

Research Article

Investigation of Dynamic, Mechanical, and Thermal Properties of *Calotropis procera* Particle-Reinforced PLA Biocomposites

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The thermal behavior of the biodegradable *Calotropis procera* (CP) particle-reinforced polylactic acid (PLA) biocomposites was investigated. The injection molding process was used to make the composites, and the CP particle weight percentage was varied during the process (0%, 5%, 10%, 15%, and 20%). The melt flow index, heat deflection temperature, Vicat softening point, and the thermal properties of the composites were determined using dynamic mechanical testing. The results were analyzed and compared to the thermal properties of the neat PLA. The results revealed the increase in thermal stability of the PLA due to the addition of CP particles. The CP particles aided in the restriction of polymer mobility, which elevated the glass transition temperature of the composite. Incorporating CP particles in the PLA can increase the PLA/CP composite utilization in heat dissipation applications.

1. Introduction

Ecofriendly natural-based composites are the spotlight in today's sustainable world. Global efforts are initiated to avoid the usage of fossil-based polymers and composites, which can endanger the environment. The global waste of polymeric materials has caused severe environmental issues which have severely impacted the global environment [1]. Natural-based reinforcement and bio-based polymer matrix are revealed as sustainable solutions for developing high-

strength bio-based polymer composites, replacing traditional polymers and their composites [2, 3]. For example, the use of natural fiber in polymer matrices has increased the biodegradability of the polymers and made them more sustainable without reducing their strength [4]. The natural fibers derived from polysaccharides (cellulose and hemicellulose) can be used as fiber and filler. The research mentioned in this paper outlines the development of natural filler-based biocomposites. *Calotropis procera* (CP) is a shrub whose stem can be used to extract natural cellulosic

fibers. These fibers have cellulose material which possesses desirable elongation and strength characteristics. Compared to cotton and jute fibers, the CP variants have elevated weight per square centimeter and enhanced tensile and abrasive capacities [5]. The CP is a commonly grown plant in India and can be used as a low-cost source of cellulose fibers to supplement the existing fibers. In the current study, the CP fiber was converted into particles and used to develop composites.

Plastics cannot be substituted easily by other materials due to their unique properties, such as good mechanical performance, low density, transparency, low cost, heat sealability, chemical resistance, and barrier capability [6, 7]. Researchers are striving hard to develop an environment-friendly material to replace plastic. Polylactic acid (PLA) is one of the most productive and promising environment-friendly polymers due to its appealing mechanical properties, renewability, biodegradability, and low cost [8]. Although the PLA has many advantages, its brittle nature, impact strength, and thermal properties are not conducive for its usage in several industrial applications [9]. The inclusion of filler material to the PLA polymeric material improves its thermal and mechanical properties, facilitating its usage in various applications [10, 11]. Bio-fillers have invoked the researcher's interest due to their low cost and environmental-friendly nature. It facilitates the easy manufacturing of polymer composites, making them suitable for automotive, structural, and other applications [12, 13]. Several studies have found that the addition of bio-fillers to polymer composites was found to augment thermal stability. For instance, PLA-based biocomposites developed using rice husk, wheat husk, and wood fiber exhibited thermal properties. The composites prepared using rice husk revealed a least thermal conductivity of 0.08 W/m.K [14]. In another study, Chun et al. reported that the addition of coconut shell particles to the PLA elevated the glass transition temperature of the composite, thereby increasing its thermal stability [15].

The dynamic mechanical analysis (DMA) is used to determine the storage modulus, loss modulus, $\tan \delta$, and the glass transition temperature of natural fiber-reinforced polymer composites as a function of temperature [16]. By determining these parameters under dynamic loading conditions concerning temperature, the viscoelastic nature of the fabricated composites can be derived [17]. The DMA details the transition zone of composites, where the polymer molecule movement is initiated [18–21]. The melt flow index (MFI) affects the mixing efficiency of the filler and plastic materials. Plastics with higher MFI were found to improve flow and distribution [22]. The MFI determines the average molecular weight and reverses the melt viscosity. Hence, the elevation of MFI is proportional to its melt flow. The MFI is desirable for predicting and regulating the composite fabrication process [23]. The Vicat softening temperature parameter is essential when the fabricated composite finds utility in potential applications like construction industries. The Vicat softening temperature will establish the material's ability to withstand penetration under increased temperatures [24]. The Vicat softening point (VSP) is a measurement

