GO. Increase in particle loading leads to creation of more nanodimensional interfaces that may generate a strong polymer network enhancing the mechanical properties. Nanocomposites with the highest f-GO loading (1 wt %) exhibited the highest tensile strength (39 MPa), corresponding to an enhancement of 5 times that of pristine polyester. The values were higher than those of the reported polyester nanocomposites such as polyester resin/GO16 and epoxy/GO26 and so forth. Further, it is most interesting to observe that the nanocomposites not only exhibited higher tensile strength but also improved elongation at break over the pristine system. The enhancement can be ascribed to the good interfacial interactions upon the homogeneous dispersion of f-GO in the polyester matrix. There is a chance of direct linkages among various oxygen-containing groups of f-GO and the polyester by physicochemical interactions. This significantly enhances the compatibility of f-GO with the polyester matrix, which facilitates the direct transfer stress to f-GO. This improves the strength of the nanocomposite. Furthermore, the values of Young’s modulus are calculated from the slope of the elastic region of the stress–strain curves, and the values are given in Table 1. On the introduction of f-GO, the values of Young’s modulus were found to be enhanced because of the chain stiffening effect which is further increased with the loadings of f-GO.

The well-established Halpin–Tsai model can be utilized for the prediction of Young’s modulus of a composite system, where the reinforcing agent was distributed either randomly or parallelly. The same may be employed for the prediction of Young’s modulus of graphene-based nanocomposites where graphene nanosheets may be aligned parallel or distributed randomly. To estimate the Young’s modulus of such nanocomposites, the following equations were utilized:

\[
E_{nc} = E_P (1 + \eta_s V_C)/(1 - \eta_s V_C)) \\
+ [s/8((1 + 2\eta_T V_C)/(1 - \eta_T V_C))]
\]

where \( s = [(E_{GO}/E_p - 1)/(E_{GO}/E_p + \zeta)] \), \( \eta_s = [(E_{GO}/E_p - 1)/(E_{GO}/E_p + \zeta)] \), \( E_{NC}, E_P, E_{GO} \) are the Young’s moduli of the nanocomposite, pristine polyester, and GO, respectively, \( \zeta \) is the diameter to thickness ratio, and \( V_C \) is volume fraction of GO. The density and Young’s modulus of GO were 2.2 g cm\(^{-3}\) and 215 GPa, respectively, as reported in the literature. The density of WHP was evaluated as 1.12 g cm\(^{-3}\), and the calculated Young’s moduli of the WHP nanocomposites were compared with the experimental obtained results at different GO concentrations, and they are shown in Figure 6b. From this figure, it is clear that the experimental modulus values are much closer to the theoretical results of parallelly aligned nanosheets.
compared to randomly distributed ones. This result demonstrated that the graphene nanosheets in the studied nanocomposites are mostly aligned in the parallel direction.

2.6. Thermal Properties. The thermal behaviors of the nanocomposite as well as GO and f-GO are presented in Figure 7a. GO is thermally unstable owing to the presence of a huge number of oxygeneous functional groups such as carboxyl, carbonyl, and hydroxyl, and its TGA curve revealed a two-step degradation pattern (Figure 7a). The weight loss near 100 °C is attributed to the evaporation of absorbed water molecules. The first step degradation at 178 °C is owing to the loss of epoxy, hydroxyl, and carboxylic groups as well as residual water molecules. The next step of degradation (430 − 520 °C) is due to the pyrolysis of the remaining oxygeneous functional groups yielding CO, CO₂, and H₂O vapors, as well as due to the decomposition of the ring carbon. The thermal degradation temperature of GO was slightly increased after functionalization, which indicates that the thermally labile oxygeneous functional groups took part in the functionalization process (Figure 7a). Further, the degradation temperature of the nanocomposites was shifted to temperatures higher than those of the pristine system as well as f-GO (Figure 7b). This signifies good dispersion of f-GO in the polyester matrix and strong interactions between them, thereby resulting in significant enrichment of the thermal stability. The thermostability of the nanocomposites was further enhanced with the increased f-GO loading. This is due to the fact that through the various physicochemical interactions with f-GO, the polymer chain motions are restricted. The enhancement in thermostability can be ascribed to the so-called “complicated path” effect of graphene platelets. GO acts as a barrier in the polymer matrix to delay the escape of volatile degradation products and retards the propagation of heat from the extraneous surroundings into the polyester matrix. Further, the glass transition temperature ($T_g$) of the nanocomposite was evaluated from differential scanning calorimetry (DSC) analysis, as shown in Figure 7c. The nanocomposite showed two different $T_g$ values, one in the range of 42−55 °C which is due to $\alpha$-transition and another, sub $T_g$, at a lower temperature (0−9 °C) which is due to $\beta$-transition. More confined polymer chains in the nanocomposites were achieved because of the strong interfacial interaction which led to a significant change in the $T_g$ and contributed to the detection of the second glass transition. In $\alpha$-transition, local segments of the polymer become mobile, while $\beta$-transition is resulted because of the side group motions or other types of in-chain motion. This demonstrated a measurable chain segmental motion which exists as a secondary relaxation process in the polymer chain. The segments such as ester linkages and aliphatic moieties actually took part in such $\beta$-transition. $T_g$ of the nanocomposite slightly increased after the incorporation of f-GO and further increased with the loading of f-GO, indicating the restriction of the mobility of...
polymer chains. This restriction may be due to different physicochemical interactions of the polyester matrix with the nanomaterial.\textsuperscript{32–34}

