



Biocomposite composed of PVA reinforced with cellulose microfibrils isolated from biofuel industrial dissipate: *Jatropha Curcus* L. seed shell



Manjula Puttaswamy*, Govindan Srinikethan, Vidya Shetty K

Department of Chemical Engineering, National Institute of Technology Karnataka, Surathkal, Mangalore PIN-575025 India

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ABSTRACT

Biofuel production by *Jatropha Curcas* L. (JC) seeds result in large quantities of unused seed shells contributing as an extensive potential source for cellulose production. Present work consummates on isolation of cellulose microfibrils (CMF) from JC seed shell by chlorination treatment and were characterized using Scanning Electron Microscope (SEM), Fourier Transform Infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and ^{13}C NMR. Removal of hemicellulose and lignin were confirmed from FTIR results. Cellulose microfibrils with diameter 0.23–1.04 μm demonstrated considerable increase in crystallinity and thermal stability by chlorination treatment. Procured cellulose microfibrils were reinforced in Poly-vinyl Alcohol (PVA) by solution casting in water to form biocomposites. Mechanical properties and thermal stability of these biocomposites increased on addition of cellulose microfibril, ensuring the potentiality of cellulose fibers as filler in biocomposites which can reinstate traditional plastics.

1. Introduction

Jatropha Curcas L. (JC) seed oil is one of the extensive sources for biofuel production and is widely cultivated in Africa, America (central and south region), India, and South-East Asia [1]. Large amount of JC seed shell as residue from biofuel production [2] are generally discarded in leachate fills, and few are utilized as source for energy [3] and activated carbon [4].

Several researchers have exploited different sources for cellulose; Rice husk [5], Astragalus gummifer (fabaceae) trunk [6], Rice straw [7], Jerusalem artichoke stem [8], Arecanut husk fiber [9], Eucalyptus sawdust [10], Cotton stalk bark [11], and Grape fruit peel [12]. Exiguous publications are reported on extraction of cellulose fibers from JC seed shell. Distinct methods like chemical, mechanical and chemo-mechanical methods have been employed in extraction of cellulose fibers. Chlorination treatment is one of the chemical methods where in sodium chlorite, bleaches the fibers to remove the lignin matrix [13] and the resulting holocellulose is further alkali treated with NaOH to separate hemicellulose from cellulose [14].

Cellulose due to its high crystalline nature when used as filler in biocomposites result in improved mechanical properties [15]. The most challenging task is dispersion of the cellulose, due to presence of –OH groups and their hydrophilic nature. To overcome this problem, PVA a biodegradable and hydrophilic polymer can be incorporated as matrix which is compatible with cellulose fibers [16]. Solution casting aids in

preparation of composites at less energy consumption compared to hot pressing and compression molding methods. Thus, the biocomposites were prepared by solution casting isolated cellulose microfibrils and PVA in water.

In the present work cellulose microfibrils were isolated from JC seed shell by chlorination treatment. Assorted weight percent of procured cellulose microfibrils were reinforced in PVA matrix by solution casting and their effect on the thermal stability and mechanical properties were analyzed.

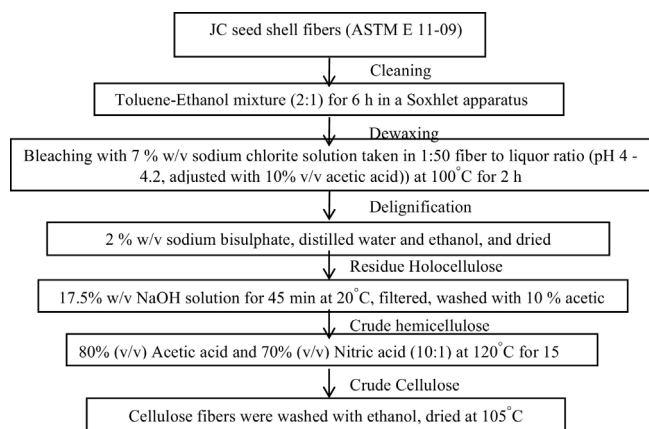
2. Materials and methods

2.1. Materials

Jatropha Curcas L. seed shells were received from the “SEEDS” Research Centre, University of Agricultural Sciences, Bangalore, India. Acknowledged shells were water washed to remove mud particles and were sundried. Further they were grounded, passed through 60 mesh sieve and stored in polythene bags. Poly-vinyl Alcohol (PVA) (typical average molecular weight 85000 to 124000, degree of hydrolysis 86–89%) was procured from Central drug house (CDH) Pvt. Ltd India. All the other chemicals used were of Laboratory grade.