that is used to compare the heat softening properties of the composite materials [25]. The systematic literature survey revealed various investigations initiated by researchers for identifying a suitable biodegradable polymeric composite for various applications. In this study, the *Calotropis procera* fiber-reinforced polylactic acid composite was fabricated using the injection molding technique and investigated for analyzing its thermal performance. The dynamic mechanical analysis, melt flow index, Vicat softening point, and the heat deflection temperature were determined using suitable procedures to determine the thermal performance of the fabricated natural fiber-filled PLA composites.

2. Materials and Methods

2.1. Materials. The PLA used in the present investigation was purchased from Nature-Tech India Pvt. Ltd, Chennai, India, having a specific gravity of 1.24, the relative viscosity of 3.3, glass transition temperature in the range of 55–60°C, and an MFI of 14 g/10 min (210C, 2.16 kg). The CP particles were prepared manually from the CP fibers extracted from the twig of a two-to-three-year-old CP plant. Initially, the CP fibers were manually extracted from the twig of the CP plant (Figure 1(a)) with the help of the retting process. The extracted fibers were cleaned in water to remove contaminants and unnecessary impurities. The fibers were then sun-dried for 4 hours before being oven-dried for 24 hours at 60°C to ensure an absence of moisture in the fiber. The well-dried fibers were cut to 0.3–0.5 mm length and placed in the desiccator. The cut-fibers were converted into particles using the ball milling process, which was done for 8 hours at 800 rpm with a ball ratio of 10:1. The powdered particles were collected and kept in an oven which was maintained at 60°C for 24 hours and used for composite fabrication. Figure 1 shows the CP plant, pellets, and the composite samples used in the DMA test.

2.2. Fabrication of Composites. The biocomposite fabrication was done in two steps. In the first step, the preparation of PLA/CP pellets (Figures 1(b) and 1(c)) was done with the help of a twin-screw extruder. The second step involved developing biocomposite samples (Figure 1(d)) as per ASTM Standards (plates) using the injection molding process. The PLA/CP pellets were developed using the twin-screw extruder (Coperion-ZSK26), operated at a screw rpm of 100. The extrusion temperature was maintained in a range between 160 and 180°C. The temperatures above the mentioned range were found to degrade the CP particles. The extruded blend was then pelletized. The PLA/CP pellets were then oven-dried at 60°C to avoid moisture content. Using the injection molding machine (JSW-J75E), the composites specimens were fabricated at 7 bar back pressure, 60 mm/sec screw speed, 175°C temperature, and 30°C molding temperature.

2.3. Dynamic Mechanical Analysis. The three-point flexural method of DMA testing was done to measure the composites' storage modulus and loss modulus. A DMS 6100