2.7. Biodegradation Study. Most interestingly, apart from the enhancement in mechanical and thermal properties arising from the incorporation of GO, the corresponding nano-composite showed a noticeable biodegradation behavior against the \textit{Pseudomonas aeruginosa} bacterial strain. The bacterial growth profiles for the nanocomposites obtained after 45 days are shown in Figure 8a. All the nanocomposites demonstrated significant bacterial growth against \textit{P. aeruginosa} with time. The factors such as flexible moieties, amorphous nature of the polyester, polar linkages, and hydrophilic character are mainly responsible for such biodegradation.\textsuperscript{35,36}

In the case of polyester, the major mode of degradation is a hydrolytic random chain scission. The degradation involves various phenomena of diffusion reaction, including ester hydrolysis, solubilization of soluble species, water absorption, and diffusion. Further, the ester cleavage is auto-catalyzed by end groups of carboxylic acid originally present in the polymer or nanomaterials or produced by hydrolytic degradation. The representative SEM images (Figure 8b–e) of PFGN0.5 demonstrated the morphologies of the nanocomposite before and after biodegradation and established broad surface erosion after degradation. However, the degree of degradation of polyester in the vicinity of the graphene sheets is less compared to the bulk. GO itself is nondegradable, but its incorporation in the polyester matrix has a marginal effect on the overall biodegradability of the nanocomposite.\textsuperscript{33,35} This is due to the increase of polar and flexible linkages including ester linkages which are prone to microbial attacks. Further, the hydrophilic character and the amorphous nature are the key factors responsible for this biodegradability.\textsuperscript{35} Though GO reduces the enzymatic hydrolysis rate in biodegradation,\textsuperscript{33} in this case, the effect was not observed, as no enzyme was directly used during the biodegradation study. Further, because of the functionalization of GO, this effect was not noticed though some enzymes may be released during the degradation process.

2.8. Nanocomposites as a Catalyst for Aza-Michael Addition Reaction. The nanocomposite was used as a catalyst for the addition of an N–H bond across a multiple bond to give important nitrogen-containing compounds. The reaction between diethylamine and acrylonitrile was carried out using different catalyst systems (Table S1, Supporting Information). The reaction was completed with highest conversion (98\%) within 3 min using PFGN1 as a catalyst. The yield was found to be higher than that reported for GO-based catalytic reaction.\textsuperscript{18}

The aza-Michael addition reaction in the presence of GO is favorable because of the presence of oxygenous functional groups in its surface which play a role in the activation of this reaction. Thus, the observed higher yield of the reaction by the nanocomposite is due to the presence of a huge number of functional groups than bare GO and f-GO. Further, the catalyst (PFGN1) concentration was optimized by varying its concentration from 0.00125 to 0.05 g (Table S2 of the Supporting Information, entry 1–5). The enhancement in the yield of the product was observed with the increase in the loading of the catalyst amount. This is due to the increase in the GO concentration with the increase in the loading of PFGN1, and hence, the increase in the number of oxygenous functional groups showed an excellent result. Further, the reaction was studied using different amines with different $\alpha,\beta$-unsaturated compounds under described conditions to obtain the desired products. The reactants were converted to the corresponding $\beta$-amino compounds without the formation of any byproducts with excellent yields within the short reaction time. These results are given in Table 2. The obtained products were characterized by NMR spectroscopy, and the corresponding NMR spectra of the products are provided in the Supporting Information (Figures S1–S3) and compared with the reported literature.