* Corresponding author.

E-mail address: manjuchintoo2@gmail.com (M. Puttaswamy).



Scheme 1. Isolation of cellulose microfibrils from JC seed shell.

2.2. Experimental methods

2.2.1. Isolation of cellulose microfibrils

Cellulose microfibrils were isolated from the JC seed shell fibers by chlorination treatment [17] presented as schematic diagram in Scheme 1.

2.2.2. Biocomposites preparation

Biocomposites films were prepared by casting cellulose microfibrils

and PVA in water. 10 wt% PVA solution was prepared under mechanical stirring for 12 h at room temperature. PVA solution and cellulose fiber dispersed solution were mixed by further stirring for an hour. The filler-matrix mixture was cast onto a Petri dish and was dried at 37 °C in oven for removal of water [18]. The composite films were casted such that the cellulose microfibril concentration in the final composites was 0, 5, 10, and 20 wt.% with respect to the polymer.

2.3. Characterization

2.3.1. SEM

The JC seed shell and isolated cellulose microfibril were washed with distilled water, filtered and dried in oven at 105 °C, until consistent weight of fibers was measured. Later the fibers were stored in desiccator until taken for the analysis. The morphological structure of gold sputtered JC seed shell and isolated cellulose microfibrils were observed under SEM (JSM-6380LA, JEOL, EVISA). The micrographs were recorded at acceleration voltage of 5–8 kV.

2.3.2. FTIR spectroscopy

JC seed shell and isolated cellulose fibers mixed with KBr were pressed to form transparent thin pellets. The FTIR spectra of the fibers were recorded in the range of 400–4000 cm^{-1} with resolution of 4 cm^{-1} using FTIR instrument (Jasco 4200, Jasco analytical instruments, USA).

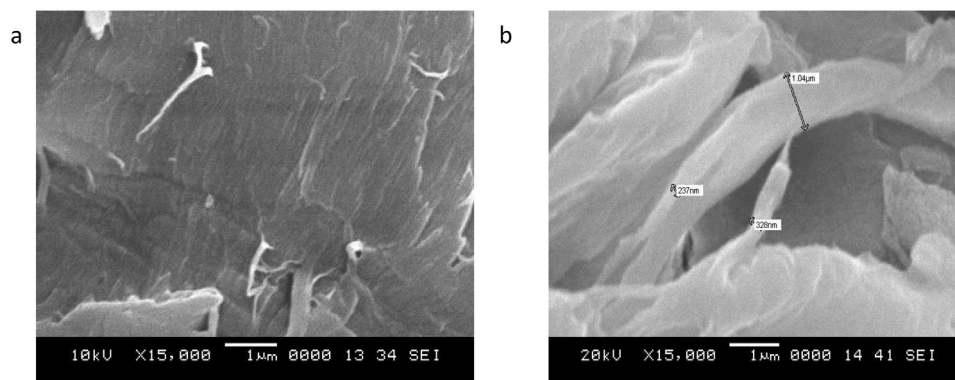


Fig. 1. SEM micrographs of the a) JC seed shell fibers seed shell and b) cellulose microfibrils.