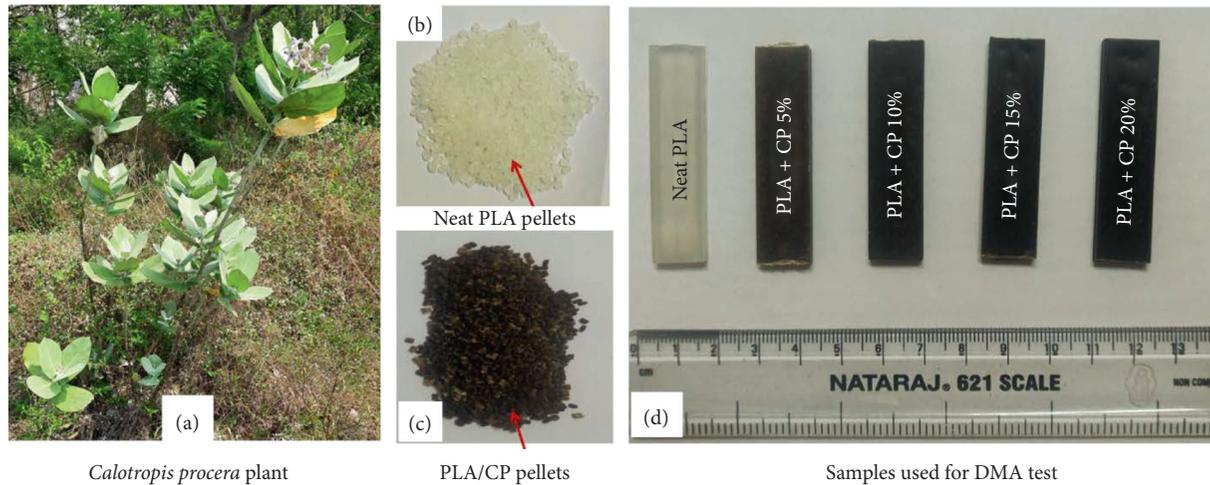


FIGURE 1: (a) *Calotropis procera* plant. (b) Neat PLA pellets. (c) PLA/CP pellets. (d) Samples used for DMA test.

instrument (SII Nano Technology, Japan) was used for conducting the dynamic mechanical test. The neat PLA and PLA/CP composite specimens (size- $52 \times 13 \times 3$ mm) were subjected to a temperature range between 30°C and 130°C and a frequency of 20 Hz. During the experiments, the samples were heated at a rate of $3^\circ\text{C}/\text{min}$.

2.4. Melt Flow Index. The MFI of the PLA/CP composites was measured using the Ametek Davenport MFI 10 equipment at a temperature of 210°C and a load of 2.16 kg following the ASTM D1238-04 protocol.

2.5. Heat Deflection Temperature. The heat deflection temperature (HDT) was measured in a three-point bending manner using the Presto HDT/VSP Tester (model: HDT/VSP-500) following ASTM D648. A specimen having the dimensions of $125 \text{ mm} \times 12.5 \text{ mm} \times 3 \text{ mm}$ was used. The HDT was obtained for each sample at a deflection of 0.25 mm and a heating rate of $2^\circ\text{C}/\text{minute}$ under a load of 0.5 MPa.

2.6. Vicat Softening Point. The Vicat softening point test for the fabricated CP-filled PLA composites was done following the ASTM D1525-17e1 standard. The specimens with dimensions of $10 \times 10 \times 3$ mm were used for testing. The specimen was placed in the testing apparatus (Presto HDT/VSP Tester: HDT/VSP-500) with the penetrating needle at approximately 1 mm from the surface's edge. After this, the specimen was immersed in an oil bath heated to 230°C , followed by applying a force of 10 N. The bath temperature was gradually increased by 50°C every hour until the needle penetrated 1 mm.

3. Results and Discussion

3.1. DMA Results. The results of the DMA test are revealed in Figure 2. The effect of the CP particle reinforcement on the storage modulus of PLA composites is depicted in Figure 2(a). Three distinct regions, namely, the glassy,

transition, and rubbery regions, were identified from the storage modulus curve at temperatures ranging from 30 to 125°C . The glassy region occurred between ca. 30 and 60°C , the transition temperature occurred between ca. 60 and 75°C , and the rubbery region occurred between ca. 75 and 125°C . The storage modulus of the PLA/CP composites was found to increase after ca. 85°C , except for the neat PLA, which was due to the cold crystallization of the PLA/CP composites. In general, cold crystallization occurs when the polymer chain gains sufficient mobility to arrange itself into an ordered structure (i.e., crystalline structure) due to chain folding. The storage modulus of composites and neat PLA decreased between 60 and 75°C . In general, the transition temperature for PLA is 60°C . The drop in storage modulus after the glassy region was caused by a change in the material's elastic behavior to viscoelastic behavior, visible in the transition region. Compared to neat PLA, the storage modulus of the PLA composites increased in both the glassy and rubbery regions. The 20 wt.% CP-added composite had the highest storage modulus, followed by the 15 wt.%, 10 wt.%, and 5 wt.% CP-added composites. At 5°C , the storage modulus of the 20 wt.% CP composites were 35% higher than the neat PLA. This was due to an increase in the composite stiffness in all three regions, which was a function of the reinforced CP particles. The increased stiffness of the composites resulted from the better compatibility of the CP particles with the matrix, which can be understood from Figure 3.

