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Development of novel sustainable biocomposite from polycaprolactone and *Sesbania rostrata* fiber

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Abstract

The best way to accelerate the application of polymer composites is by making them an environmentally friendly material that can degrade naturally without harming the environment. Hence, this work focuses on the development of biocomposite by reinforcing bark fibers of *Sesbania rostrata* (SRF) with polycaprolactone (PCL) biopolymer. Composite samples were fabricated by reinforcing untreated SRF and sodium bicarbonate-treated SRF to PCL at different weight proportions of 10, 15, 20, and 25%. The compressing moulding technique was used to develop the test specimens, and samples were subjected to mechanical, thermal, water absorption, wear, and morphological tests. Biocomposites made of 20 wt.% of chemically treated SRF with PCL yield better mechanical strength than other combinations. The thermal properties of biocomposite were not affected by the inclusion of untreated fibers and were improved by the inclusion of treated fibers. An increased fiber volume fraction in the biocomposites accounts for higher water absorption properties, whereas chemically treated fibers show a significant increase in water resistance. Wear test results expose that the weight loss of the biocomposites is mainly dependent on the contact temperature and adhesion between the SRF surface and the PCL matrix. Scanning Electron Microscope (SEM) analysis of the fractured biocomposites reveals that failure occurs primarily due to fiber pull-out, debonding, and agglomeration.

Keywords: *Sesbania rostrata* fibers – Polycaprolactone – Biocomposite - Mechanical Characterization – Water absorption – Wear test

1 Introduction

Composite materials made by reinforcing fiber with a polymer matrix are used in wide fields like automobile, structural, packaging, toys, etc. because of their beneficial characteristics like high strength-to-weight ratio, tailored-made properties, low cost, better shape formability, etc. However, the non-biodegradable nature of the synthetic polymer composites creates a huge impact on the environment, which in turn limits their consumption [1]. Due to the rising interest in this problem, a new material was developed called "Green Composite". Green composites are made of a completely biodegradable polymer matrix and natural fibers [2]. Currently, polyhydroxybutyrate (PHB), polylactic acid (PLA), and polycaprolactone (PCL) are the most commonly used biopolymers for developing biocomposites. In general, natural fibers are extracted from different segments of plants like the stem, leaf, fruit, and seed. Other than their biodegradable nature, natural fibers are cheaper, readily available, save energy on processing, and light weight than synthetic fibers. Biopolymers are a little costlier than synthetic polymers, but this can be compensated by adding a measurable weight proportion of natural fiber that reduces the overall cost of the biocomposite [3, 4].

Polycaprolacton is a synthetic biopolymer with the property of biocompatibility, which allows it to be used in biomedical applications as a carrier for antibiotic local delivery, microcapsule support in agriculture, bone implants, and soft tissue applications. Apart from biomedical applications, PCL is used in light-weight structural fields, food packaging, and making degradable bottles. Poor mechanical strength and melting properties of PCL restrict its usage [2, 5, 6]. Meanwhile, the incorporation of natural fibers/ fillers into PCL improves its strength and degradability. Chemically treated natural fibers/ fillers exhibit better adhesion with PCL when compared to untreated natural fibers/ fillers. With the help of chemical treatment, impurities and a partial fraction of hemicellulose content are removed from the natural fibers/ filler, and its surface turns rough. A chemical treatment of natural fibers and fillers improves adhesion with PCL and mechanical strength over untreated natural fibers/fillers [3, 7, 8].

Siqueira et al. [3] reported that the addition of Macaíba fiber with PCL biopolymer enhances the thermal stability and mechanical behaviour of biocomposite composites. Chemical treatment of Macaíba fiber with maleic anhydride gives better results when compared to sodium hydroxide and silane. Lima et al. [8] suggested that a 20% coir filler/80% PCL biocomposite shows better tensile strength when compared to neat PCL biopolymer and other weight proportions of filler/PCL. By incorporating chemically modified coir fiber into biocomposites, the tensile strength can be further enhanced. Aguiar and Maria (2018) found that a 5% weight fraction of H₂SO₄ treated curauá and jute fibers in PCL showed good mechanical strength when compared to 2% and 20% fiber weight addition, respectively.

Sesbania rostrata is a nitrogen fixation plant, and it is cultivated in the turmeric field of 500 acres around Kodumudi, Erode, Tamil Nadu, India, as an intercrop. It helps increase the nitrogen level in the soil and acts as green manure. It also provides natural shade for the turmeric plant from the sunlight. In summary, *Sesbania rostrata* fibers (SRF) are widely available locally and can be used for composite reinforcement purposes for a variety of reasons. Only a few studies have been conducted on the fiber [9, 10]. This article examines the effect of reinforcement of sodium bicarbonate-treated and untreated SRF with PCL at different weight proportions (10, 15, 20, and 25 wt.%) on mechanical, thermal, water absorption, and tribology (specific wear rate) in order to discover SRF reinforced polycaprolacton biocomposite for engineering applications.

2 Materials and Methods

2.1 Materials

PCL biopolymer was supplied by Bhejo, Mumbai, India, and its properties are presented in Table 1. The strip form of PCL biopolymer is used as a matrix for making the biocomposite. *Sesbania rostrata* fibers were extracted from the stem of *Sesbania rostrata* plants by submerging their skin for a period of 12 days at room temperature. Wetted fibers were cleaned with fresh water multiple times to remove the impurities and then dried for 7 hours in a conventional oven at a temperature of 60°C. The dried raw SRF is shown in Fig. 2a.

Table 1 Property of PCL biopolymer

Property	Value
Chemical formula	(C ₆ H ₁₀ O ₂) _n
Form	Strip
Dimension	25.4 X 203 X 1.58 mm (Width,Length,Thickness)
Weight/ Strip	9.24 gram
Density	1145 kg/m ³ at 25 °C
Melting point temperature	57 °C

2.2 Methods

2.2.1 Eco-friendly chemical treatment on *Sesbania rostrata* fibers

The eco-friendly chemical solution was prepared by mixing 10% wt. of powdered NaHCO₃ with 90% vol. of deionized water. The fibers were completely immersed in the solution for a period of 72 hours at 30°C. The chemical reaction that happened in the fiber is presented in Eq. (1). The treated fiber was then washed with deionized water to completely remove the NaHCO₃ left over on the surface of SRF. Finally, the chemically treated SRF was dried in the convention oven at a temperature of 40°C for 24 hours [10]. The dried and treated SRF are shown in Fig. 1a, b.

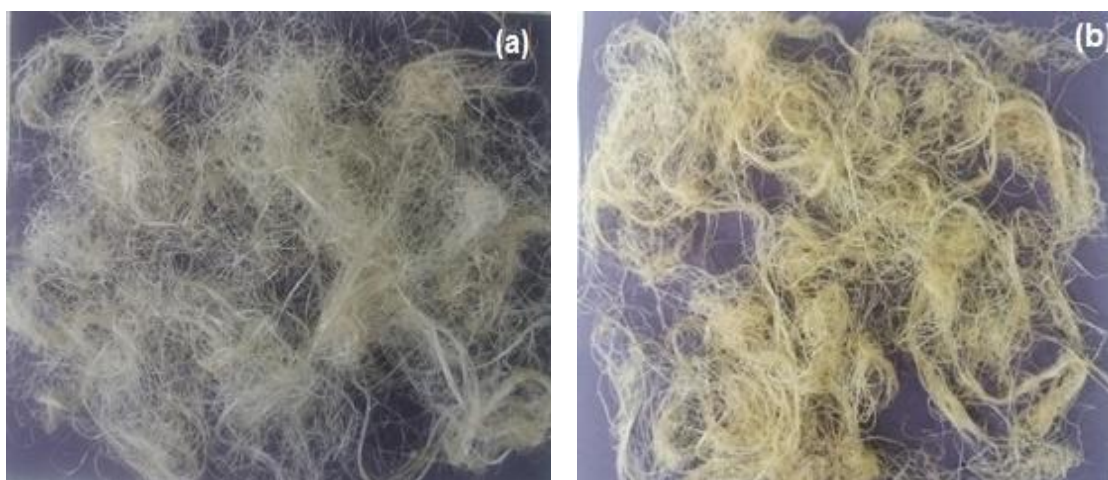
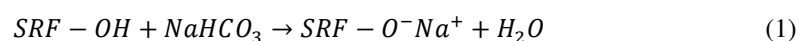


Fig. 1 *Sesbania rostrata* fiber **a** untreated SRF and **b** sodium bicarbonate treated SRF

2.2.2 Preparation of Bio composites

A compression moulding machine was used to prepare PCL/SRF biocomposite specimens at different weight proportions, as mentioned in Table 2. The procedure adopted to prepare the PCL/SRF biocomposite panel is illustrated in Fig. 2. 5 mm of chopped SRF (Fig. 2b) was placed between the strips (Fig. 2d, e) of PCL biopolymer matrix (Fig. 2c) and compressed (Fig. 2a) under a load of 10 kN at 65°C for a period of 50 minutes. The mould was kept at room temperature for curing, and Fig. 2f depicts the final form of PCL/SRF biocomposite.

