Load Bearing Properties of Environment Friendly Green Pea Pod Cellulose Toughened Sunn Hemp Polyester Composite

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Research Article

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Abstract

This study focuses to develop an environmental friendly polymer composite for various technological applications. The primary objective of this study was to determine the load bearing effect of green pea pod cellulose addition into the polyester resin along with sunn hemp fiber. The microcrystalline cellulose was developed from the waste green pea pods and the composites were fabricated using hand layup method. The results revealed that adding 2 and 35 vol.% of cellulose and fibre increased the tensile strength, tensile modulus, flexural strength, hardness, Izod impact, and ILSS for PSC3 composite by 136 MPa, 3.85 GPa, 190 MPa, 5.72 GPa, 83 Shore-D, 4.77 J, and 27.4 MPa respectively. Moreover, the composite PSC3 gave maximum fatigue life counts of 30862, 28041 and 24384 for 30%, 60%, and 90% of UTS. The composite designated as PSC3 which has cellulose contains of 2.0 vol.% was found to significantly increase the storage modulus. Similarly, the drop load impact testing demonstrated that composite PSC3 shows the highest energy absorption up to 12.2 J. SEM fractograph revealed improvement in toughness as well as enhanced fiber-matrix interface. These load bearing properties improved eco-friendly composites could preferable in industrial, automotive, defense, aero structure and domestic architectural applications with high environmental safety concern.

1. Introduction

The rising environmental pollution and human safety concerns caused by the extensive use of petroleum-based polymers for food packaging film applications have caused scientists to investigate for eco-friendly and safe alternatives. In recent century it has seen an increase in interest in the studies and creation of renewable biodegradable composites [1]. As novel and innovative items that are well-received by consumers gain market share, the demand for these materials has been rising over time. Typical biocomposite products have been created using diverse natural fibres and binder methods to adapt to varied end-use applications [2]. Since before starting of modern civilizations, when straw was used to support mud bricks in construction, natural fibers have been incorporated into composite items. Natural fibers continue to be of interest because of the many qualities they provide when employed as reinforcement within composite materials, as well as the significant environmental advantages [3].

Natural fibers can be characterized as organic composites made primarily of natural fiber imbedded in lignin matrix. Natural fibers are split, nevertheless, according on whether they come from plants, animals, or minerals. Plant fibers can be found in seed, fruits, wood, cereal straw, bast (or stem or soft sclerenchyma) fibers, leaf or hard fibers, and various grass fibers. The oldest crop producing fibers in India is sunn hemp (Crotalaria juncea), which is a significant source of lignocellulose and a member of the Fabaceae family [4]. The plant has significant economic value due to a number of traits including high biomass yield, weed management, non-host wealth for a number of diseases and pests, increases a soil organic matter, symbiotic relationship, and effective nitrogen fixation in collaboration with Rhizobacteria [5]. Sunn hemp fibers are bast fibers that are harvested from the stem of the sunn hemp plant. The sunn hemp plant contains 13% of its dry weight in fiber and 3% of its total green weight in fiber. Waste hemp fibers/epoxy composites: mechanical and thermal characteristics were studied by
Jadhav et al. [6]. At 30% loading, it was found that the strongest tensile strength for 127% grafted sunn hemp fibres was 68.73 MPa, while the strongest impact strength, interlaminar shear strength, and microhardness were 128%, 4.6 J, 68.9 MPa, and 63%, respectively. Utara et al. [7] researched on influence of surface treatments and filler loading on the characteristics of hemp fiber/natural rubber composites. Author observed silane treated hemp fiber filled natural rubber composites demonstrated better tensile strength and crosslink density at 5 phr fibre loading. SEM images showed good interfacial contact between the rubber matrix and the silane-treated hemp fiber.