Figure 2(b) depicts the loss modulus of the PLA/CP composites with varying wt.% of CP particles. In general, the loss modulus increased until it attained the glass transition temperature, followed by a precipitous fall. The CP/PLA composites followed a similar pattern. The sudden drop in the loss modulus after the glass transition temperature was due to increased polymer mobility, which increased the viscosity of the composite. For the composite with 20 wt.% CP, the loss modulus increased steadily until the peak value (66°C), followed by a sharp decrease up to 82°C . A small peak at 90°C was observed, which was due to cold crystallization. In both the glassy and transition regions, the magnitude of the loss modulus was more significant for the composites

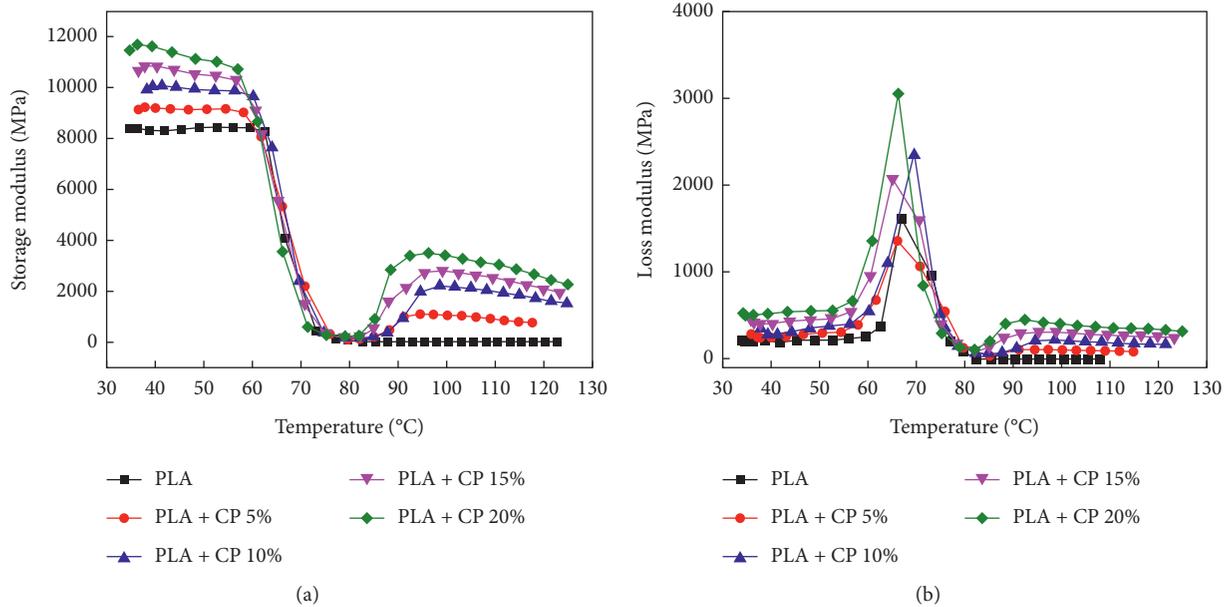


FIGURE 2: Storage modulus and loss modulus of PLA/CP.

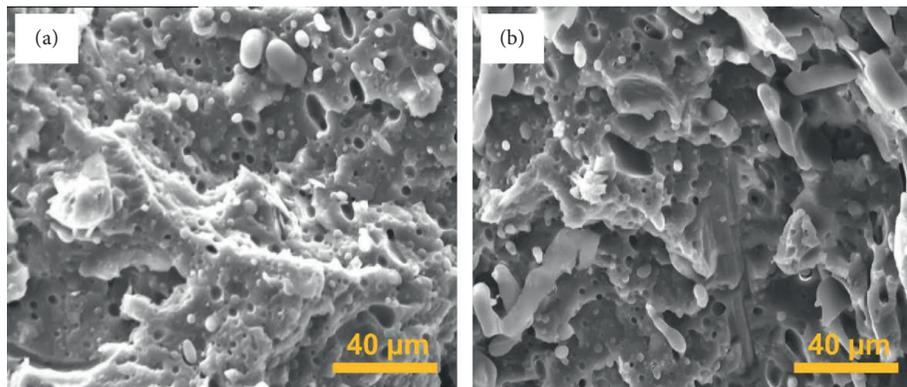


FIGURE 3: SEM image showing interaction of CP with PLA: (a) 15% CP composite and (b) 20% CP composite.

than the neat PLA. The peaks of the composites were found to be broad with distinct amplitude and temperature positions, owing to the development of complex relaxation behavior as a result of the polymeric matrix's restricted chain mobility. The displacement of the peak of the composite was observed at lower temperatures compared to neat PLA, owing to the increased flexibility of the composites that resulted from the addition of CP particles.