Table 2 Weight proportions and labeling of PCL/SRF biocomposites

S.No	Fibers	PCL/SRF (Weight %)	Labeling
1	--	100 / 0	PCL
2	Untreated SRF	90 / 10	PCL/ 10USRF
3		85 / 15	PCL/ 15USRF
4		80 / 10	PCL/ 20USRF
5		75 / 25	PCL/ 25 USRF
6		90 / 10	PCL/ 10TSRF
7	Sodium bicarbonate Treated SRF	85 / 15	PCL/ 15TSRF
8		80 / 10	PCL/ 20TSRF
9		75 / 25	PCL/ 25TSRF

PCL polycaprolactone, USRF untreated *Sesbania rostrata* fiber, TSRF 10% sodium bicarbonate treated *Sesbania rostrata* fiber

PCL/USRF untreated *Sesbania rostrata* fiber reinforced polycaprolactone biocomposites

PCL/TSRF sodium bicarbonate treated *Sesbania rostrata* fiber reinforced polycaprolactone biocomposites



Fig. 2 Making of PCL/SRF biocomposite Panel (a) Compression moulding machine **b** Chopped SRF **c** PCL strips **d** SRFs on PCL strips **e** Arrangement of PCL strips and SRFs and **f** Biocomposite panel

2.2.3 Characterization of PCL/SRF bio composites

The tensile strength, percentage of elongation and Young's Modulus of PCL/SRF bio composites at different weight proportions was tested in accordance to ASTM D3039-14 standard. The PCL/SRF bio composites specimens were tested in KALPAK UTM (Universal Testing Machine) Maharashtra, India, model of KIC-2-1000-C, Capacity of 100 KN. The tensile test of the specimen was done at 30°C (room temperature) with a loading value of 3 mm/min. 5 samples were tested in each category and the average of 5 samples value is presented as the final value.

The flexural strength of PCL/SRF biocomposite was found by testing 5 specimens on KALPAK UTM (Universal Testing Machine) Maharashtra, India, model of KIC-2-1000-C, Capacity of 100 KN. ASTM: D790-15 standard was followed to investigate the flexural properties. 50 mm length composite specimen was placed between the supports in the middle position and load was applied at a rate of 3 mm/min.

According to ASTM: D4812 standard, impact test of PCL/SRF bio composites were performed in digital Izod impact tester of model TEXC-22D, Capacity 1- 22 J, Jinan, China. The samples were tested at 30° C (room temperature). The thermal properties of PCL/SRF biocomposite was presented with the results of Differential Scanning Calorimetry (DSC) analysis of TA Instruments, Model of Q20, New Castle, United States. 3 samples of PCL/SRF biocomposite in powder form were tested by heating and cooling at a rate of 10 °C/min under nitrogen flow as per ASTM E794 standard. Test samples were heated from -20 °C to 100 °C and then held at 100 °C for 5 minutes, then it was cooled to 20 °C followed by heating to 100 °C [6]. By substituting the following parameters in Eq. (2) gave crystallinity Index (X_c %) of PCL/SRF bio composite. ΔH_m (measured enthalpy of melting of the sample (J/g)), ΔH_o as 139.5 J/g and weight percentage of fiber as W_{fiber} .

$$X_c \% = \frac{\Delta H_m}{\Delta H_o(1-W_{fiber})} \times 100 \quad (2)$$

The water absorption property for PCL/SRF bio composites was investigated in accordance to ASTM D570 standard. Each sample weighed on an electronic weighing gauge of 1×10^{-3} gram accuracy and it recorded as W_{ds} (Weight of dry sample). The samples were dried inside an oven at a temperature of 60 °C for 6 hours before weighing. Then, the samples were immersed in a water bath at 30 °C (Room Temperature). After every week, the samples were taken out from the deionized water and wiped with tissue paper. It is then weighed and recorded as W_{ws} (Weight of water absorbed sample). The same procedure is repeated for 6 weeks [3]. The water absorption percentage (W_{wa} %) of bio composite is calculated by substituting W_{ds} and W_{ws} in Eq. (3).

$$W_{wa} \% = \frac{(W_{ws} - W_{ds})}{W_{ds}} \times 100 \quad (3)$$

The wear behaviour of PCL/SRF bio composites was studied through abrasive wear test using Pin-on-disk, Ducom made, TR-20LE Model, Bohemia, United States. The sample was tested in accordance to ASTM G99 by sliding it against a rotating disc (Steel of Hardness 64 HRC) of $8 \times 8 \times 50$ mm³. The wear test was performed at normal load of 10, 15, 20, 25 and 30 Newton. Sliding distance and speed were maintained as 500 meter and 0.5 meter/second respectively. After each test, weight loss of the specimen was measured with electronic weighing gauge of accuracy 1×10^{-3} gram [11]. Scanning electron microscope (SEM) captured the images of fractured bio composite specimens under different mechanical test at various magnification. A gold-coated fractured specimen was imaged in vacuum using a SUPRA Zeiss SEM, Oberkochen, Germany.

3. Result and Discussion

3.1 Tensile strength of PCL/SRF

Using the Stress-Strain curve in Fig. 3a, it is clearly evident that PCL biopolymer has high ductility properties. Stress-Strain curve of PCL biopolymer reveals that deformation occurs in three stages during tensile testing. In the first stage, stress and strain have linearly changed by elastic behaviour till the yield point. During the second stage, the neck formed (Fig. 4a), whereas the changes in strain and stress have almost been constant. According to Sarasini et al. [12], the cold drawing characteristic of PCL biopolymer causes macromolecular mobility. Due to the greater extension of PCL in the third stage, biopolymer became thinner (Fig. 4b). No failures have been reported till the grip end of the sample. Dhakal et al. [4] have also observed the same result. Incorporating 10 and 15% wt of untreated SRF in PCL biopolymer exhibits similar strain behavior, however, the tensile stress value has improved compared to PCL biopolymer. Brittle fractures were observed in the tensile test of PCL/SRF bio composite only after adding 20 and 25% wt of untreated SRF. Stress-strain characteristics of the bio composite have been greatly impacted by the increasing amount of untreated SRF [12]. With a 25% weight contribution, fibers no longer contribute to the increase in tensile stress of the bio composite. As shown in Fig. 3b, PCL treated with SRF exhibited similar Stress - strain behavior to PCL untreated with SRF,

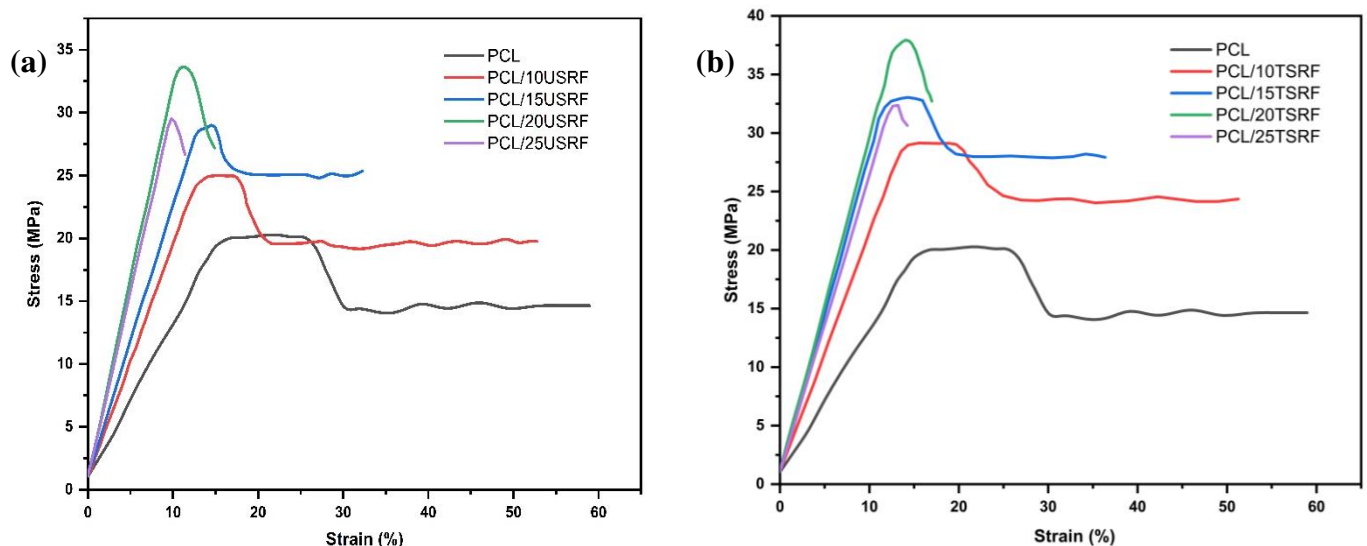


Fig. 3 Tensile Curve of **a** PCL and PCL/USRF biocomposites and **b** PCL and PCL/TSRF biocomposites