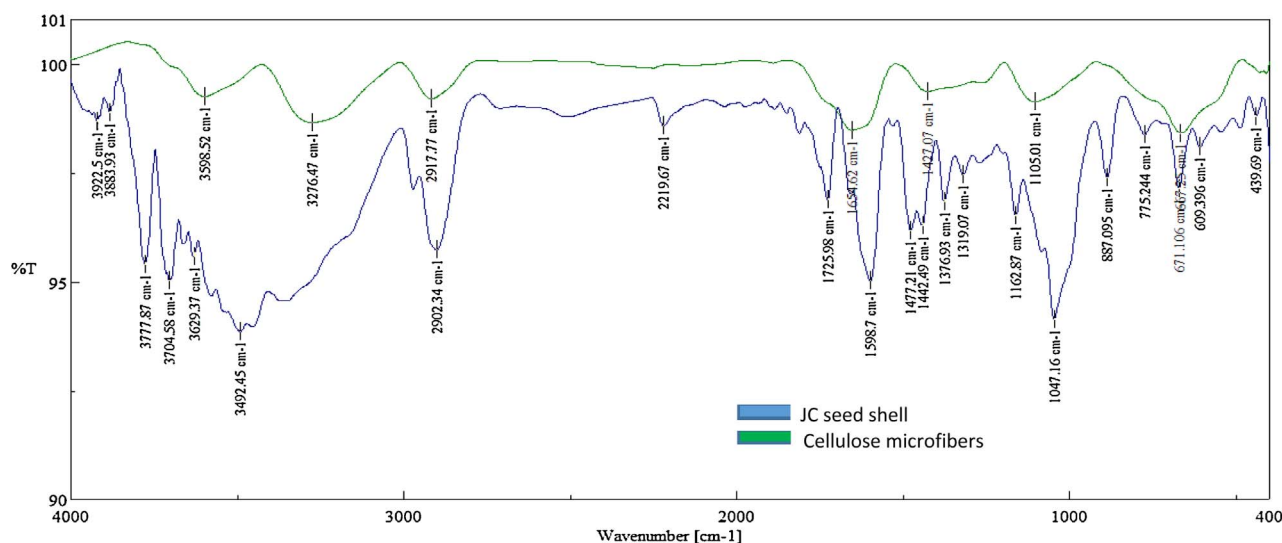


Fig. 2. FT-IR spectra of purified JC seed shell fibers and cellulose microfibrils.

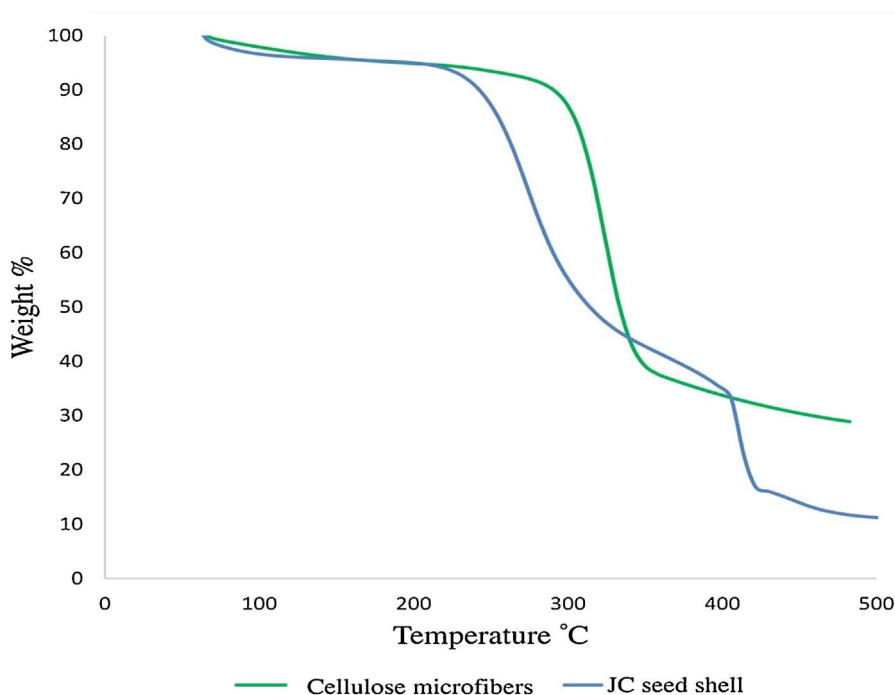


Fig. 3. Thermograms of JC seed shell fibers and cellulose microfibrils.