### Table 2. Aza-Michael Addition of Different Amines and $\alpha,\beta$-Unsaturated Compounds in the Presence of PFGN1 as the Catalyst\textsuperscript{a}

| Entry | Amine | $\alpha,\beta$-unsaturated compounds | Reaction time (min) | Yield (%) |
|-------|-------|-------------------------------------|---------------------|-----------|
| 1     | ![Amine Image](image1.png) | ![Unsaturated Compound Image](image2.png) | 3                   | 97        |
| 2     | ![Amine Image](image3.png) | ![Unsaturated Compound Image](image4.png) | 5                   | 96        |
| 3     | ![Amine Image](image5.png) | ![Unsaturated Compound Image](image6.png) | 35                  | 62        |

\textsuperscript{a}Reaction condition: amine (1 mmol), $\alpha,\beta$ unsaturated compound (1.2 mmol), and the desired amount of the catalyst were stirred under daylight at room temperature.

\textsuperscript{23,33} 3-(Diethylamino)propanenitrile. \textsuperscript{1}H NMR (400 MHz, CDCl$_3$, $\delta$): 2.67 (t), 2.40 (q), 2.30 (t), and 0.92 (t).
The values are similar to the reported literature.\textsuperscript{37} \textsuperscript{13}C NMR (400 MHz, CDCl$_3$) $\delta$: 119.6, 50.4, 47.2, 17.1 and 15.4 (Figure S1a,b). These are supported by the SciFinder results.

2.8.2. 3-(Diethylamino)2-methyl Methyl Ester. \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$: 1.19, 1.13, 2.42, 2.59, 2.84, and 3.67. \textsuperscript{13}C NMR (400 MHz, CDCl$_3$) $\delta$: 175.8, 56, 51.2, 48, 38.5, 15, and 13.4 (Figure S2a,b). The values are supported by the SciFinder results.

2.8.3. 3-(Phenylamino)propanenitrile. \textsuperscript{1}H NMR (400 MHz, CDCl$_3$) $\delta$: 2.58 (t), 3.47 (t), 6.75–6.78 (m), and 7.2–7.25 (m). These are in accordance with the reported literature.\textsuperscript{37–39} \textsuperscript{13}C NMR (400 MHz, CDCl$_3$) $\delta$: 147.7, 129.6, 117.7, 113.5, 40, and 19 (Figure S3a,b). These values are supported by the SciFinder results.

Further, recovery of the catalyst is a key factor to determine whether it has the potential for large-scale application in the industry or not. Thus, the recyclability of the catalyst was studied using the same aza-Michael addition reaction of acrylonitrile and diethylamine as a model reaction, and the results provided in the Supporting Information, Table S3. The catalyst was easily recovered by simple filtration after completion of the reaction. However, in the reported reaction by GO, the catalyst was recovered by extraction with dichloromethane from the reaction mixture.\textsuperscript{18} Thus, the aza-Michael addition reaction in the presence of the nanocomposite has an added advantage than the reported GO nanoparticle.\textsuperscript{18} It is seen from Table S3 that the yield of the product was found to be constant up to the fourth cycle during the recycling process, establishing the efficient recyclability of the catalyst.

Thus, the nanocomposite is an efficient heterogeneous catalyst for the synthesis of different amino-substituted compounds through the aza-Michael addition of $\alpha$,$\beta$ unsaturated compounds and amines. Further, it was also easily recoverable as well as recyclable with the constant catalytic activity.

3. CONCLUSIONS

The present study established a facile, green, and eco-friendly in situ fabrication method to obtain a sustainable tough WHP thermosetting nanocomposite with functionalized GO. More interestingly, this sustainable material was fabricated from biobased raw materials, and the process does not involve any additional catalyst and compatibilizing agent. Furthermore, such a facile approach provides opportunity to produce high-performing nanocomposites in a large scale. The nanocomposite exhibited significant enhancement in mechanical and thermal properties at a low nanomaterial loading. In addition, the nanocomposite showed a biodegradation behavior toward the P. aeruginosa bacterial strain. This nanocomposite can be utilized as an efficient heterogeneous catalyst for the aza-Michael addition reaction. Thus, the study stimulates new opportunities for the fabrication of waterborne polymer/graphene nanocomposites for a wide range of potential applications.

4. METHODS

4.1. Materials. Glycerol (Merck, Germany), citric acid (Merck, Germany), BD (Merck, Germany), 2,2-bis-(hydroxymethyl)propiolic acid (Sigma-Aldrich, Germany), and poly(ethylene glycol) (PEG-200, $M_n$ = 200 g/mol, Merck, Mumbai) were used after drying in a vacuum oven. Graphite flakes (60 mesh, purity 99%, Loba Chemie, India), hydrogen peroxide ($\text{H}_2\text{O}_2$, 30%, Merck, India), concentrated sulfuric acid (98%, Merck, India), TDI (Merck, Germany), potassium permanganate (KMnO$_4$, Analytical Rasayan, India), diethyamine (Merck, Mumbai), methyl methacrylate (Sigma-Aldrich) acrylonitrile (SRL, Mumbai), and poly(amide amine) hardener (Asian Paints, Mumbai, amine value 5–7 equiv/kg) were used as received. The other reagent grade chemicals were used in this study without further purification.