As a bar chart, the tensile properties of PCL/SRF bio composite such as tensile strength (Fig. 5), Young's modulus (Fig. 6) and strain at break (%) have been plotted in relation to SRF weight (%) on untreated and treated samples. The tensile strength of PCL biopolymer is 20 ± 2.45 MPa. Inclusion of untreated SRF has increased the tensile strength value after including 10, 15, 20 and 25% of unstained SRF by 25.3 MPa, 28.9 MPa, 33.6 MPa and 29.5 MPa. Table 3 lists the tensile properties of untreated and treated SRF. SRF was chemically treated with sodium bicarbonate to remove impurities and improve tensile strength [10, 13]. Accordingly, treated SRF inclusions showed better tensile strength for bio composites as well as percentage improvements of 15.5, 14.2, 12.8 and 9.8 at 10, 15, 20 and 25% respectively. Both treated and untreated SRF inclusions have shown a decrease in tensile strength at 25% wt. The uneven distribution of SRF results in the bio composites being unable to withstand prolonged tensile loads and failing less than 20% wt. of SRF [14]. The fibers-rich zone appeared on the SEM image of PCL/ 25 USRF (Fig. 8a) which clearly confirmed the agglomeration of fibers happened which falls down the strength compared with PCL/ 20 USRF. The maximum strength of PCL bio composite (37.9 ± 3.3

MPa) was achieved with the addition of 20 % wt of treated SRF and it has 89.5% greater strength than PCL biopolymer.

Table 3 Tensile strength of untreated and treated SRF [10]

Fiber	Tensile strength (MPa)	Elongation at Break (%)	Young Modulus (GPa)
Untreated SRF	353.5±28.15	1.43±0.54	40.17±10.05
Treated SRF	439±26.31	1.65±0.61	42.83±6.92

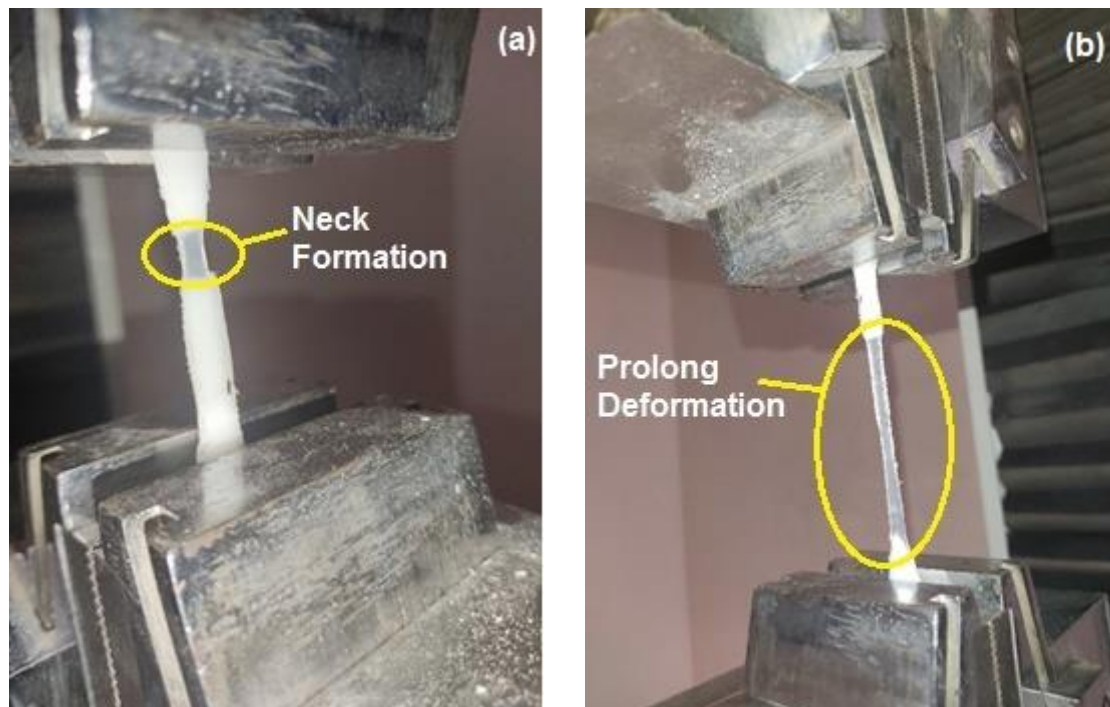


Fig. 4 PCL biopolymer tensile test at UTM **a** neck formation and **b** prolong Deformation