2.3.3. XRD analysis

XRD measurements for JC seed shell fibers and isolated cellulose microfibrils were obtained by X-ray Diffractometer (D/max 2200, Rigaku, Japan) using Cu K α radiation (1.5406 Å) with Ni-filtered at 40 kV, 15 mA. Scattered radiations were recorded in the range of $2\theta = 10^\circ\text{--}30^\circ$ at a scan rate of $2^\circ/\text{min}$. The Segal method (Eq. (1)) was used to calculate crystallinity Index (CI) considering heights of 2 0 0 peak (I_{200} , $2\theta = 22.6^\circ$) and the intensity minimum between the 2 0 0 and 1 1 0 peaks (I_{am} , $2\theta = 18^\circ$), Where I_{200} represents intensities of crystalline and amorphous material and I_{am} for the amorphous material.

$$CI\% = \left(1 - \frac{I_{am}}{I_{200}}\right) \times 100 \quad (1)$$

2.3.4. TGA

Thermograms for JC seed shell, cellulose microfibrils and biocomposites were determined using a thermogravimetric analyzer (Extra 6000, TG/DTA6300, SII nano technology Inc., Japan) at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere.

2.3.5. ^{13}C NMR (CP/MAS)

Spectra of JC seed shell fibers and isolated cellulose microfibrils were run on solid-state NMR spectrometer (Bruker DSX 300 MHz). Operating frequency was fixed at 75.46 MHz for ^{13}C nuclei. Fibres were spun at 7.5 kHz spinning rate with filled 5 mm rotor at room temperature.

2.3.6. Tensile properties of composites

Tensile properties of the cellulose microfibrils –PVA composites were measured at room temperature (25°C) using universal testing machine (AG-X plus, Shimadzu, Japan) with 100 kN load and

$15\text{--}20\text{ mm}/\text{min}$ cross head speed. The specimen dimension was $40 \times 22 \times 0.1\text{ mm}$ and at least 5 sample specimens for each set were tested as per ASTM D882-02 [19] to get the average value.

3. Results and discussion

3.1. Characterization results

The cellulose fibers isolated from JC seed shell by chlorination treatment were characterized for their morphological features, thermal stability and also to ensure removal of matrix components lignin and hemicellulose. The scanning electron microscope images of JC seed shell fibers as presented in Fig. 1a show compact arrangement of hemicellulose and cellulose in lignin matrix whereas in case of isolated cellulose microfibrils shown in Fig. 1b, individual cellulose microfibrils of diameter ranging from $0.23\text{--}1.04\ \mu\text{m}$ are observed. However, in

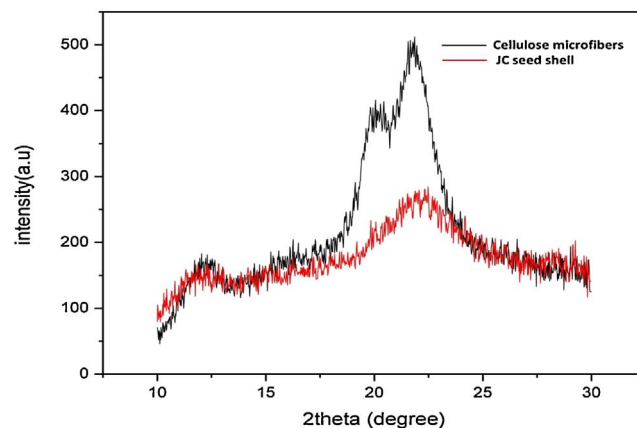


Fig. 4. Powder X-ray diffraction patterns of cellulose microfibrils isolated from JC seed shell fibers.