Additionally, the cellulose was used as filler to explore the characteristics of cellulose and its crystallinity. A-cellulose, hemicellulose, lignin, waxes and pectins make up the majority of natural fibers and fillers structures [8]. D-anhydroglucose (C$_6$H$_{11}$O$_5$) repeating units are connected by 1,4-b-D-glycosidic connections at the C$_1$ and C$_4$ positions to form the natural polymer known as cellulose. Three hydroxyl groups are present in each repeating unit. The crystalline packing of these hydroxyl groups and their capacity to form hydrogen bonds also significantly influence the physical characteristics of cellulosic materials [10]. Our aim is to utilize the bio waste in composite materials to reduces the hazardous environmental effects. Around the world, pea and broad beans are frequently grown and consumed. This kind of leguminous peas are typically consumed, with a quick industrial procedure when the pod is removed to make the seeds into frozen, canned, or fresh food [11]. The core component is isolated, resulting in an abundance of inexpensive, unwanted remnants. Very few researchers have only studied on the utilization of such bio waste into composite material applications. Agro-industrial residues from pea (Pisum Sativum) and broad bean (Vicia Faba) pods were the subject of research by Kassab et al. [12]. Purified Cellulose microfibers and nanocrystals have diameters of 10.68 $\pm$ 1.28 m and 14.67 $\pm$ 2.29 m, respectively, and crystallinities of 79% and 70%. Additionally, the thermal stability and great crystallinity was observed for these cellulose nanocrystals. Utilizing trash from the pea industry to create biodegradable products studied by Upasana et al. [13]. The study’s findings showed that waste pea peels are rich in ash (7.87%), fat (2.27%), and fibers (1.84%), as well as a significant amount of crude protein (19.79%). The biofilm created for this study had good thickness (70 m), water solubility (2.46%), and tensile strength (5.96 MPa).

According to literature studied it is observed that green pea pods were a great source of cellulose and not studied by any researcher in combination with sunn hemp fiber and polyester resin. Hence this study aims to study the effect of green pea pods cellulose inclusion in sunn hemp fiber reinforced polyester composites. The investigation focused on mechanical, fatigue, DMA and drop load impact properties of cellulose and sunn hemp fiber reinforced polyester composites. These composites prepared by utilizing hand layup process and characterized in accordance appropriate ASTM standards. Further such mechanically strong and highly toughen composite could be use in for a variety of applications, including industrial and automotive sectors, food packaging drug delivery as well as for domestic applications.

2. Experimentation
2.1. Materials

Huntsman India Ltd. provided unsaturated polyester resin (maleic anhydride) with a molecular weight of 2400g/mol, viscosity of 600cps, and density of 1.13g/cm\(^3\). Merck India Ltd. supplied Methyl-Ethyl-Ketone-Peroxide (catalyst) with a density of 1.17g/cm\(^3\) and a molar mass of 210.1g/mol, as well as Cobalt Naphthenate with a density of 0.95g/cm\(^3\). Sunn hemp fiber mat with fiber diameter 20µm and density of 1.28g/cm\(^3\) designed for continuous use at temperatures up to 300°C and green pea pod source to produce cellulose was purchased from metro composites research and development centre in Chennai, India.

2.2. Cellulose Preparations

For this process waste green pea pods were collected by local food processing industry. The washed green pea pods are gathered and arranged on a tray set out in the sun to dry. After thoroughly drying, the green pea pods are ground into a fine powder using a grinder. From which 4 g of powdered green pea pods are collected in a beaker. The beaker is then filled with 12ml of 1mol NaOH and 88ml of distilled water and whirled for 2 h at a steady 80°C temperature using a hot plate magnetic stirrer.