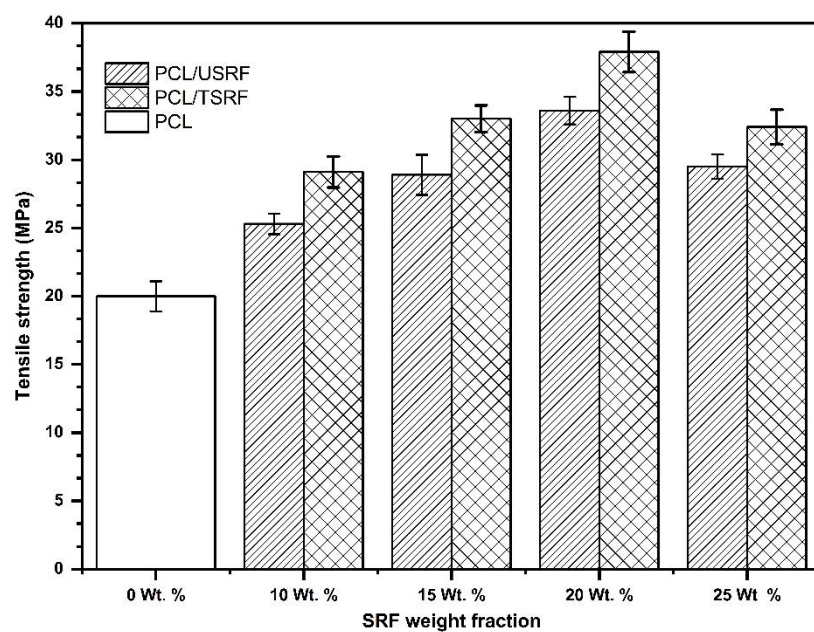


Fig. 5 Tensile strength of PCL and PCL/SRF biocomposites

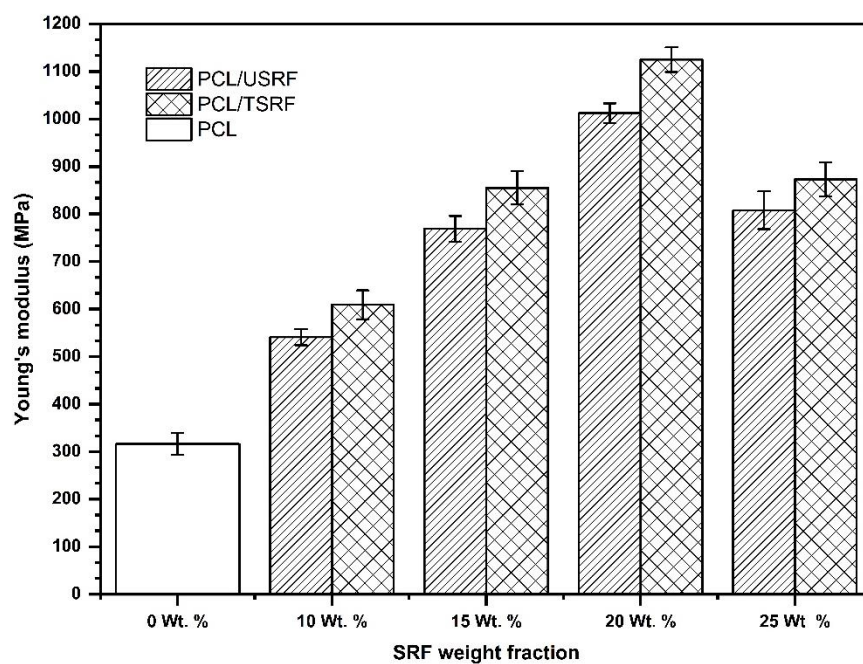


Fig. 6 Young's modulus of PCL and PCL/SRF biocomposites

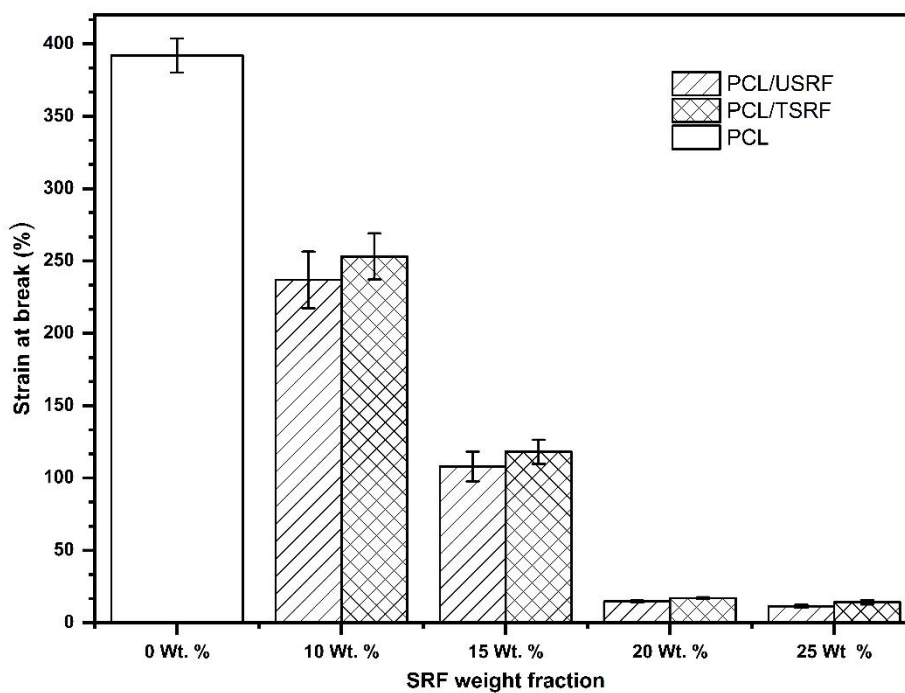


Fig. 7 Strain at Break (%) of PCL and PCL/SRF biocomposites

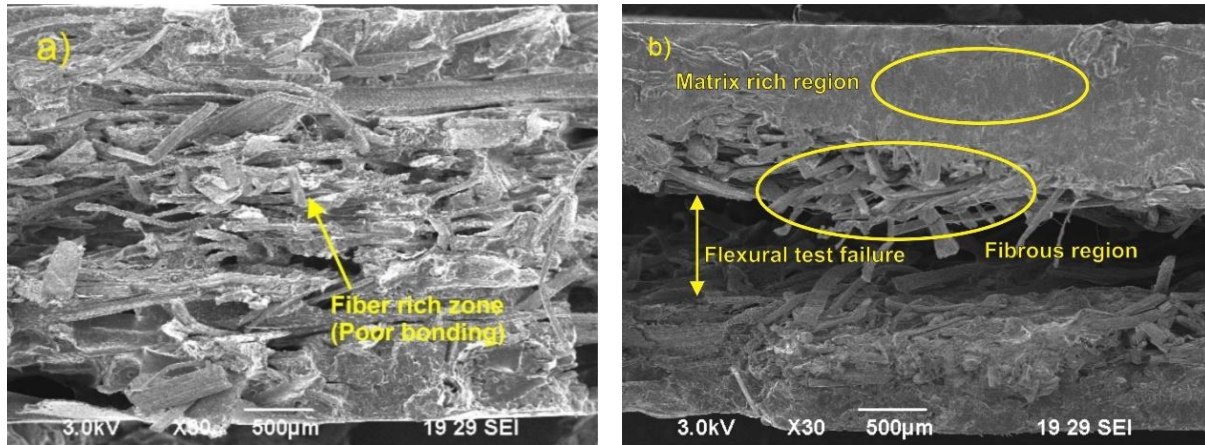


Fig. 8 SEM images of PCL/25USRF composite **a** tensile fractured sample and **b** flexural fractured sample

A similar pattern of increases in Young's modulus was observed (Fig. 6) in PCL/SRF bio composites when SRF was added (untreated/treated). Also, the addition of treated SRF improved the Young's modulus value in comparison with untreated SRF. The 20 % wt treated SRF PCL biocomposite has a Young's modulus value of 1125 ± 57.9 MPa and it is the maximum among PCL/SRF biocomposites. Its value is 3.56 times greater than PCL biopolymer and 11.16 % greater than PCL/ 20 USRF bio composite.

During the tensile test, the PCL biopolymer did not fail because of its extremely high ductility. It was subjected to elongation up to the UTM fixture end [15]. The PCL biopolymer has achieved a final strain (%) value of 392 ± 26.3 %. By incorporating brittle SRF with PCL, the strain (%) value was significantly reduced, as illustrated in Fig. 7. The strain at break (%) is noted as $237 \pm 43.4\%$, 108 ± 22.7 , $14.8 \pm 1.73\%$ and 11.4 ± 2.45 at 10 %, 15 %, 20 % and 25 % loading of untreated SRF in the PCL bio composite. It was found that the stiffness and strength properties of SRF restricted the continuous elongation of the PCL bio composite and that the strain at break (%) value was minimized when SRF was added to the PCL bio composite at an increased weight percentage [3, 15, 16]. Sarasini et al. [12] have also observed a similar reduction in strain at break (%) value when ramie fibers are combined with PCL biopolymer. 550 % strain at break of 100 wt% of PCL biopolymer is significantly reduced to 40% and 5% after 20% and 30% ramie fiber is added with PCL. A slight increase in Strain (%) value has been observed for PCL/TSRF bio composites when compared to PCL/USRF bio composites. As a result of the chemical treatment, the ductility property of SRF was marginally enhanced by rearranging the fibrils in the fiber [10].

3.2 Flexural Strength of PCL/SRF Biocomposites

During the flexural test, tensile, compression, and shear forces act cumulatively to determine the value of the flexural strength. A bar chart (Fig. 9) illustrates the effect of incorporating treated and treated SRF with the PCL on the flexural strength of bio composites. SRF has continued to increase in flexural strength as the loading of both treated and untreated has been increased up to 20% weight loading of SRF. It was noticed that the flexural strength of PCL biopolymer has improved from 19.1 ± 1.11 MPa to 24.4 ± 1.5 MPa after the addition of 20 % weight of untreated SRF, which represents an improvement of 28 %. The results indicate that SRF has given a positive effect to the PCL biocomposites, as well as a good bonding nature to PCL, which has resulted in a greater flexural strength. PCL's flexural strength decreases when fiber loading is increased from 20% to 25%. Uneven distribution of SRF (Fig. 8b) occurs at the 25% weight loading point and leads to the formation of a high tension region that causes earlier failure [14]. The maximum flexural strength of PCL composite is 26.8 ± 2.67 MPa at a loading of

20% weight treated SRF. As compared to untreated SRF, treated SRF increased the flexural strength of PCL composite by 9.8% at 20% weight. As a result of the chemical treatment, the interfacial adhesion between the fiber and biopolymer was enhanced, enabling the fiber to withstand the higher loading under test [17].

The flexural modulus of PCL biopolymer and PCL bio composites with various weight proportions of both untreated and treated SRF is shown as a bar chart in Fig. 10. The modulus of the bio composite is improved after the addition of both treated and treated SRF at all weight percentages. Based on the bar chart, it can be clearly seen that the PCL bio composites loaded with treated SRF have a higher modulus compared with those that are loaded with untreated SRF. As a result of the chemical treatment, fibers were defibrillated, improving the surface contact between SRF and PCL. The maximum flexural modulus of PCL bio composite is found as 1314 ± 127 MPa at 20 wt. % loading of treated SRF. It is 3.02 times higher than PCL biopolymer and 1.30 times higher than 20 PCL/USRF.