4.2. Functionalization of GO. Functionalization of GO consists of two steps. In the first step, GO was prepared according to the well-established Hummers method\textsuperscript{4} by the oxidation of graphite using sulfuric acid (concentrated) and KMnO$_4$. The resultant suspension of GO was centrifuged repeatedly and washed by dilute HCl solution. Further, ultrasonically, the exfoliated GO was made water-dispersible and dried in a vacuum oven. This GO was functionalized in the second step by the following method. Functionalization was done by reacting GO with a requisite amount of TDI and BD. In brief, 0.5 g of GO was dispersed in 25 mL of THF by mechanical shearing followed by sonication. The dispersed GO was placed in a three-necked flask outfitted with a Teflon septum, mechanical stirrer, and nitrogen inlet. TDI (0.82 mmol) was added dropwise into the abovementioned GO suspension at room temperature. The reaction was again continued at 70 ± 4 °C for 2–3 h to achieve the isocyanate-terminated GO. Then, BD (0.41 mmol) was added into the abovementioned mixture, and the reaction was further continued for another 1 h, which resulted in the desired functionalized GO (f-GO). The free reactants/components were separated by centrifuging and washing f-GO with THF. The obtained f-GO was dried in a vacuum oven.

4.3. Fabrication of WHP/f-GO Nanocomposites. WHP nanocomposites were fabricated using different amounts of f-GO for the first time through an in situ technique without using a compatibilizing agent and an organic solvent. The first step of this fabrication process was the reaction of citric acid and PEG-200 at 140 °C for 1 h, which resulted in the prepolymer. In the second step, the requisite amount of bis-MPA and glycerol was added to it along with the required amount of f-GO after cooling this reaction mixture to 60 °C, and then, again the reaction was carried out at 140 °C. This product can be diluted by water to the desired extent. Further, to achieve the thermosetting nanocomposite, the resultant polyester nanocomposite was mixed with hyperbranched epoxy and poly(amide amine) hardener homogeneously at room temperature in the ratio of 1:0.5:0.25 by wt. The mixture was cast on glass plates and cured at 150 °C for a specified time period. The cured films were peeled out by using warm water and used for mechanical testing after conditioning for 48 h. Three different compositions of nanocomposites were fabricated using different wt % (0.1, 0.5 and 1) f-GO by following the similar preparative protocol, and they are denoted as PEGN0.1, PEGN0.5, and PEGN1, respectively. The nanocomposite of polyester with GO (0.1 wt %) was also prepared for comparison purposes and coded as PGN0.1.

4.4. Characterization. The nanomaterials and nanocomposites were characterized by different spectroscopic techniques as used earlier for the characterization of the carbon dot-based polyester nanocomposite.\textsuperscript{24}

4.5. Biodegradation Study. A biodegradation study was performed using the McFarland turbidity method against P.
aeruginosa as the bacterial strain,40,41 and the detail method is given in the Supporting Information.

4.6. Method for the Aza-Michael Addition Reaction.

The nanocomposite was tested as a heterogeneous catalyst for the aza-Michael addition reaction (Scheme S1). A mixture of 1.2 mmol of α,β-unsaturated compound and 1 mmol of the amine substrate was stirred at room temperature in the presence of 0.0025 g of catalyst (PFGN1). The completion of the reaction was confirmed by thin-layer chromatography, and the product was extracted from the reaction mixture using ethyl acetate. The catalyst was recovered by simple filtering after completion of the first cycle. Further, to check the recyclability of the catalyst for this reaction, a set of experiments were performed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01551.

PROCEDURE FOR BIODEGRADATION, TABLES FOR PERFORMANCE OF DIFFERENT CATALYSTS IN THE AZA-MICHAEL ADDITION REACTION, FIGURES FOR 1H AND 13C NMR OF 3-(DIETHYLAMINOLPROPAENITRILE, 3-(DIETHYAMINO)2-METHYL METHYL ESTER, AND 3-(PHENYLAMINO)PROPANENITRILE, AND SCHEME FOR THE AZA-MICHAEL ADDITION REACTION (PDF)

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Notes

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