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Graphene-based nano-functional materials for surface modification of wheat straw to enhance the performance of bio-based polylactic acid composites

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ABSTRACT

To enhance wheat straw compatibility with the polylactic acid (PLA) matrix, several graphene-based materials (GBMs) derivatives, including graphene nanoplatelets, graphene oxide, and nano graphite particles with a constant fraction of 0.1 wt.-%, were employed for the surface functionalisation of wheat straw. Wheat straw surface quality was assessed by comparing PLA bio-based composites' mechanical and thermal performance with and without GBM surface functionalisation. All the resulting composites with surface functionalised straw particles exhibited higher thermal stability, flexural strength, tensile strength, and tensile toughness than those with pristine straw. This could be associated with the improved straw/PLA matrix interfacial bonding induced by the existence of GBMs on the surface of straw particles which was confirmed through morphology assessments. The mechanical properties investigations revealed maximum enhancements of 27%, 66%, and 322% for flexural strength, tensile strength, and tensile toughness, respectively, for bio-based composites consisting of graphene oxide-functionalised straw particles compared to control samples.

1. Introduction

As a result of the increased costs of petrochemical-based polymers and growing environmental concerns, there has been a surge in demand for bio-sourced degradable polymer manufacturing in recent years [1,2]. Polylactic acid (PLA), which originates from renewable crops, has already attained worldwide recognition and research interest as the most promising solution among numerous bio-sourced degradable polymers [3,4]. PLA has a wide range of applications attributable to its thermo-plasticity, good mechanical performance, biocompatibility, biodegradability, and thermal stability [5–7]. Nevertheless, this material has yet to be widely utilised commercially. This can be due to PLA's higher cost than petroleum-based rivals, which significantly hinders its commercial feasibility [8]. Lignocellulosic-based materials, e.g., jute strands, wheat straws, and rice husks, have been found to be a feasible, low-cost, and eco-friendly substitute for PLA matrix, lowering the total price of bio-based composites [3,9]. These items are currently classified as waste agricultural materials [10]. Allowing these waste products to be combusted as a means of disposal, whether in farmlands or as household fuel, may jeopardise the environment [11].

The authors' previous research has confirmed the potential of employing wheat straws to partially replace the PLA polymer matrix. This renewable biomass comprises various chemical elements, some of which (e.g., inorganic silica, extractives, and waxy cuticle layers) are considered highly hydrophobic substances [12–14]. The presence of such hydrophobic components on the surface of wheat straw particles leads to impeding the wheat straw/polymer binder interface bonding. Chemical pre-treatment, eco-friendly physical pre-treatment and surface modifications are required to improve the straw/PLA bonding quality, hence enhancing the mechanical properties of bio-based composites [3,9]. However, when sustainability factors are considered, chemical pre-treatments would have fewer favourable environmental effects than physical pre-treatments. It is reported that despite the fact that chemical pre-treatments significantly alter the structure of biomass, they are not economically viable, and the required chemicals (e.g., alkaline chemicals) are hazardous to handle on large scale [15]. In addition

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to pre-treatment methods, a variety of coupling agents, including graphene nanoplatelets [3], attapulgite clay [3], maleic anhydride [16], silane [17], and polydopamine [18], have been utilised to enhance the interface compatibility between cellulosic biomass and polymer matrices. In order to link with polymer matrices, the mechanism is generated by a reaction between hydroxyl groups at one end, and natural fibre surface and another functional group at the other end [9,19].

In this study, the wheat stem's internodes were subjected to a physical pre-treatment (H + S) to modify the surface chemical functional groups and reduce the hydrophobic components, such as waxes and extractives. Based on the authors' previous studies, the H + S pre-treatment minimises undesirable chemical content, making a suitable substrate for nano surface functionalisation. The aim of this work is to strengthen the interfacial bonding of the straw/PLA matrix by functionalising the surface of the pre-treated straw particles using 0.1 wt.-% graphene-based materials (GBMs). The originality of this study offers the possibility of using extra-low-dosage 2D graphene-based materials as crosslinking agents to enhance the mechanical and physical properties of straw/PLA. For this aim, first, the attachment of functionalising agents to the straw surface is confirmed using morphology assessment, and then, the performance of bio-based composites with 20 vol.-% wheat straw replacement, before and after functionalisation, is evaluated in terms of flexural strength, tensile strength, tensile toughness, and thermal and dimentional stability. In this study, graphene-based nanoparticles were only used to functionalise the surfaces of H + S pre-treated straws, as the author's previous study confirmed the superiority of the graphene surface functionalisation system on the H + S pre-treated straws over their non-functionalised counterparts [3]. To the best of the authors' knowledge, no studies have investigated various derivatives of graphene-based materials as a surface functionalisation agent in the production of wheat straw bio-based composites.