Green pea pod powdered particles are separated using a filtration procedure after delignification, and it is then dried for 24 h [14]. For bleaching these powdered green pea pods, a solution of 50ml Sodium Hypochlorite (NaOCL) and 50ml distilled water is required. The hot plate magnetic stirrer is heated to 80°C, dwelled for 1 hour, and then naturally cooled. The particles are collected on filter paper, and the remaining solution is placed in the proper container. To make cellulose, the particles are cleaned with distilled water and dried in a hot air oven for 3 h to neutralized and retain the pH level [15]. The particle size of the cellulose is kept constant at 5µm, with a density of 1.48 to 1.51g/cm\(^3\). The steps of cellulose perpetration are shown in Fig. 1. Figure 2 displays the X-ray diffraction analysis (XRD) for the cellulose synthesized in this investigation. A considerable crystalline phase with (110), (200), and (004) planes is shown by the diffraction peaks at 2 = 12.9, 22.4, and 35.33 degrees it is clearly indicate that cellulose has a crystalline structure according to their peak values and degrees.

2.3. Composite Laminate Preparation

Prior to hand layup process fiber was surface treated as per the reference [16]. The lay-up surface is cleaned as part of the mould preparation process before to the creation of the composite, and wax is then applied to facilitate with laminate removal. Silicon-rubber is wrapped around the perimeter of the laminate to define the lamination zone. After preparing the mold, 97.5 wt.% unsaturated polyester resin (maleic anhydride) is collected in a cleaned glass beaker and green pea pod cellulose is added. Assured that there were no lumps in the mixture and that it had been well combined. After thoroughly mixing the cellulose derived from green pea pods and unsaturated polyester, the Methyl Ethyl Ketone Peroxide (catalyst) is added up to 2 wt.% with 0.5 wt.% cobalt naphthenate as an accelerator [17]. The sunn hemp fiber layers are placed on the mold in the order specified, and the resin mixture is carefully poured on top of each fiber layer. The hand-lay-up technique is used to introduce the resin into the fiber layup. Because
of the slow polymerization, the cure time provided at room temperature is 10 hours. The composite is then post-cured in a hot air oven at 70°C for 4 h. Sunn hemp fiber was mixed with unsaturated polyester and green pea pod cellulose to generate a composite with a thickness of up to 3mm [18]. Table 1 displays the various materials combined to make a composite with different designation. Figure 3 shows the composite laminates prepared with combination of 0.5 vol. % of cellulose.

Table 1
Composite designation for various material combinations

<table>
<thead>
<tr>
<th>Composite designations</th>
<th>Unsaturated polyester resin (Vol. %)</th>
<th>Sunn hemp woven fiber (Vol. %)</th>
<th>Green pea pod Cellulose (Vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PS</td>
<td>65</td>
<td>35</td>
<td>0</td>
</tr>
<tr>
<td>PSC1</td>
<td>64.5</td>
<td>35</td>
<td>0.5</td>
</tr>
<tr>
<td>PSC2</td>
<td>64</td>
<td>35</td>
<td>1</td>
</tr>
<tr>
<td>PSC3</td>
<td>63</td>
<td>35</td>
<td>2</td>
</tr>
<tr>
<td>PSC4</td>
<td>61</td>
<td>35</td>
<td>4</td>
</tr>
</tbody>
</table>

3. Characterizations

The polyester-based bio cellulose as filler and sunn hemp fiber reinforced composite is visually evaluated further to trace any noticeable surface flaws. At least three test specimens are drowned out of the laminate utilizing abrasive water-jet machine, Maxiem Water Jets, 1515 KENT, in line with the ASTM. Throughout the procedures, the machine settings were maximum 220 psi jet pressure, 0.3 g/sec abrasive flow-rate, 1.1 mm nozzle diameter, and 3 mm SOD [19]. Surface defects were removed by polishing the specimen faces using P320 grit emery paper. The mechanical, fatigue, DMA and flammability tests were carried out in accordance with Table 2. For the purpose of determining the mean, five identical test samples were evaluated. Figure 4 shows the specimens prepared from composite designation PSC1.
Table 2
ASTM standards with test specification

