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Effect of Maleated Compatibilizer on the Mechanical Properties of PLA/Mustard Waste Biocomposites

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Natural fiber polymer composites of biodegradable poly(lactic acid) (PLA) and mustard waste were fabricated with the addition of various amounts (0.25-2.00 wt.%) of maleic anhydride grafted PLA (PLA-*g*-MA), which was used as a coupling agent to improve interfacial adhesion between the components and thereby enhance the mechanical features of the biocomposite. PLA-*g*-MA was synthesized in-house by reactive melt grafting using dicumyl peroxide as a free grafting initiator. Preparation of the biocomposite samples was carried out using a twin screw extruder and an injection molding machine. The effect of PLA-*g*-MA concentration on the samples' mechanical traits and surface hardness was investigated. Mechanical properties were determined using uniaxial tensile tests, flexural tests, and Charpy impact tests; additionally, the surface hardness was tested with a Shore D indenter. The tensile tests revealed that even the lowest amount (0.25 wt.%) of PLA-*g*-MA was sufficient to effectively improve the interfacial adhesion between PLA and mustard waste, as manifested in an increased tensile strength (34 to 39 MPa). Similarly, the flexural and the Charpy impact strength also exceeded that of neat PLA/mustard waste biocomposite by 31 % and 45 %, respectively. The addition of compatibilizer in higher concentrations than 0.25 wt.% did not improve the mechanical properties further, ascribed to the excess PLA-*g*-MA plasticizing the composite. Based on Shore D testing, the compatibilization did not affect the surface hardness of the biocomposites significantly.

1. Introduction

Over the past century, there has been a dramatic increase in the production of plastic-based goods owing to their versatility, low weight, beneficial mechanical properties, and outstanding water resistance. In 2022, the annual production of plastics exceeded 400 million tons (Kabeyi et al., 2023). Considering the fact that approximately half of that ends up as plastic waste (Chai et al., 2022), the "white pollution" caused by these materials has become a major issue in recent years (Lendvai et al., 2024). Society has been striving to overcome this problem for decades, which has greatly facilitated research in the corresponding field over the past few decades (Lendvai et al., 2017).

Consequently, there is a growing interest in using green alternatives to substitute synthetic and petroleum-based materials (Peidayesh et al., 2021). Among the commercially available bioplastics, poly(lactic acid) (PLA) is the most diffused. It is a thermoplastic polyester derived from renewable resources and is, in many respects, superior to commodity plastics. For instance, PLA has a strength of ~50 MPa, which is considerably higher than that of polypropylene (25-35 MPa), and its Young's modulus (2.5-3.5 GPa) is similar to that of poly(ethylene terephthalate). Besides being derived from green sources, it is also biodegradable and biocompatible, serving as an excellent material for medical implants. Furthermore, PLA's crystallinity can be controlled on a wide scale by choosing appropriate cooling rates when cooled down from its molten state. Solidifying it in an amorphous structure, it can exhibit excellent optical transparency. On the other hand, PLA has major drawbacks, such as brittleness, low thermal stability, and high production costs (Patti et al., 2023). To mitigate these disadvantages, extensive research and development have been carried out, most of which address the issue by combining PLA with other polymers or various fillers and reinforcements. Among the studies dealing with the property-tailoring of PLA by combining it with different additives, the ones investigating the potential of vegetable-based natural fillers are of great significance (Wang et al., 2016). Mustard seed waste, the solid residue of mustard after oil