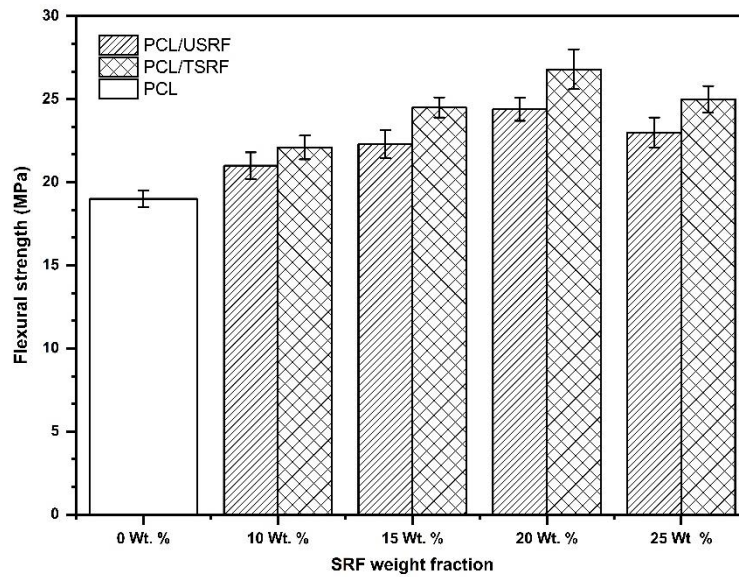


Fig. 9 Flexural Strength of PCL and PCL/SRF biocomposites

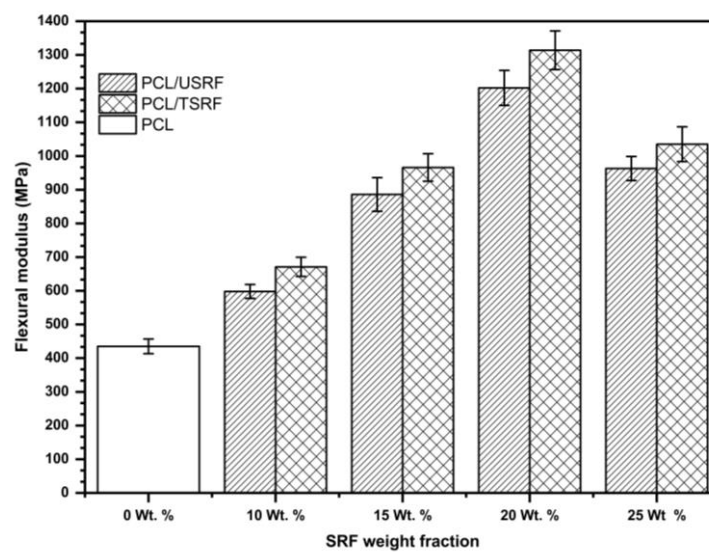


Fig. 10 Flexural modulus of PCL and PCL/SRF biocomposites

3.3 Impact Strength of PCL/SRF Biocomposites

An impact test has been performed on the PCL composite to determine its resistance to impact loads. Figure 11 shows the impact strength of PCL polymer with weights of 10%, 15%, 20%, and 25% for both untreated and treated SRF PCL composites. As shown in the figure, the PCL/SRF composites, both treated and untreated, have improved impact strength as fiber weight percentages increase up to 20 percent. Further increasing the SRF weight percentage (25%) in the PCL composite has resulted in a reduction in strength due to the stress concentration caused by the irregular distribution of fiber clusters during composite processing. All weight percentages of PCL/TSRF composites have greater impact strength than PCL/USRF composites. By chemically treating the fiber, the impurities on the surface were removed, and the roughening of the surface creates a stronger bond between the fiber and polymer. 20PCL/TSRF biocomposite has obtained maximum impact strength of 327 ± 36 J/m which is 29.7% greater than PCL biopolymer and 7.5% greater than 20PCL/USRF biocomposite.

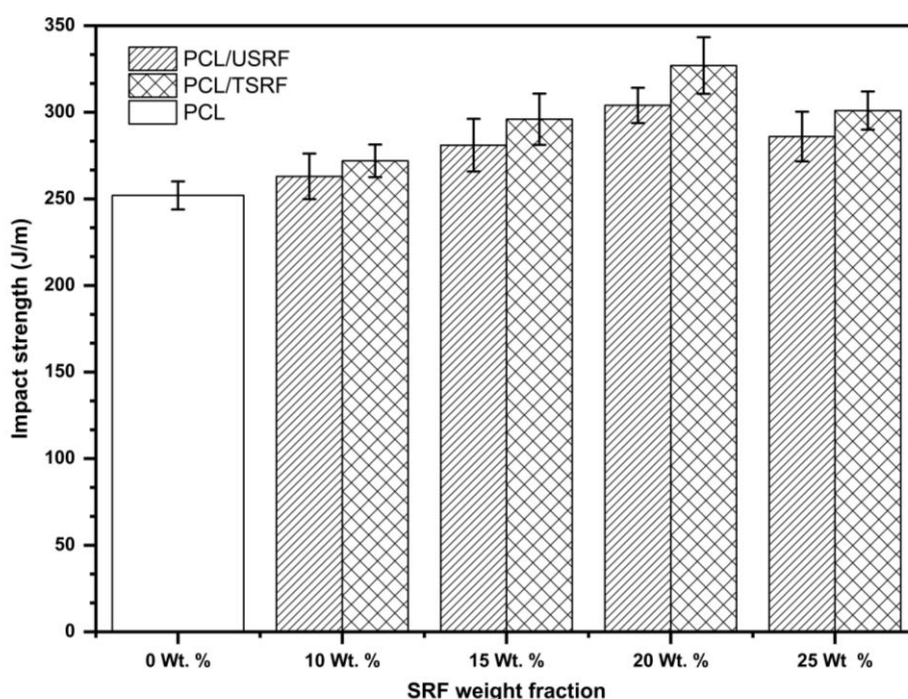


Fig. 11 Impact strength of PCL and PCL/SRF biocomposites

3.4 Thermal Analysis of PCL/SRF Biocomposites

Analyzing the thermal properties of biopolymer composites is crucial to understanding and producing various products for automotive, packaging, and biomedical applications. A thermogram of PCL, PCL/USRF, and PCL/TSRF composites is shown in Fig. 12 (Heating Curve) and Fig. 13 (Cooling Curve). Table 4 shows parameters such as degree of crystallinity (calculated using Eqn. 2.2) melting temperature (T_m) and crystallization temperature (T_c) derived from DSC thermograms. A transition from an exothermic crystallization to an endothermic melting of the PCL and PCL/SRF biocomposites was observed when the PCL and PCL/SRF biocomposites were cooled and heated, respectively.

PCL is a semicrystalline biopolymer with a crystallization temperature (T_c) of $27.4 \pm 0.6^\circ\text{C}$. As compared to PCL, the crystallization temperature of PCL/USRF and PCL/TSRF composites is higher at all weight percentages of fiber content, since biocomposite fibers form more nuclei due to heterogeneous nucleation [16].

PCL/SRF biocomposites have a lower enthalpy of crystallization (ΔH_c) than PCL biopolymers due to the physical presence of SRF, which accelerates the exothermic crystallization process. Matching PCL/USRF cooling curves (Fig. 12a) with PCL/TSRF curves (Fig. 12b) revealed that PCL/TSRFs have narrower curves and peaks at higher crystallization temperatures. As a result of sodium bicarbonate treatment, the surface of the SRF was modified, which led to positive nucleation effects in the exothermic process [18].

There was no significant difference between PCL/SRF biocomposites (57°C) and PCL (57°C) after the addition of non-treated SRF content with the PCL biopolymer. It was also observed by Cocca et al. [19] that the melting temperature of PCL was not affected by the addition of 10, 20 and 30% of amorphized cellulose. The results of this experiment indicate that non-treated SRF has no effect on the melting temperature of PCL biocomposite. The incorporation of SRF with PCL has reduced the endothermic melting area of the composite compared to PCL, as well as the enthalpy of melting (ΔH_m) value of PCL/SRF composites.

By replacing the weight fraction of fiber (0 wt%) and the enthalpy of melting (65.3 J/g) in Eqn. 2.2, the degree of crystallinity of PCL-neat composite is predicted to be 46.8%. For the untreated SRF at loadings of 10, 15, and 20%, the degree of crystallinity increased by 48.4, 49.3, and 51.2%, respectively. The melting temperature of PCL, PCL/USRF and PCL/TSRF biocomposites are found in Fig. 13a, b. The nucleating action of SRFs at various biocomposite sites has a favourable impact on PCL/SRF composites [3]. PCL/25SRF has a noticeably lower melting temperature, enthalpy of melting, and degree of crystallinity than PCL/20SRF. Higher fiber loading prevents PCL chains from being rearranged into their lattice, which restricts the lowering of thermal characteristics [16]. The highest melting temperature ($58.4 \pm 0.7^\circ\text{C}$) and crystallinity ($52 \pm 0.5\%$), which are 2.45% and 11.24% higher than PCL, respectively, are found at PCL/ 20TSRF. From this, it may be inferred that the NaHCO_3 treatment enhances crystallinity by enhancing the biocomposite ability of fibers to form crystals.