<table>
<thead>
<tr>
<th>Tests</th>
<th>ASTM</th>
<th>Machines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile</td>
<td>3039</td>
<td>INSTRON 4855, UK,</td>
</tr>
<tr>
<td>Flexural</td>
<td>790 − 17</td>
<td>Traverse speed of 1.5 mm/min</td>
</tr>
<tr>
<td>Izod impact</td>
<td>256–10</td>
<td>Krystal equipment Ltd., India</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Maximum load capacity of 20 J</td>
</tr>
<tr>
<td>Hardness</td>
<td>2240</td>
<td>Durometer (shore-D)</td>
</tr>
<tr>
<td>Fatigue</td>
<td>3479</td>
<td>MTS Landmark 370 load frame, USA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Working stress values are 30%, 60% and 90% of UTS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>frequency of 5 Hz, stress ratio of 0.1 and temperature of 28°C</td>
</tr>
<tr>
<td>DMA</td>
<td>4065</td>
<td>Dual cantilever mounted DMA analyser with sweep mode</td>
</tr>
<tr>
<td>Drop load impact</td>
<td>7136</td>
<td>SPRANKTRONICS Pvt, Ltd. Bengaluru India, with 2.5 m/s velocity and 1.5 m drop height</td>
</tr>
<tr>
<td>SEM</td>
<td>-</td>
<td>HITACHI, S1500, Japan</td>
</tr>
</tbody>
</table>

In impact testing using a hemispherical impactor nose, the composites were pierced. A finite element numerical investigation was conducted using ABACUS 3.0 with a 1L node capacity to demonstrate how the composites' ballistic reactions improved. During the analysis, the von-Mises stress-strain relationship was followed. Figure 5 shows the composite 3D model and the hemi-spherical impactor prepared using ABACUS along with meshing. This drop load impactor has diameter of 12.7 mm.

4. Result And Discussion

4.1. Mechanical Properties

The mechanical behavior of green pea pod cellulose and sunn hemp fiber reinforced polyester composite was shown in Fig. 6. Figure 6 (a) shows the tensile properties (b) represents the flexural properties (c) demonstrates the hardness and Izod impact values and (d) shows the interlaminar shear strength. It is observed that composite designation P gives very lesser tensile strength, tensile modulus, flexural strength, flexural modulus, hardness and Izod impact values about 44 MPa, 1.68 GPa, 82 MPa, 2.88 GPa, 76 Shore-D and 0.32 J respectively. The reason behind these lower values is pure resin content of composite designation P which is always extremely brittle and shows the flat fractures on surface as represented in Fig. 7 (a). But further incorporation of sunn hemp fiber by 35 vol. % in pure polyester resin enhances the mechanical properties of composite designation PS. Tensile strength and modulus, flexural
strength and modulus, hardness, Izod impact, as well as interlaminar shear (ILSS) values increased up to 78 MPa, 2.71 GPa, 136 MPa, 3.8 GPa, 77 shore-D, 3.84 J, and 22.4 MPa for composite designation PS. Silane-treated hemp fibers in polyester resin, which enhanced the adhesion bonding mechanism between the fiber and the matrix [20], is what resulted to this significant enhancement as shown in Fig. 7 (b). When a fiber has good wetting ability with matrix and sunn hemp fibers has high wettability, statistically dispersed fibers flaws are overcome [21]. Furthermore, increased in mechanical properties is noted with inclusion of green pea pod cellulose by 0.5, 1.0, 2.0 and 4.0 vol. % for composite designation PSC1, PSC2, PSC3, and PSC4 correspondingly. PSC3 exhibits the highest values of tensile, flexural strength and modulus, hardness, Izod impact, as well as ILSS when compared to all other composite designations up to the 136 MPa, 3.85 GPa, 190 MPa, 5.72 GPa, 83 Shore-D, 4.77 J, and 27.4 MPa. It is due to the evenly dispersed cellulose shows the resistance to crack propagation in the sunn hemp fiber reinforced polyester composites as shown in Fig. 7 (c) and (d).