2. Material and methods

2.1. Materials

The polylactic acid (PLA) (Tecnaro GmbH, Germany) was used as the binder matrix. Wheat straw (*Triticum aestivum* L.) harvested in the summer of 2021 was provided from a residential farm in Middlesex, United Kingdom. The straw used in this study is comprised of leaves (15%), internodes (61%), nodes (10%), rachis (5%), and chaffs (9%) by mass, which results in inconsistent chemical distribution. The author's earlier research has detailed the chemical composition of each component [20]. Three categories of graphene-based materials (GBMs), including Graphene nanoplatelets (G), Graphene oxide (GO), and Nano Graphite (nG), have been provided by Nanesa, Italy, to serve as surface modifying agents. Water suspension GO was used, with the GO content being 4 g/l, while G and nG particles were employed in powder form. The characteristics of GBM and their morphology appearances are presented in Table 1 and Fig. 1, respectively. Previous works by authors provide detailed information on the characteristics of GBMs used in this study [21–23].

2.2. Pre-treatment and surface functionalisation

Based on the authors' previous studies [9,24], the internode sections of the wheat straw stems were shredded by means of a Retsch SM 100 cutting mill (size range of 65–2000 μm) and subjected to an eco-friendly pre-treatment (H + S) combining hot water (H) and steaming (S). Pre-treated straw particles were then loaded into the pre-dispersed 0.1 wt.-% GBM aqueous solutions to perform the surface functionalising process. The authors' previous studies [3,24] and other research conducted by Scaffaro et al. (2020) [25] confirmed the 0.1 wt% GBM dosage as the optimal GBM concentration for efficient surface functionalisation. A hot plate and magnetic stirrer were used to mix the straw particles with the GBM solutions at 80 °C until a semi-dried mixture was obtained. Finally, semi-dried straw particles were oven-dried for 24 h at 100 °C. This provides GBM particles' attachment to the outer surface of the H + S straw particles. The microstructure comparison of straw particles before and after GBM surface functionalisation is depicted in Fig. 2, which confirms the successful attachment of GBM particles to the outer surface of the pre-treated straws.

2.3. Sample preparation

PLA polymer pellets (80 vol.-%) and H + S wheat straw particles (20 vol.-%), with and without GBM surface functionalisation, were first dry-mixed and pre-heated at 180 °C for 15 min using a hot-air oven. Thereupon, the pre-heated PLA/straw compositions were placed in a steel mould of 20 mm × 100 mm × 100 mm and subjected to a constant pressure of 10 MPa for 20 min at 180 °C employing a hot-press device. Five 20 mm × 10 mm × 100 mm strips were cut to be used for tensile and flexural experiments. Fig. 3 presents the mix composition and testing procedure used in this research.

2.4. Experimental tests

The tensile and flexural strengths were performed for each composition according to the ASTM D3039/D3039 M standard using an Instron 5969 universal testing machine with a load rate of 1 mm/min. The integration of the area under the stress-strain curve was used to evaluate tensile toughness.

The surface morphological variation of wheat straw particles following GBM surface functionalisation was investigated using Scanning Electron Microscopy (SEM). Moreover, each composition's PLA/straw interfacial bonding was assessed by employing fractured portions of specimens (about ~10 mm^3) in the tensile test. All the pieces were gold-coated before analysing them on the SEM to provide a satisfactory electrical conductivity. For every morphological investigation, a minimum of 10 areas were snapped to ensure reliable conclusions.

The straw PLA composites' dimension stability was assessed following BS 5669-1:1989. This included thickness swelling (TS) and water absorption (WA) tests. A batch of six samples of size 100 × 20 × 20 mm^3 were analysed for each composition. The samples were immersed in water (20 ± 2 °C) for the WA test. Using a digital scale with a 0.01 g accuracy, the weight of each sample was

Table 1
Characteristics of graphene-based materials. (*) measured by BET for dry powders, and (**) estimated value considering that GO in water solution showed about 95% monolayer. (courtesy of Nanesa srl).