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extraction, might also serve as an excellent low-cost filler in biopolymers, as suggested by Rani et al. (2023). Natural filler-containing polymer composites (NFPCs) have significant potential to promote the development of the circular economy, especially if the fibers are embedded into a renewable polymer, such as PLA (Singh et al., 2022). This way, entirely compostable materials can be achieved for products that pose little to no threat to the environment after their useful lifecycle. It is important to note, however, that the mechanical traits of natural fiber–reinforced polymer composites are greatly dependent on the interfacial adhesion between components, i.e., the polymer matrix and the natural fiber (Ponnusamy et al., 2023). Most polymers, including PLA, tend to have a hydrophobic nature due to their non-polar molecules. In contrast, lignocellulosic fibers are highly polar, ultimately leading to poor mechanical load transfer capacity between the matrix and the reinforcement in such composites. Thus far, the literature has reported several procedures intended to overcome the issues related to the limited interfacial interactions in NFPCs (Väisänen et al., 2016). The various treatments applied to improve the adhesion between the polymer and natural particles are usually classified into two groups: surface modification of the bio-fillers and compatibilization through the addition of a coupling agent.

Fang et al. (2022) investigated bamboo fiber as a potential filler for PLA. The authors fabricated biocomposites with a 3:7 (filler:matrix) mass ratio. Bamboo fibers were treated with a mixture of choline chloride and oxalic acid. The result showed that as a consequence of surface treatment, the tensile strength of the composite increased from 43.9 MPa to 75.6 MPa. The enhancement in mechanical strength was further supported by an improvement of flexural strength, which was 35.3 MPa for the composite containing untreated fiber, while it was 46.9 MPa for the one fabricated with surface-treated fibers. A slight improvement in stiffness was also reported, with the Young's modulus growing from 757.3 MPa to 806.9 MPa.

Tham et al. (2022) fabricated bamboo and jute fabric (30 wt.%) reinforced polymer composites with PLA as the matrix material. The authors analyzed the effect of maleic anhydride grafted PLA (PLA-*g*-MA) as a coupling agent in the range of 0-10 wt.%. Adding 3-5 wt.% enhanced the interfacial adhesion between the components, which was manifested in lower water absorption, higher glass transition temperature, and crystallinity, as well as higher strength, modulus, and impact toughness. However, further addition of PLA-*g*-MA led to adverse effects, which were attributed to excess PLA-*g*-MA acting as a plasticizer.

Currently, the applicability of mustard seed waste as a filler for biodegradable polymers is an underexplored area. Therefore, the main objective of this present study is to develop mustard waste-filled PLA composites and analyze the effect of the amount of coupling agent. For this purpose, PLA-*g*-MA was synthesized through reactive melt blending and then added in concentrations of 0.25, 0.5, 1, and 2 wt.% to PLA/mustard waste composites with a bio-filler content of 10 wt.%. The resulting biocomposites were characterized by their mechanical properties (tensile, flexural, and impact) and hardness.

2. Materials and methods

2.1 Materials

PLA Ingeo 2003D, obtained from NatureWorks (Minnetonka, MN, USA), with a D-isomer content of 4 %, a density of 1.24 g/cm^3, and a melt flow rate of 6 g/10min (210 °C, 2.16 kg) was used as the polymer matrix. The mustard seed waste, with a size of <70 mesh, used as filler, was collected from local farmers in Dehlwin village (Himachal Pradesh, India). Dicumyl peroxide (DCP) and maleic anhydride (MA), used for the grafting process, were purchased from Merck (Budapest, Hungary).

2.2 Synthesis of maleic anhydride grafted PLA

PLA-*g*-MA was synthesized through melt grafting, carried out using a Brabender Plastograph PLE331 internal mixer (Duisburg, Germany) equipped with a 50 cm^3 chamber. The synthesis was performed following the reactive maleation route described by Phetwarotai et al. (2021). The kneading chamber was heated to 170 °C, and the rotor speed was set to 60 1/min. In the first step, PLA was added into the mixer and maintained until melting, which took approximately 1 min. This was followed by the addition of DCP (at a concentration of 0.6 wt.%), which acted as a free radical initiator. After 1 min, MA was added at a content of 3 wt.%, and kneading continued for another 4 min to obtain PLA-*g*-MA. Before further use, the resulting material was ground into particles of approximately 4 mm using a plastic shredder.