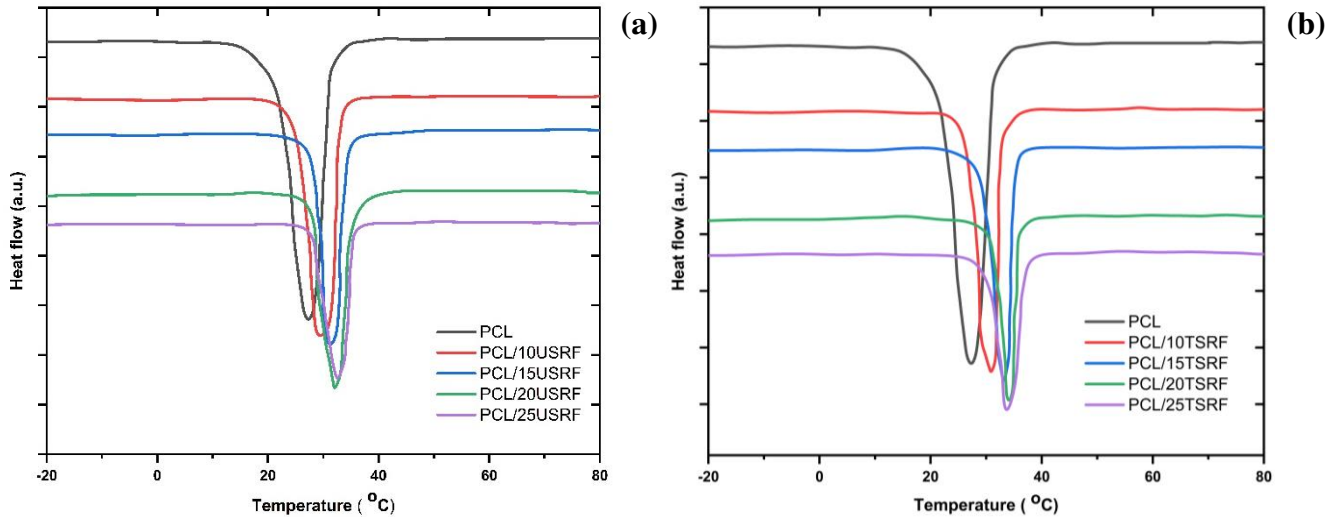


Fig. 12 DSC cooling curve of **a** PCL/USRF composites and **b** PCL/TSRF composites

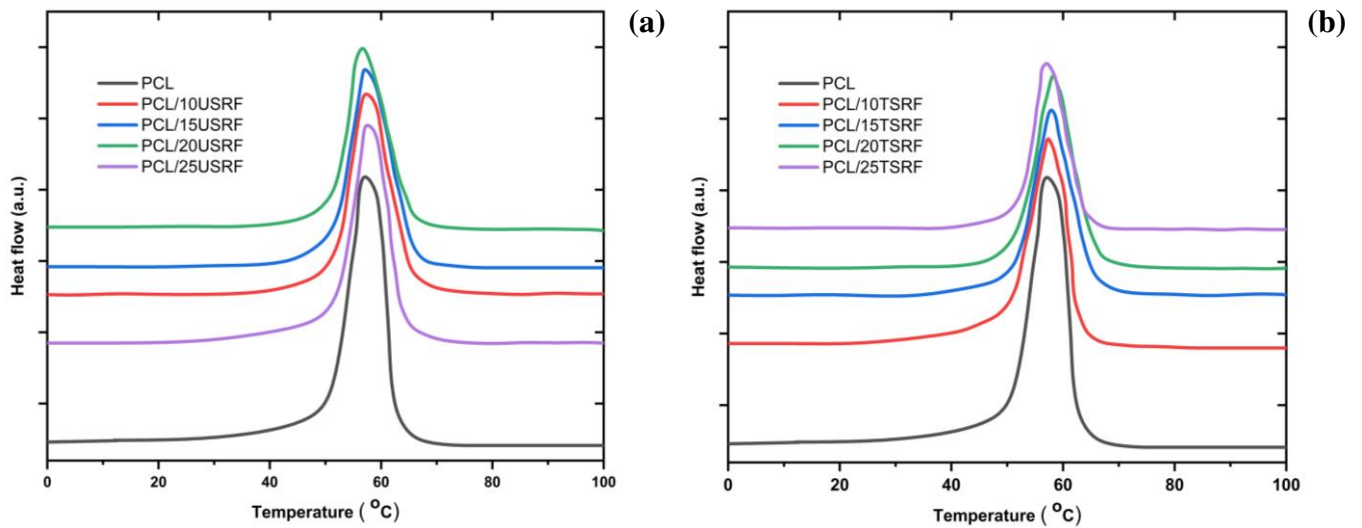


Fig. 13 DSC heating curve of **a** PCL/USRF composites and **b** PCL/TSRF composites

Table 4 Crystallization and melting temperature with the corresponding enthalpy for PCL, PCL/USRF and PCL/TSRF composites

Samples	Crystallization temperature (T_c) °C	Enthalpy of crystallization (ΔH_c) J/g	Melting temperature (T_m) °C	Enthalpy of melting (ΔH_m) J/g	Crystallinity Degree (X_c) %
PCL	27.4±0.6	63.2±0.3	57±0.1	65.3±0.5	46.8±0.4
PCL/ 10USRF	29.8±0.3	58.5±1.7	57±0.7	60.8±0.5	48.4±0.7
PCL/ 15USRF	31.4±0.5	56.2±0.6	57±0.8	58.5±0.2	49.3±0.3
PCL/ 20USRF	32.1±0.7	53.7±1.3	57±0.5	57.2±0.8	51.2±1.1
PCL/ 25 USRF	32.5±1.3	55.1±0.5	55.2±0.2	51.4±0.6	49.1±0.6
PCL/ 10TSRF	30.9±0.5	56.4±0.3	57.5±0.7	61.9±2.1	49.3±1.8
PCL/ 15TSRF	33±0.4	54.1±1.1	57.8±1.4	60.2±0.7	50.7±0.8
PCL/ 20TSRF	34.3±0.5	51.5±0.7	58.4±0.7	58.1±0.4	52±0.5
PCL/ 25TSRF	34±0.8	53.2±0.7	57.2±0.4	52.6±1.1	50±1.3

3.5 Water absorption characteristic of PCL/SRF composites

It is essential to study the water absorption characteristics in biocomposites, as the water absorbed in the composite may reduce the bonding between natural fibers and polymers, thereby affecting the mechanical strength of the composite. These characteristics are crucial for determining the biocomposite's potential applications. In Figure 14, water gain percentage values for PCL, PCL/USRF, and PCL/TSRF biocomposites are indicated with fiber loadings of 10, 15, 20, and 25 wt.%. Figure 15 illustrates the equilibrium water gain percentage value of PCL, PCL/USRF, and PCL/TSRF biocomposites as a function of fiber loading.

Over a period of six weeks, the PCL biopolymer absorbs very little water, and the water gain percentage (0.21 ± 0.02) is almost at equilibrium after three weeks. The results show that PCL biopolymer is hydrophobic [19]. For PCL/SRF biocomposites with different fiber loadings, the water gain percentage curve shows three well-defined sections. Due to the hydrophilicity of SRFs and the fact that more water permeated the spaces between

fibers and matrix in the initial section of the biocomposites (time up to two weeks), the rate of water absorption was extremely rapid [20]. The second section consists of an interim interval during which water is progressively absorbed (2 weeks < time < 4 weeks). The rate of water absorption is extremely sluggish and nearly reaches saturation in the final segment (time greater than 4 weeks). The proportion of water gain in PCL/SRF biocomposites curves has gradually increased by 10, 15, 20, and 25 weight percent of fiber loading, as shown in Fig. 14. This is because composite materials now contain hydrophilic SRFs. In comparison to PCL and biocomposites, 25% PCL/SRF biocomposites showed higher water gain percentages.