Agent	Carbon content	Average lateral size	Thickness (nm)	SSA (m^2/g)	Physical state
G	>97 (C:O = 49:1)	D50: 42 μm	8	56*	Powder
GO	49-56 (C:O = 1.660)	D50: 5 μm	1	30*, 2,200**	Colloidal liquid suspension 4 g/l
nG	>97.5	D50: 3.4 μm	6–7	26*	Powder

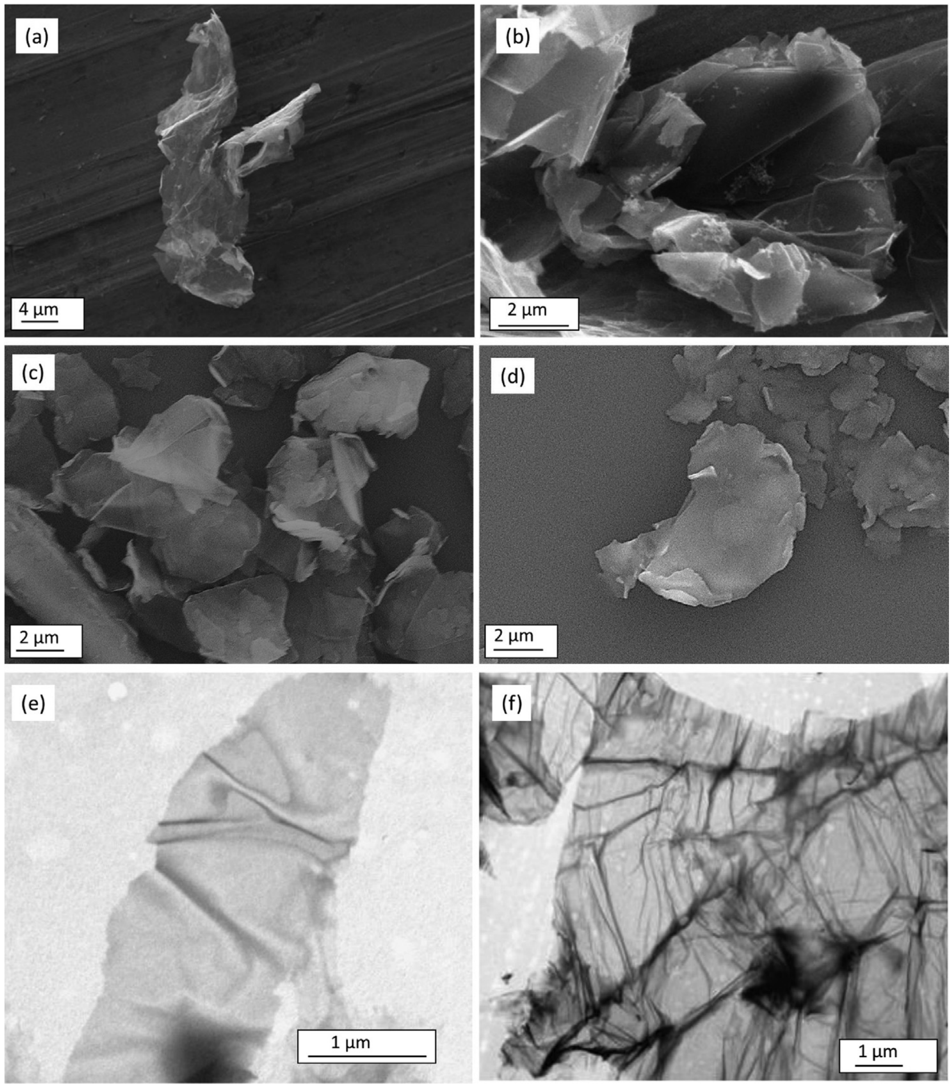

Fig. 1. SEM Images of (a and b) Graphene, (c and d) nano graphite, and (d and e) TEM micrograph of graphene oxide nanoparticles. (courtesy of Nanesa srl).

determined after exposure to water for 1, 2, 3, 4, 5, 6, 12, and 24 h. The percentages of water absorption were calculated using Eq. (1). For the TS test, the samples were submerged in water for 3 h and 24 h. The thickness of each sample was precisely measured using a digital calliper with a 0.001 mm accuracy. The TS % was determined via the formula Eq. (2).

$$WA\ (\%) = \left[\frac{M_2 - M_1}{M1}\right] \times 100 \quad (1)$$

where: WA is water absorption (%), M_1 (g) and M_2 (g) are the weights of samples before and after water immersion, respectively.

$$TS\ (\%) = \left[\frac{T_2 - T_1}{T1}\right] \times 100 \quad (2)$$

where: TS is water absorption (%), T_1 (g) and T_2 (g) are the weights of samples before and after water immersion, respectively.