2.3 Composite fabrication

Prior to melt compounding, PLA, PLA-*g*-MA, and the mustard waste were oven-dried at 80 °C for 4 h to remove any moisture in the components. Melt mixing of the biocomposites was performed using a Labtech LTE 20-44 co-rotating twin-screw extruder (Samutprakarn, Thailand) with a 44 L/D ratio and a 20 mm diameter screw. The extruder was operated with a temperature profile of 155-185 °C from the feeder to the die. The extrudates were pelletized with a Labtech LZ120 grinder (Samutprakarn, Thailand). The designation and the composition of the

compounded biocomposites are summarized in Table 1. Before further processing, the pellets were oven-dried once more at 80 °C for 4 h.
The granulates were then injection molded into suitable specimens using an Arburg Allrounder 420C injection molding machine (Lossburg, Germany) equipped with a 35 mm diameter screw. The injection molding conditions used were: injection temperature: 195 °C; injection rate: 40 cm^3/s; holding pressure profile: 750-650-250 bar (15 sec); cooling time: 60 sec; and mold temperature: 30 °C.

Table 1: Designation and composition of the prepared PLA-based biocomposites

Sample designation	PLA [wt.%]	PLA-*g*-MA [wt.%]	Mustard waste [wt.%]
PLA_10M	90.00	-	10.00
PLA_10M_0.25MA	89.75	0.25	10.00
PLA_10M_0.5MA	88.50	0.50	10.00
PLA_10M_1MA	89.00	1.00	10.00
PLA_10M_2MA	88.00	2.00	10.00

2.4 Characterization

Tensile and flexural properties were measured using an Instron 3382 universal testing machine (Norwood, MA, USA) equipped with a 10 kN sensor, according to ISO standards 527 and 178, respectively. The crosshead speed was 5 mm/min for both tests. For the tensile test, specimens conforming to the ISO 527-2 standard's 1A geometry were used, with an initial gauge length of 100 mm. For the 3-point bending test, rectangular specimens measuring 10×4×80 mm were applied, with a span length between the supports set to 64 mm. The average values and standard deviations were calculated from the results of five consecutive measurements.
Charpy impact strengths of the composites were determined using a Ceast 6545 impact tester (Torino, Italy), following the ISO 179 standard. Unnotched specimens measuring 10×4×80 mm were used, with a span length of 62 mm, and a 2 J pendulum was employed to impact the samples. The average values and standard deviations were calculated from the results of five consecutive measurements.
The Shore D hardness of the samples was measured with a Sauter HDD 100-1 (Balingen, Germany) digital hardness tester, following the ISO 868 standard. The average values and standard deviations of hardness were calculated from the results of seven consecutive measurements.
The obtained results were evaluated using the one-way analysis of variance (ANOVA) method, followed by Tukey HSD post hoc tests at a significance level of 5 % ($p < 0.05$).

3. Results and discussion

3.1 Tensile mechanical properties

The tensile mechanical properties of any engineering materials are of critical importance, as the derived data allows the understanding of how the material behaves under uniaxial mechanical loads. Figure 1 shows the tensile strength and Young's modulus of PLA/mustard waste biocomposites filled with various amounts of PLA-*g*-MA. The PLA/mustard waste biocomposite exhibited a tensile strength of 34±2 MPa, which is considerably lower than what has been reported for neat PLA in the literature (~50 MPa) (Juhász et al., 2024). In filler-containing composites, the failure mechanism is more complex than in unfilled polymers due to the role played by the filler-matrix interface when exposed to mechanical loads. Stress concentration sites form around the filler particles, leading to earlier failure when exposed to mechanical stresses. Meanwhile, the strength was observed to grow with the addition of 0.25 wt.% compatibilizer to 39±1 MPa, which was relatively 14 % higher than that of the non-compatibilized composite. Further increasing the amount of PLA-*g*-MA still enabled some improvement in tensile strength; however, according to the statistical tests, the changes were not significant. For samples PLA_10M_0.5MA, PLA_10M_1MA, and PLA_10M_2MA, the tensile strength values varied within the small range of 39-40 MPa. Based on the literature (Tham et al., 2022), it can be assumed that above a certain concentration of PLA-*g*-MA, there is an excess uncoupled portion, which acts more as a plasticizer rather than improving adhesion any further. The stiffness of the samples was not affected by the presence of PLA-*g*-MA, as Young's modulus values of all biocomposites were within the deviation range. Even between the samples with the lowest (2.61 GPa) and highest (2.67 GPa) modulus (samples PLA_10M_0.25MA and PLA_10M, respectively), the difference was insignificant. The reason for the modulus not increasing along with the tensile strength is that this property is more dependent on the individual traits of the components rather than the strength of interactions between them. Accordingly, the enhanced adhesion achieved by the compatibilizer was not expected to affect the modulus.