The percentages of water gain for PCL biopolymer, PCL/10USRFs, and PCL/ 10TSRF biocomposite were 0.14, 1.6, and 1.01%, respectively, throughout the two-week immersion period. According to this finding, sodium bicarbonate treatment reduced SRF hydrophilicity and enhanced fiber adhesion to matrix, preventing the formation of microvoids or gaps within the biocomposites. As a result, PCL/10TSRF had a significantly lower water gain percentage than PCL/10USRF [10]. At remaining fiber loadings of 15, 20, and 25 wt.%, respectively, PCL/USRF and PCL/TSRF biocomposites have comparable water gain percentages.

PCL/10TSRFs ($2.63 \pm 0.3\%$) and PCL/TSRF ($6.92 \pm 0.55\%$) are the biocomposites' minimum and maximum water gain percentages, respectively. The largest difference seen in the equilibrium water gain percentage between PCL/20TSRFs and PCL/TSRFs is observed to be 1.86%. In the composite, there are more voids or gaps because the fibers are unable to adhere to the matrix well at higher loadings (25 wt.%).

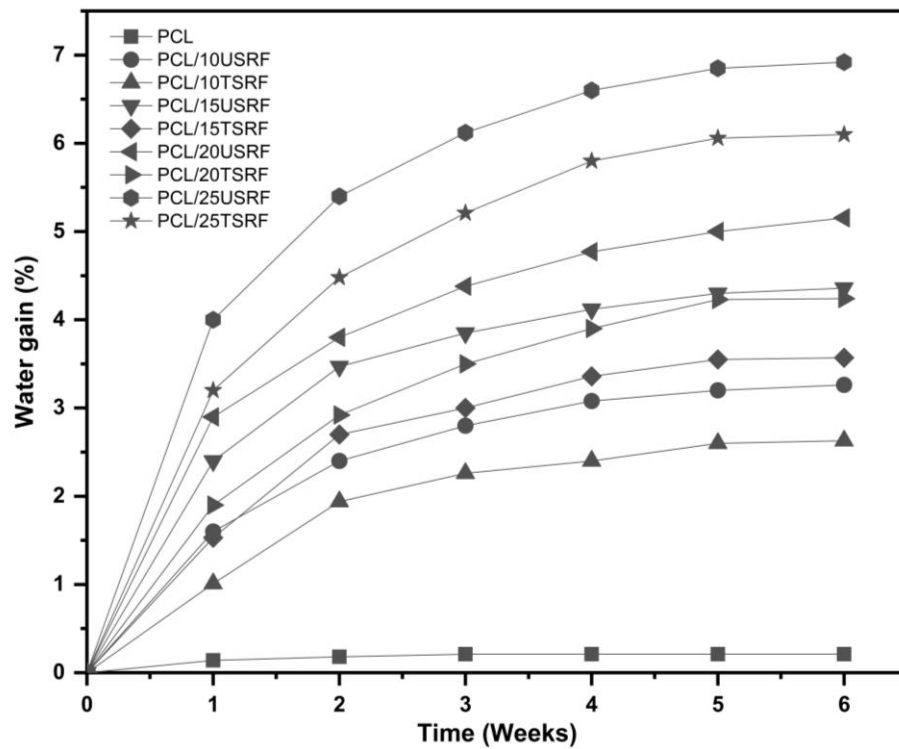


Fig. 14 Water gain percentage of PCL, PCL/USRF and PCL/TSRF biocomposites

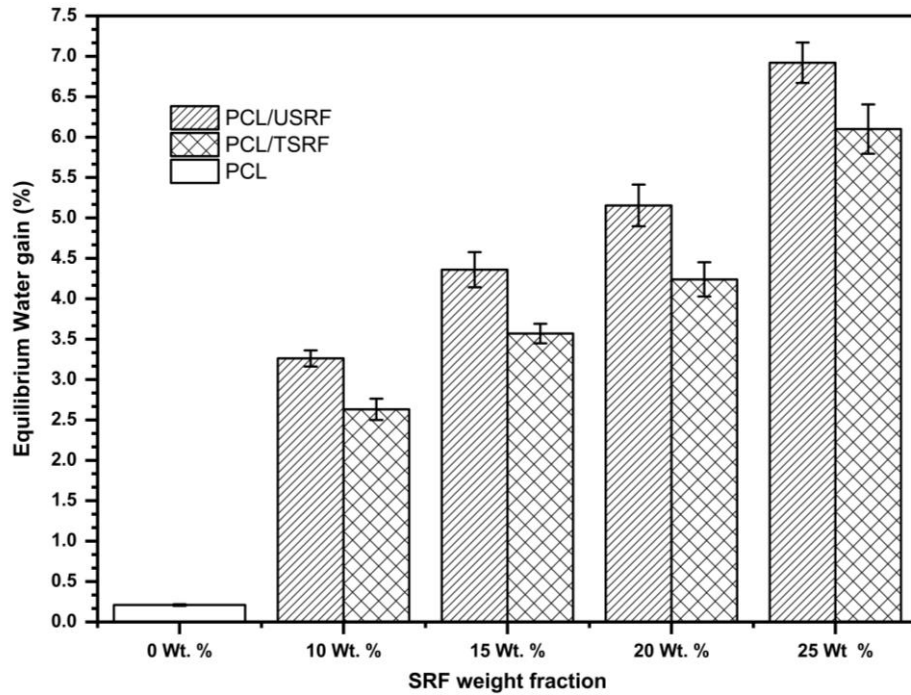


Fig. 15 Equilibrium Water gain percentage of PCL/USRF and PCL/TSRF biocomposites

3.6 Wear characteristic of PCL/SRF composites

When tribological loads cause biocomposites to fail due to wear effects as a result of wear effects, they are frequently employed in automotive and structural applications [21]. To comprehend how biocomposite fibers and fiber treatments affect weight loss under various loading and treatment situations, such as normal load, sliding velocity, and sliding distance, it is vital to analyse the wear characteristics of biocomposite fibers and fiber treatments. When subjected to various normal loads (10 to 30 N) and fiber loads (10, 15, 20, and 25%) at a sliding velocity of 0.5 m/sec and a sliding distance of 500 m, the weight loss (in grammes) of PCL, PCL/USRF, and PCL/TSRF biocomposites is shown in Fig. 16.

Figure 16 shows the PCL biopolymer has higher weight loss compared to PCL/SRF biocomposites at all normal loading conditions. It is evident from this that SRF combined with PCL biopolymer makes the biocomposite resistant to wear (weight loss). It has been demonstrated that the rate of wear (weight loss) of biocomposites is largely determined by their stiffness, hardness, and fiber-matrix adhesion characteristics [22]. Increasing the weight percentage of SRFs in the biocomposites has reduced the weight loss of PCL/SRF composites under all normal loading conditions. As the normal load of PCL/SRF biocomposites has been increased, the weight loss has increased. When the normal load is increased from 10 to 30 N, the weight loss of PCL/SRF biocomposites increases non-linearly. By increasing the normal load from 10 to 20 N, mild wear has been observed on the biocomposites, as the strong bond between SRF and PCL has been able to resist wear to a greater extent [23]. The weight loss behaviour changed from mild to severe wear on PCL/SRF biocomposites when normal load exceeds 20 N. This causes the biocomposite to lose weight (g) at an increasing rate due to an increase in the contact temperature between the biocomposite and the rotating disc, resulting in elastic deformation occurring at the biocomposite's surface asperities. PCL/TSRF biocomposites exhibit minimal weight loss when compared with PCL/USRF biocomposites at all weight percentages. The results demonstrated that sodium bicarbonate chemical treatment improved SRF-PCL adhesion bonding and protected the biocomposite against

wear [24]. The minimum weight loss has been found in the PCL/ 20TSRF biocomposite. Compared with PCL/ 20TSRF biocomposite, PCL/ 25TSRF biocomposite has a greater weight loss because improper distribution of SRF reduces stiffness and adhesion bonding [25].