The Thermogravimetric analysis (TGA) test was performed employing an SDT Q600 V8.3 Build 101 (TA instrument). Samples were heated, ranging between 25 °C and 600 °C with a heating rate of 10 °C/min in a nitrogen atmosphere. As suggested by several studies [8,26], the temperature at 10% weight loss (T_{10}) and the temperature at 50% weight loss (T_{50}) were considered to compare the degradation characteristics (i.e., thermal stability) of bio-based composites.

3. Results and discussion

3.1. Mechanical properties and microstructure analysis

The mechanical performances, including flexural strength, tensile strength, and tensile toughness of bio-based composites comprised of H + S straw particles with and without GMB surface modifications, have been reported in Fig. 4(a and b). The flexural strength results (Fig. 4-a) indicate that all three composite samples containing functionalised straw particles have outperformed the control sample. The flexural strength of GMB-modified samples increased from 40.2 MPa for control samples to 51.2 MPa, 51.4 MPa, and 47.6 MPa for G, GO, and nG samples, respectively. Fig. 4-b shows that GBM surface modifications resulted in considerable tensile strength enhancements of 47%, 66%, and 52% for G, GO, and nG samples, respectively, compared to the control sample. The graphene oxide surface modifications exhibited the maximum tensile performance at the fracture point, with a maximum value of

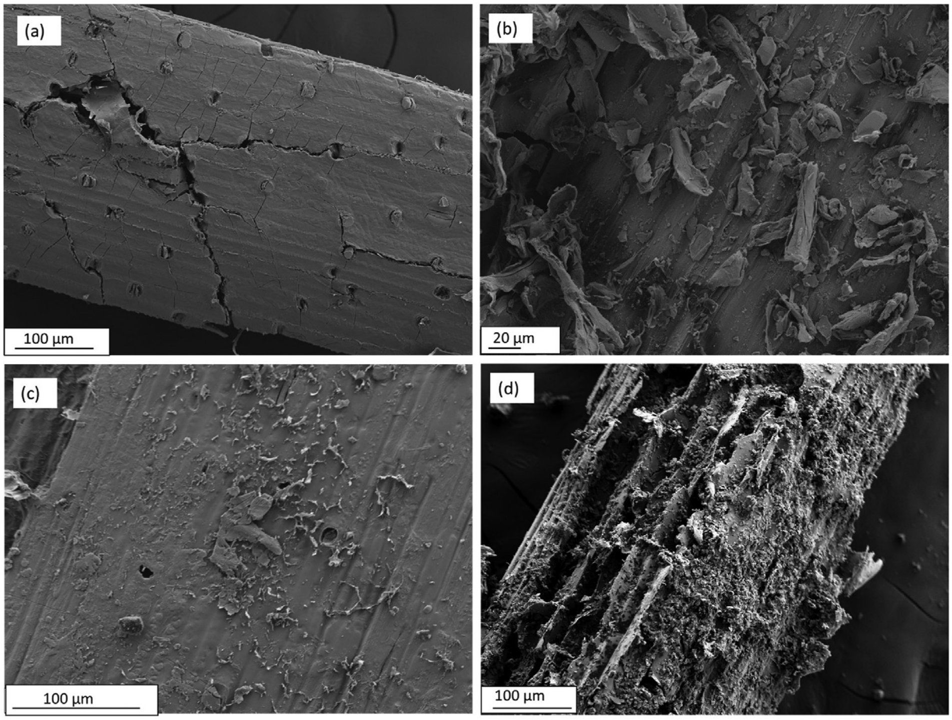

Fig. 2. (a) Control sample, (b) Graphene modification, (c) nano graphite modification, (d) graphene oxide modification.