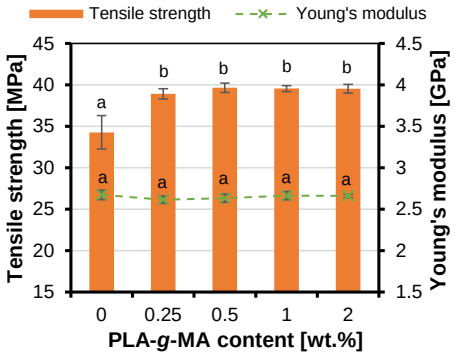

Figure 1: Tensile strength and Young's modulus of PLA/mustard seed waste biocomposites as a function of PLA-g-MA content. Identical letters at the data points indicate no significant difference according to the ANOVA and Tukey HSD test

3.2 Flexural mechanical properties

Figure 2 presents the flexural mechanical properties, i.e., flexural strength and flexural modulus, of the prepared composites. Similar to tensile strength, flexural strength values of the compatibilized samples were also superior compared to neat PLA/mustard waste (PLA_10M – 53±1 MPa). Again, the addition of small amounts (0.25-0.5 wt.%) of PLA-*g*-MA enhanced the strength, which peaked at 73±2 MPa for sample PLA_10M_0.5MA. Increasing its concentration beyond that value did not further improve the flexural strength. The flexural modulus of the composites as a function of PLA-*g*-MA content also followed the trend determined for the tensile properties, namely a consistent modulus within a small deviation range (between 3.61 and 3.68 GPa in this case). Chauhan et al. (2021) investigated the effect of PLA-*g*-MA on the flexural properties of PLA/starch composites. The authors found similar changes in flexural mechanical properties, i.e., ~90 % higher flexural strength and an unaltered modulus.

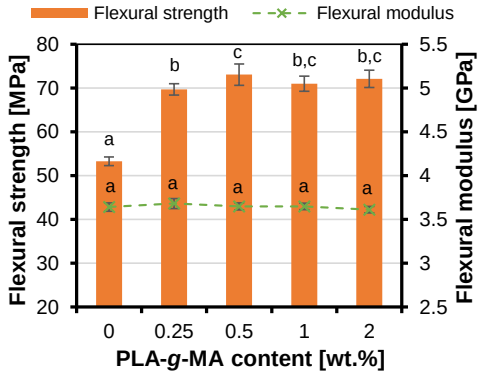

Figure 2: Flexural strength and flexural modulus of PLA/mustard waste biocomposites as a function of PLA-g-MA content. Identical letters at the data points indicate no significant difference according to the ANOVA and Tukey HSD test

3.3 Impact toughness

Impact tests allow the assessment of the toughness of engineering materials, which provides important data on their behavior when subjected to sudden forces. The effect of the compatibilizer loading on the Charpy impact strength of the PLA/mustard waste composites is graphically shown in Figure 3. The results clearly indicate that the addition of PLA-*g*-MA caused an improvement in impact toughness. The unnotched impact strength of the PLA_10M composite increased from 3.96±0.25 kJ/m^2 to 5.76±0.54 kJ/m^2 when 0.25 wt.% coupling agent was added, which represents a relative improvement of 45 %. Increasing the amount of PLA-*g*-MA to a higher level did not result in any significant enhancement in toughness according to statistical analysis, although the highest impact strength was determined for composite PLA_10M_1MA (6.21±0.65 kJ/m^2). Similar observations were reported in the literature by Panthapulakkal and Sain (2006), who found increasing impact toughness for natural filler (wheat straw) containing polymer composites when paired with a malleated compatibilizer.