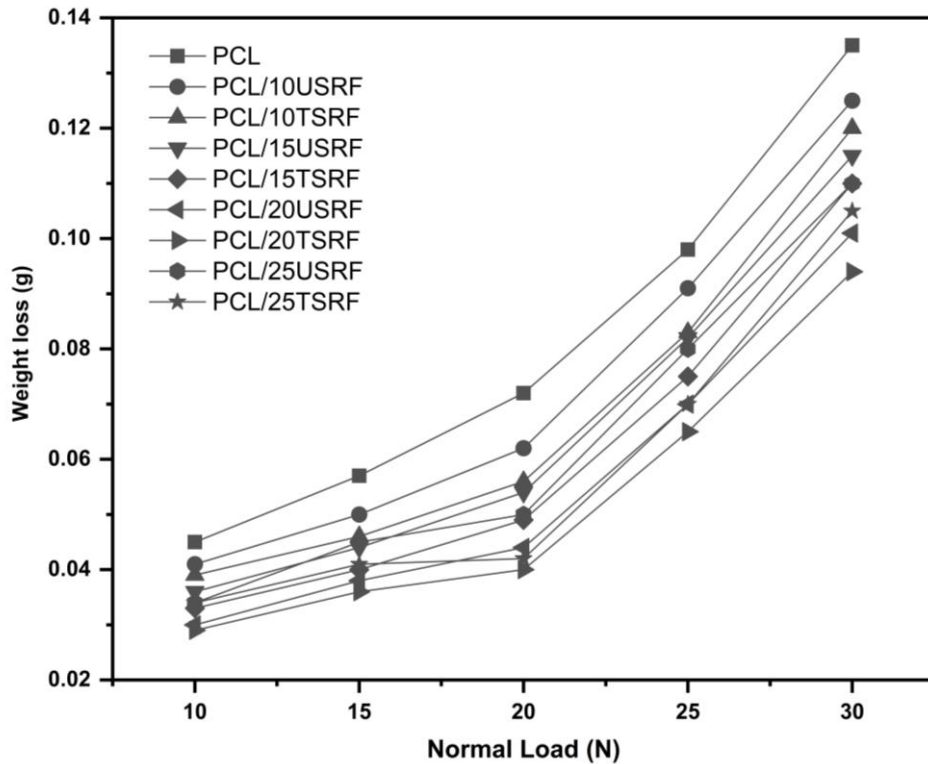


Fig. 16 Wear Weight loss of PCL, PCL/USRF and PCL/TSRF biocomposites

3.7 SEM ANALYSIS OF SRFs/PCL COMPOSITES

In order to discover the failure of samples during mechanical properties testing, the failure analysis of SRFs/PCL composites is carried out using a scanning electron microscope to ascertain the bonding between natural fibers and polymer matrix. The cracked SEM images of tensile, flexural, and impact-tested samples are shown in Fig. 17.

Fibers are clearly seen separating from the matrix and debonding from it in the SEM image of the tension fractured sample (Fig. 17a). This suggests that the link between natural fibers and the biopolymer matrix at the interface is frail. As a result, the tensile strength of composite is impacted, and unexpected failure is possible [26]. The thick and thin cell wall structures of SRFs treated with PCL biopolymer are shown in Fig. 17 b. The sodium bicarbonate treatment successfully bonded the fiber and matrix together, avoiding fiber separation. As a result, fiber fracture occurred under the maximum tensile force.

After being treated with sodium bicarbonate, the majority of SRFs are shown to be strongly bound to the PCL biopolymer matrix in Fig.17c. As a result, fiber pulling and fracture are the most likely causes of flexural failure in biocomposite materials [27, 28]. According to Fig. 17d, the failure of the impact sample is brought on by the fibers pushing out, which causes the fiber to break and the void zone to form. The various regions of fiber-matrix bonding are depicted in Fig. 17e. As a result, the impact stresses were distributed amongst the matrixes and fibers more evenly. The impact strength of composites is also impacted by the weak bonding between the fibers and matrix [29].

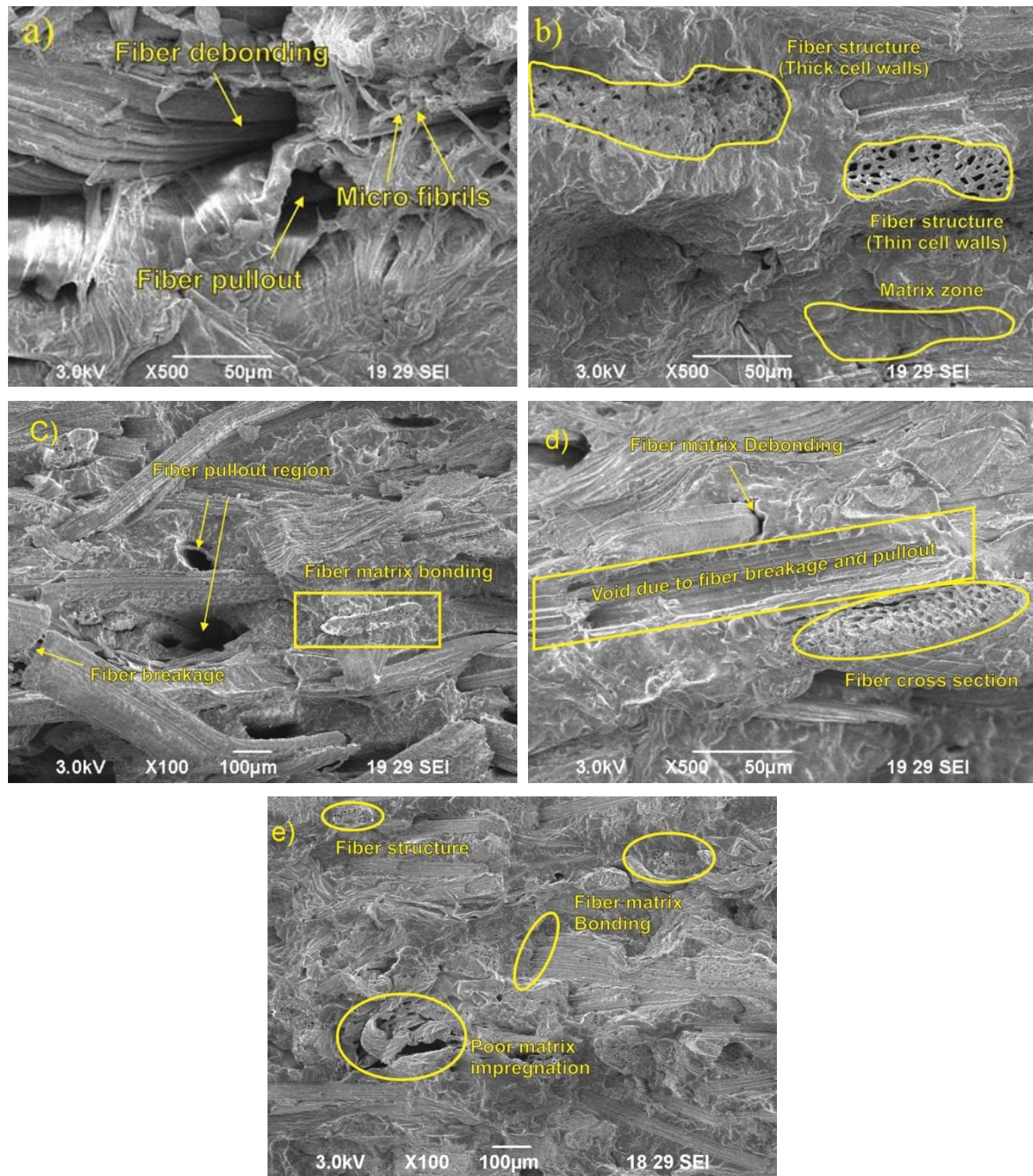


Fig. 17 SEM image of **a** fractured tensile test sample of PCL/20USRF **b** fractured tensile test sample of PCL/20TSRF **c** fractured flexural test sample of PCL/15TSRF composite **d** fractured impact test sample of PCL/15USRF and **e** fractured impact test sample of PCL/15TSRF

4. Conclusion

An advanced biocomposite has been developed by combining *Sesbania rostrata* natural fiber with polycaprolactone (PCL) biopolymer using a compression molding machine. As a result of the good interface and bonding between PCL polymer and the chemically treated SRF, the PCL/ 20 wt % PCL-treated SRF has shown the best mechanical and thermal results. The results of SEM analysis of fractured specimens confirmed this observation. A higher percentage of fiber weight resulted in a higher water absorption by PCL/SRF biocomposites. As a result of adding treated SRF to the biocomposite, weight loss was minimized and wear resistance was maximized on the wear test of the biocomposite. It is important to note that the higher fiber loading

of the PCL biopolymer (25 weight percent) decreases its mechanical properties, thermal properties, and wear resistance. This result was caused by the agglomeration of fibers, which reduced the load sharing and bonding between fibers and polymers. The inclusion of an optimum weight percentage of treated SRF fiber with the PCL has proven that it has greater mechanical, thermal, and wear resistance than PCL, with the added benefit of reducing the cost of the biocomposite and improving rural economic conditions.

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Author contribution

Raja Krishnan: Conceptualization, methodology, writing — original draft preparation. Kathirselvam Muthusamy and Senthil Kumar Marudhamuthu Shanmugam: Investigation, reviewing and editing. Santhanam Kadhiresan: visualization.

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Declarations

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