18 MPa compared to the control sample's 11 MPa tensile strength. The results (see Fig. 4-b) imply that GBMs could also serve as toughening agents in bio-based composites, enhancing fracture toughness and tensile ductility. All composites containing GBM-modified straw particles provide a considerably higher toughness, i.e., 5.2 MJ m^3 for G, 3.8 MJ m^3 for GO, and 2.4 MJ m^3 for nG, than composites containing non-functionalised straw (i.e., 0.9 MJ m^3). Compared to the control sample, the composite incorporating graphene functionalised straw (i.e., G) achieved a maximum toughness improvement of 468%. The findings of this study are supported by a study conducted by Scaffaro et al. (2020), where a substantial increase in the composites' physical properties was found after functionalising PLA particles with graphene nano-platelets, leading to a 22% increase in the tensile strength in comparison with control samples [25].

The SEM images of control samples and surface-modified composites are presented in Fig. 5(a–d). The effects of nano-functional materials and their role on improved straw particles/PLA matrix

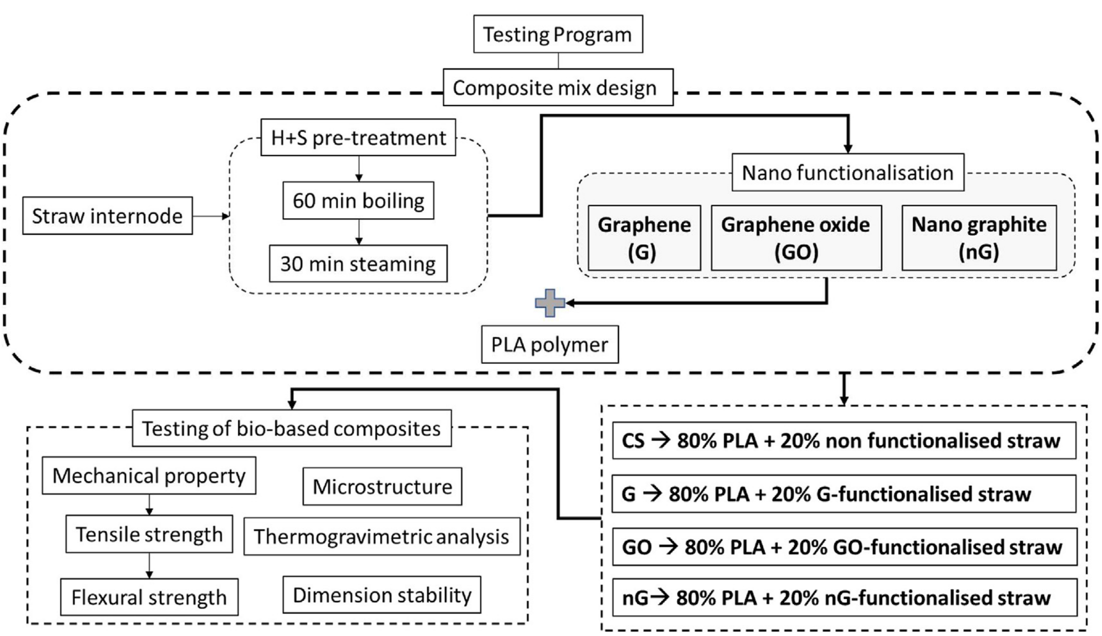

Fig. 3. Experimental framework and the testing program.

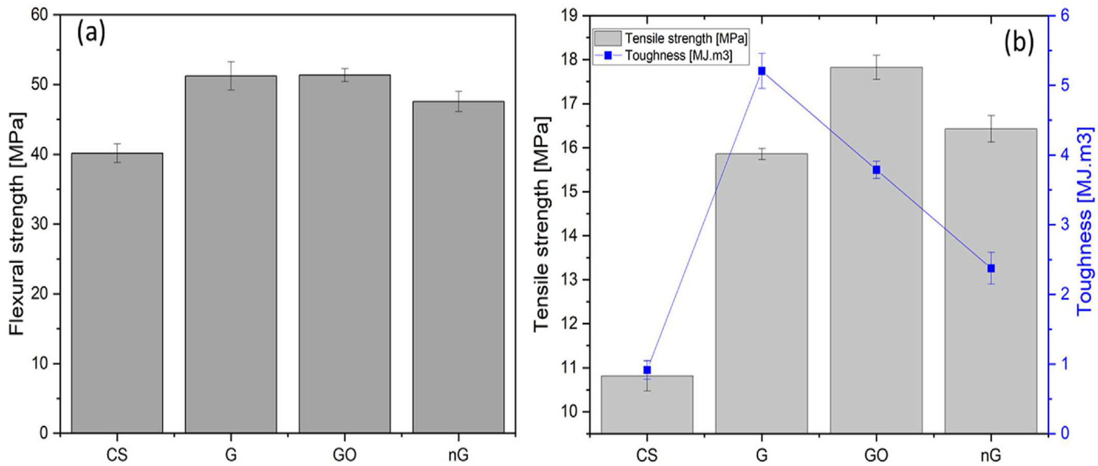

Fig. 4. Mechanical performance of bio-based composites, (a) flexural strength, and (b) tensile strength and tensile toughness.