Cellulose addition reduces the larger defects and reduces the crack propagation points due to the even distribution of particles [22] as demonstrated in Fig. 7 (e). However, further increased in vol. % of cellulose up to 4 vol. % decreased in mechanical properties is observed. Raised in vol. % of cellulose shows the agglomeration of the particles in the resin acted as stress concentration points that hastened failure and resulted in lower mechanical properties due to brittle fracture [23] as represented in Fig. 7 (f).

### 4.2. Fatigue Behavior

The fatigue behavior of green pea pod cellulose with sunn hemp fiber reinforced polyester composites was shown in Fig. 8. The composite designation P gives the lowest fatigue life counts at 30%, 60% and 90% UTS of which is about 2764, 1409, and 725 respectively. The higher brittleness of pure polyester resin is a result of this lower fatigue life count with flat brittle fracture [24] as shown in Fig. 9 (a). The reason for this is the preservation of plastic strain in the molecular chain of polyester. Furthermore, addition of sunn hemp fiber by 35 vol. % enhances the fatigue life counts for composite designation PS about 19653, 16513, and 12884 correspondingly. This could be due to the improvement of chemical bonding and mechanical interlocking between the treated fibres and matrix because of the silane surface treatment on sunn hemp fiber [25]. Figure 9 (b) shows the matrix cracks after sustaining the highest number of fatigue cycles. It is also shows the fiber matrix debonding but with improved interlocking mechanisms. Similarly, the incorporation of cellulose particles by 0.5, 1.0, 2.0 and 4.0 vol. % raised in fatigue life counts are observed. However cellulose additions show the improvement in toughness of brittle matrix which results in formation of micro cracks instead of large failures as shown in Fig. 9 (c) and (d). The maximum fatigue life counts are noted for the composite designation PSC3 about 30862, 28041 and 24384 at 30%, 60% and 90% UTS. This is because the cellulose introduction up to 2 vol. %, is scattered evenly throughout the matrix and does not deform easily, resulting in greater cross-linking [26]. This leads to better fatigue life counts with denser microcracks in matrix as shown in Fig. 9 (e). Furthermore, increased in cellulose vol. % up to the 4.0 vol. % diminishes the fatigue life counts for composite designation PSC4 due to the cluster formation within matrix materials.

### 4.3. DMA
Figure 10 demonstrates the DMA characteristics of green pea pods cellulose and sunn hemp fiber reinforced polyester composites. The composite designation P shows the lowest storage modulus characteristic, which is 2.6 GPa. As the free volume arises with temperature then vibration also increases, indicating that matrix molecules rotate rapidly and have a low storage modulus. The loss tangent is also large for pure polyester resin because the molecules cannot retain the energy that is provided as stress while they are rotating at high temperatures and frequencies [27]. When 35 vol. % of sunn hemp fiber were included in pure polyester resin it seems to have storage modulus of 3.2 GPa respectively. These rise in storage modulus offered on by the layer-sequence stacking of fibers into polyester resin. Because the surface-treated fibers structures stop the rotation of the matrix molecules, the free volume in the matrix, surrounded with fiber content, increasing the storage modulus. Similarly, inclusion of green pea pod cellulose particles by 0.5, 1.0, 2.0 and 4.0 vol. % improved values for storage modulus and decrement in loss factor is observed. The highest storage modulus and lowest loss factor was noted for the composite designation PSC3 with addition of 2.0 vol. % of cellulose particles. The reason behind this is inclusion of cellulose improves the fiber matrix bonding as well as tightly holds the secondary molecules of the resin. Hence the inertia to rotate about the primary chains is rapidly increased due to the addition cellulose and more heat energy is required to activate the same [28]. However further increased in cellulose vol. % up to 4.0 vol. % decreases the DMA characteristics because of the agglomeration of the particles in resin.