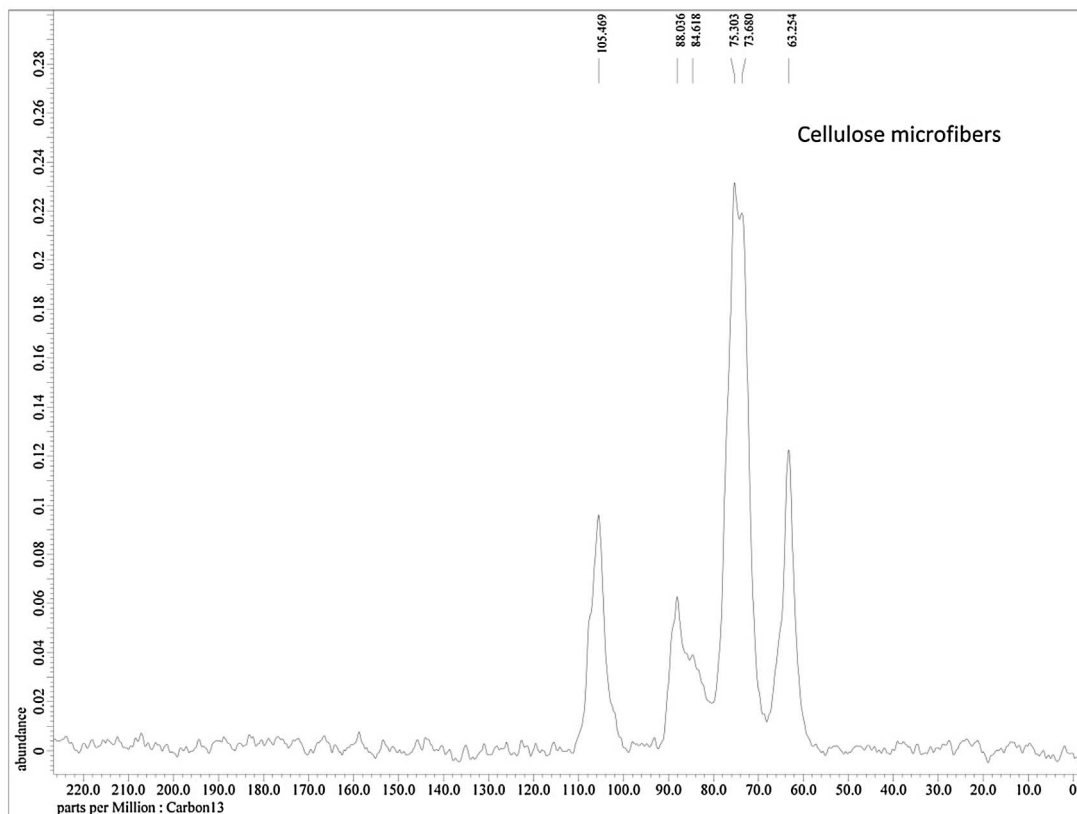
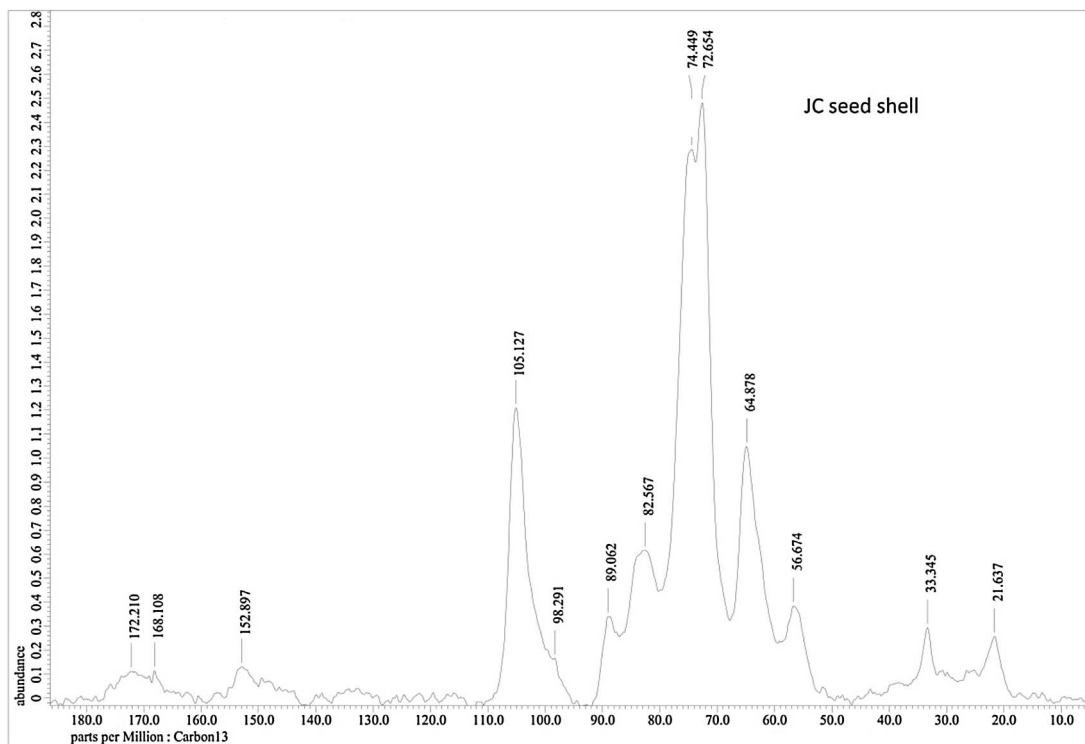