interfacial adhesion can be observed in these images. Consequently, the mechanical properties are enhanced in bio-based composites. The involvement of all GBM nanoparticles, including graphene, graphene oxide, and nano graphite, on the surface of H + S straw, offers a crosslinking effect, providing a functionalised straw particles-PLA matrix connection, thereby strengthening interfacial adhesion. This phenomenon has been confirmed in previous investigations conducted by the authors and other researchers [24,25]. Fig. 5 (a) exhibits a distinct separation gap within the PLA/straw interface, referred to as delamination. The existence of such delamination in a bio-based composite implies poor mechanical performance, which is caused by fibre pull-out resulting in composite structure failure under applied load. However, the promising contribution of GBM's surface functionalisation process in minimising the delamination phenomenon is obvious in Fig. 5 (b-d). In addition, as seen in Fig. 1, GBM particles are distinguished by their unique morphology, which results from the exfoliation of expanded graphite flakes. Isolated GBMs exhibit typical surface wrinkles and fringed shapes. Due to the distinct wrinkled topography of GBMs, the hypothesis in the mechanical property enhancement is linked to surface wrinkles, which can promote mechanical interlocking in straw/PLA matrix interface. It has been determined that a small amount of graphene-based modifying agents (0.1 wt.-%) can substantially improve the mechanical performance of straw-PLA bio-based composites. However, it has been reported that using too many functionalising agents can compromise the technique's efficiency [8]. Commercial strawboard production employs various matrices, including urea- and phenol-formaldehyde (UF) and phenol-formaldehyde (PF). Due to the hydrophobic nature of straw, these matrices develop a poor bonding quality between straw

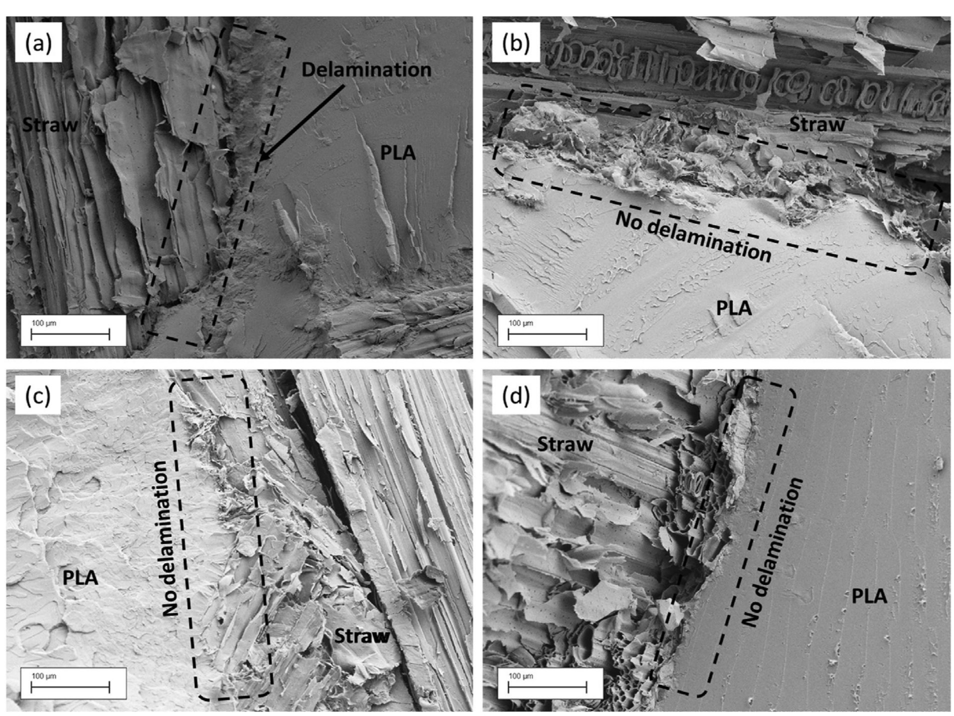

Fig. 5. (a) Control sample, (b) Graphene modification, (c) graphene oxide modification, (d) nano graphite modification.