Generally, the glass transition temperature can be determined from the loss modulus concerning temperature. However, the loss modulus was more sensitive to the molecular movements under the same deformation amplitude in this case. The glass transition temperature of the PLA/CP composites was higher than that of the neat PLA due to the restriction in polymer chain mobility caused by the addition of the CP particles.

3.2. Melt Flow Index of CP/PLA Composites. Figure 4 reveals the melt flow test results of the PLA/CP composites. The

melt flow index of the neat PLA was 13 g/10 min. The melt flow of the PLA was reduced after the addition of the CP particles in a usual manner. The reinforcement of 5 wt.% and 10 wt.% CP particle reinforcement revealed lower MFI when compared to the neat PLA. However, the composites, reinforced with 15 wt.% and 20 wt.% CP particles, possessed higher MFI than the neat PLA and the other two PLA/CP composites. The lower MFI value at 5 wt.% and 10 wt.% particle content was due to the strong interaction of the PLA and CP particles, which restricted the movement of the polymer chains, resulting in a reduction in the flowability of the PLA/CP composite.

The addition of CP particles increased the viscosity of the molten PLA while decreasing its elasticity. However, this mechanism depended on the particle loading content of the PLA composite with 20 wt.% CP having the highest MFI, which was three times higher than the neat PLA. The PLA composite with 5 wt.% CP had the lowest MFI. The MFI of the 20 wt.% CP composite increased by 332% when compared to the 5 wt.% CP-added composite. This increase was

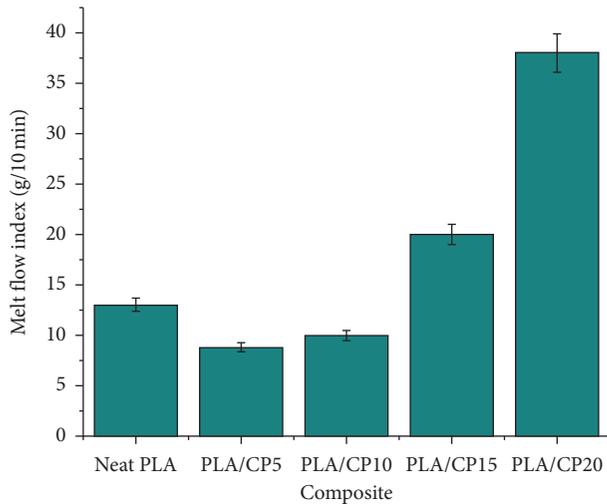


FIGURE 4: Melt flow index of PLA/CP.

primarily attributed to increased particle-to-particle interaction in the composites after the 15% and 20% CP particles, respectively. At high testing temperatures, the bioparticles lose their stability and interaction as thermal degradation begins, resulting in a weak polymer-polymer link that allows the polymer to move freely. This reduces the polymer's viscosity, which increases the MFI.

3.3. Heat Deflection Temperature of CP/PLA Composites.

The heat deflection temperature of the CP/PLA composites is shown in Figure 5. After incorporating the CP filler material into the PLA, the heat deflection temperature gradually increased. The addition of CP filler material to the PLA matrix resulted in a 4% to 20% increase in heat deflection temperature. The heat deflection temperature gradually increased from 50°C to 58°C as the filler particle content increases from 5 wt.% to 20 wt.%. Maximum enhancement was noted for the composite with 20 wt.% CP, 20% higher than the neat PLA. A minimal enhancement (4%) was noted for the composite with 5 wt.% CP added. Furthermore, lower polymer content at a higher CP content increased the polymer-to-particle interaction rather than the polymer-to-polymer interaction. The increased particle-polymer interaction probably accounted for the improved HDT at 20% CP composites.