Fig. 5. ¹³C NMR spectra of JC seed shell fibers and cellulose microfibrils.

finding the range of dimension, we have used various SEM images taken at different locations in the sample. The morphological changes observed after the chemical treatment can be accounted to the removal of lignin matrix and hemicellulose [20] by chlorination treatment. The JC seed shell isolated cellulose fibers were much smaller in diameter compared to that isolated from Coconut palm leaf sheath (10–15 μm) [17] using the similar method of isolation, from Ficus leaves (1.5 μm) [21], Palmyro palm fruits (4–11 μm) [22] and Agave (8–14 μm) [23]. Smaller diameter of cellulose fibers may prove to be an added advantage in its application to form composites as it provides large interfacial area and promotes the adhesion between filler and polymer matrix [24].

FTIR spectra of JC seed shell fibers and cellulose microfibrils were obtained as shown in Fig. 2. The peak at 1725.98 cm^{-1} (C=O carbonyl group stretching) disappeared in cellulose spectra ensuring removal of hemicellulose and lignin [25]. The removal of lignin from cellulose fiber was supported by disappearance of peaks at 1598 cm^{-1} (aromatic ring vibrations) [26,27], 1477.21 cm^{-1} (C=C stretch of the aromatic rings of lignin) [28] and 775 cm^{-1} (C-H deformations) [29]. Band around 1047.16 cm^{-1} (C-O-C stretching) in JC seed shell spectra indicates presence of xylans associated with hemicelluloses strongly bond with cellulose fibers [30]. Broadening of the band at 1105 cm^{-1} in cellulose spectra was associated with cellulose I to cellulose II transition due to the effect of chlorite and alkaline treatment [31]. Broadening of vibration at 3276.47 cm^{-1} in cellulose fiber spectra ensures presence of amorphous fraction of cellulose [32]. Absorption bands in the region of 3598 and 3276 cm^{-1} (-OH groups) represent the hydrophilicity of cellulose [33]. 2902 – 2917.77 cm^{-1} band region was assigned to C-H stretching vibrations in hemicellulose and cellulose [34]. The peak at 1654.62 cm^{-1} was associated with adsorbed water [35] which could be due to hydrophilicity of cellulose microfibrils.

Fig. 3 show thermograms obtained for the JC seed shell fibers and isolated cellulose microfibrils. Onset degradation temperature of cellulose fibers and JC seed shell fibers was recorded at $291\text{ }^{\circ}\text{C}$ and $239\text{ }^{\circ}\text{C}$ respectively. The thermograms clearly indicate increase in thermal stability by 52% which can be accounted for removal of hemicellulose and lignin through chemical treatments [33]. Major degradation peak was observed between $280\text{ }^{\circ}\text{C}$ – $360\text{ }^{\circ}\text{C}$ with 50% degradation of cellulose components and presence of residue up to $450\text{ }^{\circ}\text{C}$, indicating the presence of carbonaceous materials in the nitrogen atmosphere. Thus, the isolated cellulose microfibrils from JC seed shell could find application in thermoplastic processing, which are usually processed at temperatures above $200\text{ }^{\circ}\text{C}$ [36].

Powder XRD patterns of JC seed shell and cellulose microfibrils are shown in Fig. 4. Diffractograms obtained by analyzing the JC seed shell fibers and cellulose microfibrils show peaks at $\sim 12^{\circ}$, $\sim 16^{\circ}$, $\sim 20^{\circ}$, and $\sim 22^{\circ}$. Peaks at $2\theta = 22^{\circ}$ and 14° – 17° represent cellulose I [37] whereas peak at $2\theta = 12.5^{\circ}$ and 20° represents cellulose II [38]. Increase in crystallinity of cellulose microfibrils by 21.3%, indicates reduction of amorphous components lignin and hemicellulose in the cellulose microfibrils [39].