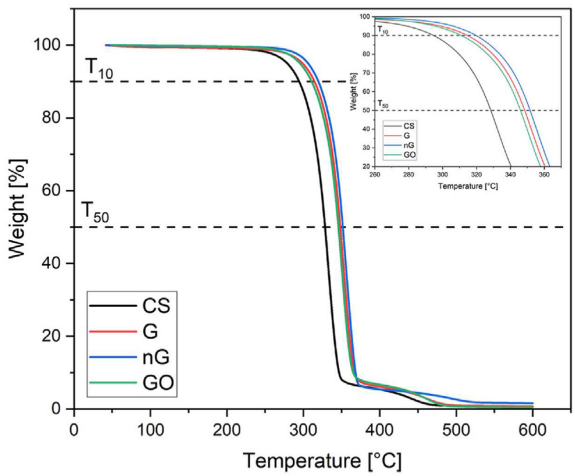

Fig. 6. Thermogravimetry analysis of bio-based composites incorporating H + S pre-treated wheat straw with and without GBM surface functionalisation.

particles. Strawboards bound with UF reportedly have an average tensile strength of approximately 6.3 MPa [27]. The developed strawboards in this study are able to compete with the available commercial products. Several investigations have obtained tensile strengths that are higher than this work. Although, their manufacturing processes (i.e., injection moulding) and preparation techniques (i.e., compounding) are highly energy-intensive and impractical for mass-producing strawboards.

3.2. Thermal and dimentional stability assessments

A direct correlation between thermal stability and degradation temperature of bio-based composites following weight loss of 10% (T_{10}) and 50% (T_{50}) has been reported in several studies [8,28]. This implies that a higher degradation temperature points to an improved composite's thermal stability [29,30]. At a weight loss of 10% (T_{10}), the decomposition temperature for the control sample (i.e., H + S pre-treated straw) was 294 °C, which was relatively lower (by up to 9%) than those of composites loaded with GBM surface functionalised straw particles (see Fig. 6). The temperature of decomposition of composites at % weight loss T_{50} followed the same trend, increasing from 328 °C for the control sample to 348 °C, 346 °C, and 352 °C for G, GO, and nG composites, respectively. A slight improvement in the composite's thermal stability can be associated with the presence of GBM particles with large specific surface areas in the bio-based composites. These particles provide a layered structure that serves as a shielding barrier resulting in increased thermal stability [31].

As seen in Fig. 7, the dimensional stability of bio-based composites with and without GBMs was evaluated using the thickness swelling (TS) test as well as the water absorption (WA) test. The results revealed that all bio-based composites, both with and without GBMs, exhibited increased water absorption and thickness swelling with time. The WA results revealed that the water infusion of bio-based composites containing GBM-functionalised straw particles was considerably lower than that of the control sample (i.e., bio-based composites containing non-functionalised straw particles) at all immersion intervals. The same trend is observed for the TS of bio-based composites in which the thichness sweilling of bio-based composites after 24 h of water exposure decreased from 0.67% for the control sample to 0.10%, 0.18%, and 0.31% for the G, nG, and GO samples, respectively (see Fig. 7b). These effects could be attributed 1) superior interfacial interaction between surface functionalised straw particles and PLA matrix, which leads to a denser microstructure, improving the dimensional stability of strawboards [3]. 2) the increased hydrophobicity of straw strands after GBM surface functionalisation. All the GBMs employed in this study are considered hydrophobic [21,22,32], preventing water uptake and increasing the dimensional stability of resulting bio-based composites. It should be noted that among all the bio-based composites containing GBM-modified straws, samples containing GO particles exhibited the highest TS and WA values. As reported in the author's previous research [32], both hydrophilic and hydrophobic functional groups were observed on the GO particles providing them an amphiphilic property. Amphiphilic properties imply edge-to-center distribution of hydrophilic and hydrophobic domains [15]. Therefore, hydrophilic functional groups on GO particles can allow more water to penetrate than other GBMs, resulting in increased water absorption and thickness swelling. Following the H + S pre-treatment of straw particles, (i) a reduction in the concentration of hydrophobic chemical functional groups, i.e., wax and silica, from the straw surface occurs [3], and (ii) partial hemicellulose and lignin degradation increase the surface porosity of straw particles, leading to easier water molecules penetration into compressed strawboards [33]. Therefore, Incorporating graphene-based crosslinking agents is crucial for