4.4. Drop Load Impact

Figure 11 shows drop load impact energy absorption for various composite designation. It is observed that the composite designation P which is a pure polyester resin gives very lower energy absorption, which is equal to 0.4 J. This lower energy absorption is the cause of high brittle nature of pure polyester resin. It is observed that the addition of sunn hemp fiber by 35 vol. % in polyester resin improved the energy absorption. This improvement is because of effective load sharing and high load bearing capability of sunn hemp fiber in polyester resin composite. As well as due to the silane functional group’s ability to tightly bind the reinforcements to the matrix, the reinforcement addition exhibit higher increases in values. Furthermore, incorporation of green pea pod cellulose particles by 0.5, 1.0, 2.0 and 4.0 vol. % enhancement in energy absorption is observed. The highest observed drop load impact values for composite designation PSC3 after addition of 2.0 vol. % of cellulose particles. The inclusion of cellulose in polyester resin improvement in impact energy is observed as results of filler materials strong hydrogen bond. This hydrogen bonding improves the ability of the composite system to absorb energy during fracture propagation and enhance the impact resistance of the composite [29]. On other hand further raised in cellulose vol. % up to 4.0 vol. % decreases the energy absorption values for composite designation PSC4 due to the cluster formation in matrix materials which makes composite brittle. Figure 12 shows the impact damage analysis for different combinations of cellulose with sunn hemp fiber reinforced polyester composites.

The impact damage analysis for composite designation P was shown in Fig. 12 (a-b). It represents the penetration of impactor up to the other end of the specimen which means this composite fails to sustain the sudden applied load. This is because of the pure polyester resin which is brittle in nature and do not
have energy absorption mechanism [30]. However, further inclusion of sunn hemp fiber shows the lesser impact damages and improvement in energy absorption as represented in Fig. 12 (c-d). It is due to the ability of the fiber to evenly distribute the load transferred by the matrix materials. Although the composite laminate distributes the majority of the impacting energy applied by sudden load, the forces are reduced at the back end. Moreover, inclusion of green pea pod cellulose up to the 2.0 vol. % the minimum damage on the composite surface is observed in Fig. 12 (e-f). Since the impactor is situated in the centre point of the composite, indicates the polyester with cellulose is responsible for absorbing most of the energy.

5. Conclusion

This research aims to investigate the effectiveness of adding green pea pod cellulose to polyester composites reinforced with sunn hemp fiber. To determine the mechanical, fatigue, DMA, and drop load impact characteristics of cellulose with sunn hemp fibers reinforced polyester composites were the objective of the study. These composites were created by hand layup process and were tested in accordance with respective ASTM standards. The outcomes of this study indicate that the highest values of tensile strength, tensile modulus, flexural strength, flexural modulus, hardness, Izod impact and ILSS observed for PSC3 about 136 MPa, 3.85 GPa, 190 MPa, 5.72 GPa, 83 Shore-D, 4.77 J and 27.4 MPa noted with addition of 2 vol. % of cellulose and 35 vol. % of cellulose. Similarly, the maximum fatigue life counts are noted for the composite designation PSC3 about 30862, 28041 and 24384 at 30%, 60% and 90% UTS. The dynamic mechanical analysis shows the highest storage modulus and lowest loss factor was noted for the composite designation PSC3 with addition of 2.0 vol. % of cellulose particles. Correspondingly, drop load impact testing shows the highest energy absorption with 2.0 vol. % of cellulose and 35 vol. % of sunn hemp fiber. SEM shows the improved toughness in matrix by addition of 2 vol. % of cellulose as well as enhanced fiber matrix bonding. However, it is noted that increased in cellulose vol. % up to 4.0 vol. % diminish the mechanical, fatigue, DMA and drop load impact properties. From all of these outcomes it is concluded that the designation PSC3 is suitable for future applications such as industrial, automotive, defence, aero structure and domestic architecture uses.

Declarations

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Conflict of Interest

Authors here by confirming that there are no conflict of interests

Author Contributions

Hassan Alshahrani – Design of research work and drafting
Acknowledgment

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Figure 8

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Drop load impact damage analysis