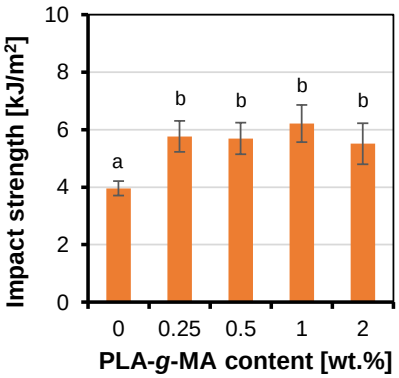

Figure 3: Charpy impact strength of PLA/mustard waste biocomposites as a function of PLA-g-MA content. Identical letters at the data points indicate no significant difference according to the ANOVA and Tukey HSD test

3.4 Hardness

Hardness is an important property of polymers, and their composites since the wear and scratch resistance of the material greatly depend on it. The effect of PLA-*g*-MA on the Shore D hardness of the PLA/mustard waste composite is shown in Figure 4. The hardness of PLA_10M was determined to be 83.4, and it was in the small range of 83.0-83.5 for all samples, with all the composite alternatives falling within the deviation range. Consequently, it can be concluded that the presence of 0-2 wt.% malleated compatibilizer does not induce considerable change in the Shore D hardness of PLA/mustard waste composites.

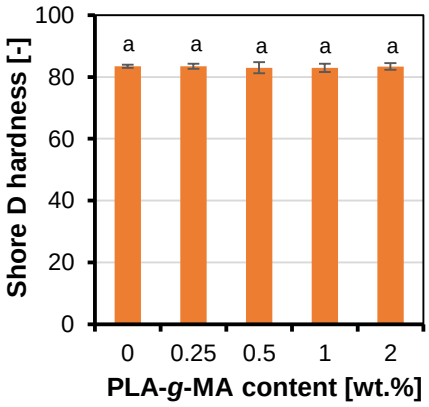

Figure 4: Shore D hardness of PLA/mustard waste biocomposites as a function of PLA-g-MA content. Identical letters at the data points indicate no significant difference according to the ANOVA and Tukey HSD test

4. Conclusions

Green renewable composites of PLA and mustard waste (10 wt.%) were prepared with the addition of PLA-*g*-MA as a coupling agent. Samples were processed *via* twin-screw extrusion followed by injection molding. The addition of the coupling agent in a concentration of 0.25 wt.% considerably increased the tensile, flexural, and Charpy impact strength of the composites. The relative improvement of these properties was found to be 14 %, 31 %, and 45 %, respectively, suggesting an effective improvement in the interfacial adhesion between the polymer matrix and the bio-filler. Further addition of PLA-*g*-MA barely affected the strength; according to the statistical analysis, there was no significant enhancement in the strength properties of composites PLA_10M_0.5MA, PLA_10M_1MA, and PLA_10M_2MA. Unlike the strength, the presence of PLA-*g*-MA had no effect on the stiffness parameters, i.e., Young's modulus and flexural modulus, of the PLA/mustard seed waste composite. This is assumed to be because the modulus is less influenced by the interactions between components than strength. Similarly, the hardness of the samples was also rather uniform, as it did not alter with the addition of PLA-*g*-MA. In summary, using PLA-*g*-MA as a compatibilizer in PLA/mustard seed waste biocomposites either improved or did not affect the investigated properties, indicating that this additive could

help promote the worldwide adoption of this eco-friendly material. Further research regarding the morphological, physical, and barrier properties is required, however, to justify the suitability of these composites for specific applications.

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