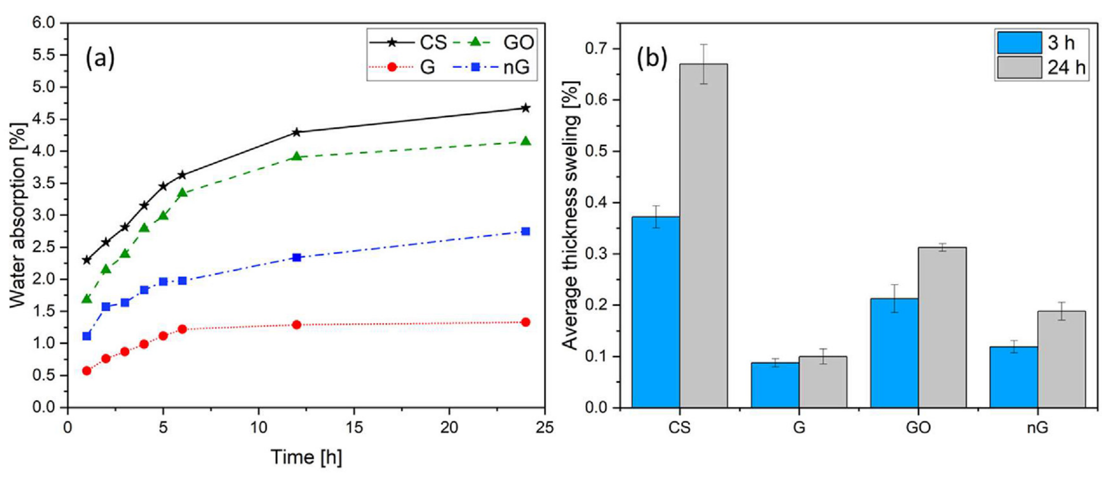

Fig. 7. Dimentional stability of bio-based composites with and without GBM surface functionalised H + S pre-treated wheat straw (a) water absorption and (b) average thickness swelling.

controlling bio-based composites' water absorption and dimensional stability.

4. Conclusions

Efficient pretreatments for the extraction, separation and fractionation of wheat straw in conjunction with understanding its microstructure and properties can be crucial for high-efficiency biorefinery process [34]. In this study, wheat straw surface was modified employing a combination of H + S pre-treatment and surface functionalisation using 0.1 wt% GBM derivatives, such as graphene nanoplatelets, graphene oxide, and nano graphite particles. Bio-based composites comprised of 80% PLA polymer and 20% pre-treated wheat straw particles, with and without surface functionalisation, were manufactured. The influence of GBM modifying agents on the straw/matrix interfacial bound quality and, as a result, thermal stability and mechanical performance (i.e., tensile and flexural characteristics) of the produced bio-based composites were investigated. The outcomes of this study have verified that.

- Using GBM modifying agents results in an improved straw/matrix adhesion quality which leads to enhanced thermal stability and mechanical efficancy. The bio-based composite's microstructure confirmed improved interfacial bonding quality between functionalised straw and PLA matrix.
- Composites made of GO-modified straw particles indicated optimum flexural strength, tensile strength, and tensile toughness of about 27%, 66%, and 322%, respectively, compared to the control sample (i.e., bio-based composites containing non-functionalised wheat straw).
- nG-modified composites exhibited the maximum thermal stability of 9% for T_{10} and 7% for T_{50}, higher than the corresponding values registered for the control samples.
- The results from both water absorption and thickness swaling tests show that GMB-modified bio-based composites maintain their dimensional stability. Following a 24-h immersion in water, samples containing G-modified straws exhibited the highest reductions in water absorption and thickness swelling by 72% and 85%, respectively.

Credit authorship contribution statement

Mehdi Chougan: Data curation, Methodology; Validation, Investigation, Writing - Original Draft, Visualization.
Seyed Hamidreza Ghaffar: Conceptualization, Methodology, Supervision, Writing - review & editing, Resources, Writing - Original Draft, Visualization, Supervision, Funding acquisition.
Mazen J Al-Kheetan: Writing - Review & Editing, Validation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Seyed Hamidreza Ghaffar reports financial support was provided by Engineering and Physical Sciences Research Council.

Data availability

Data will be made available on request.

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