3.4. Vicat Softening Point of CP/PLA Composites. The VSP of the CP/PLA composites is depicted in Figure 6. The VSP of the neat PLA was around 55°C. When the filler was added to the composites ranging from 5% to 20%, the VSP of the composites increased from 57°C to 64°C. This demonstrated the effectiveness of the CP filler particles in PLA composites against the VSP. The needle penetrated to a depth of 1 mm inside the neat PLA at a lower temperature (55°C) than the PLC/CP composites. This was because the addition of CP to the PLA increased its rigidity, which increased the hardness of the composites.

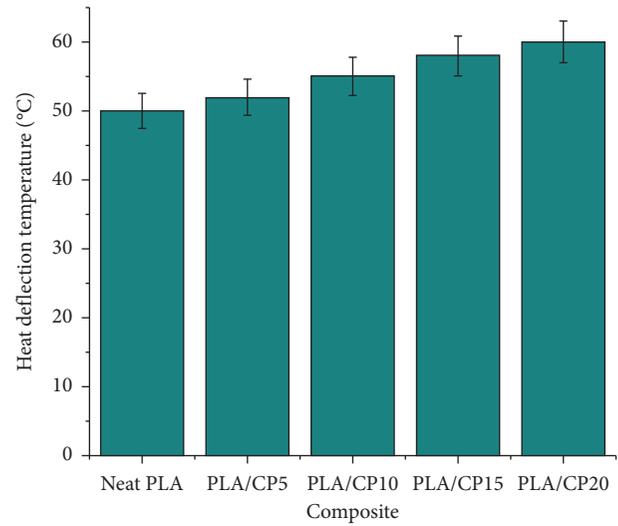


FIGURE 5: Heat deflection temperature of PLA/CP.

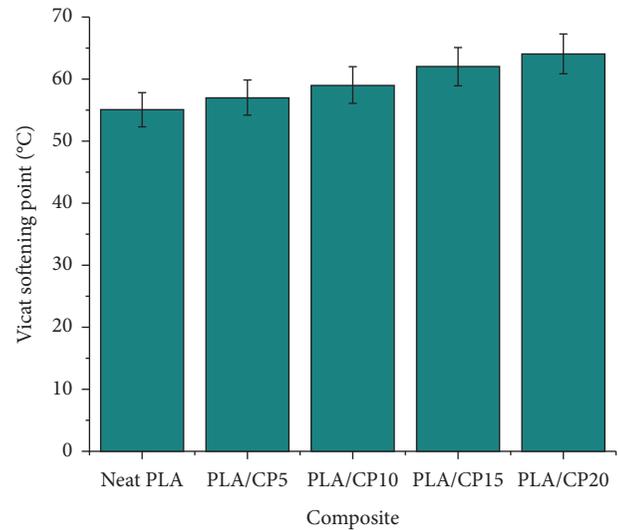


FIGURE 6: Vicat softening point of PLA/CP.

Furthermore, increasing the temperature was not sufficient to break the bonding between the PLA and CP particles because of the increased stiffness of the composites. The increased stiffness was also the reason for the composite's increased VSP. The composite's storage modulus results can explain the increased stiffness.

4. Conclusion

The PLA-based biocomposites reinforced with natural filler CP were successfully manufactured using the injection molding process. The thermal properties of the composites were studied, including the dynamic mechanical analysis, heat deflection temperature, melt flow index, and the Vicat softening point. The addition of CP particles to PLA increased the thermal stability of the composites. The 20 wt.% CP-added composite possessed the highest storage modulus, followed by the 15 wt.%, 10 wt.%, and 5 wt.% CP-added

composites. The glass transition temperature of the PLA/CP composites was higher than the neat PLA due to the restriction in the polymer chain mobility caused by the addition of the CP particles. The reinforcement of 5 wt.% and 10 wt.% CP particle reinforcement had lower MFI when compared to the neat PLA. However, the composites with 15 wt.% and 20 wt.% CP-added composites had higher MFI than the neat PLA and the other two PLA/CP composites. The heat deflection temperature of the 20 wt.% CP composites were 20% higher when compared to neat PLA. The maximum VSP for the 20 wt.% CP composites were 64°C, which was 16% higher than the neat PLA. The increased thermal stability was due to restriction in polymer chain movement due to the addition of CP particles. The findings resultant of our investigation can be used to induce enhanced thermal resistance in the PLA-based biocomposites.

Data Availability

The data used to support the findings of this study are included in the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

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