^{13}C NMR spectra of JC seed shell fibers and cellulose microfibrils are shown in Fig. 5. The absence of peaks at 168 and 33.345 ppm of lignin and 21.637 and 172.210 ppm of hemicellulose [40] in cellulose microfibrils spectra signifies effectiveness of chlorination method in isolations of cellulose microfibrils. Whereas carbon peaks are observed to be same throughout the 64–105 ppm region for both JC seed shell and cellulose spectra, which ensures unalteration of cellulose structure by chlorination treatment. With respect to the decrease in peaks at 70–80 ppm and 100–110 ppm, it can be accounted to loss of non-

cellulosic polysaccharides. Bleaching and alkaline treatments dissolve non-cellulosic polysaccharides which are associated by strong interaction with cellulose at the microfibrils surface [41] and due to strain/compression of cellulose fibers [42]. These observations are in full agreement with that of FTIR spectroscopy, XRD and TGA analysis.

3.2. Biocomposites properties

Biocomposites of pure PVA and cellulose microfibril reinforced-PVA were characterized for the thermal and tensile properties. Fig. 6 shows the thermograms obtained for the cellulose microfibril, pure PVA, and 5 wt%, 10 wt% and 20 wt% cellulose fibers reinforced PVA matrix and the onset degradation temperature was observed to be $291\text{ }^{\circ}\text{C}$, $272\text{ }^{\circ}\text{C}$, $278\text{ }^{\circ}\text{C}$, $280\text{ }^{\circ}\text{C}$ and $276\text{ }^{\circ}\text{C}$ respectively. Increase in degradation temperatures of the composites with the addition of cellulose fibers can be accounted to the presence of crystalline cellulose [43]. TGA curves show that the thermal property associated to cellulose-PVA composites are intermediate between the pure cellulose fiber and pure PVA, which can be due to poor adhesion of cellulose microfibrils in the core of PVA matrix [44].

Variation in tensile strength and Young's modulus of composites are shown in Fig. 7a and b. Increase in tensile strength from 20.69 to 29.32 MPa and modulus from 2.88 to 16.241 GPa with the increase in cellulose content indicates stress was successfully transferred from the matrix to fiber [45]. Higher tensile strength is mainly associated with effective filler dispersion and adhesion between filler and matrix [46]. This could have been achieved due to availability of large interfacial area as a result of smaller diameter cellulose fibers used as fillers [24]. Tensile modulus and strength increased by 463% and 42% respectively on addition of 20 wt% cellulose loading onto PVA. The increase is comparatively higher than the increase of 257% of tensile strength and 23% of tensile modulus reported by [47] for 20% waste cotton fabrics isolated microcrystalline cellulose loading in PVA. The stress and strain behavior of PVA and the cellulose microfibril/PVA composites are represented in Fig. 8. Thus, the cellulose fibers isolated from JC seed shell can be considered to be effective fillers in biocomposites. PVA in general is used in packaging industry for packaging detergents, dyes and industrial polarizers, due to resistance to greases oils and solvent [48,49]. Cellulose reinforcement improves the mechanical strength and structural properties of PVA [50] and the cellulose microfibril/PVA composites have been proved to meet the packaging requirements [51].

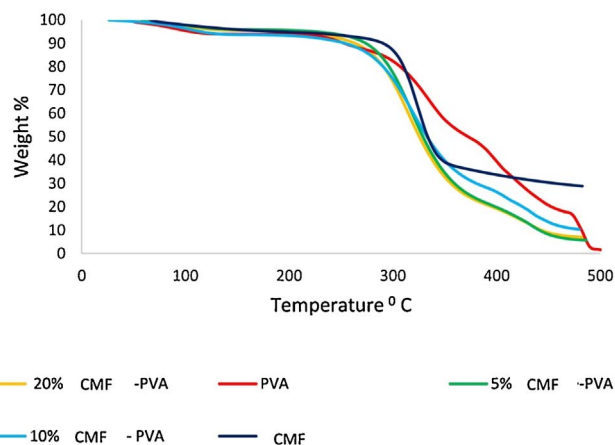


Fig. 6. Thermograms of JC seed shell fibers and cellulose microfibrils.

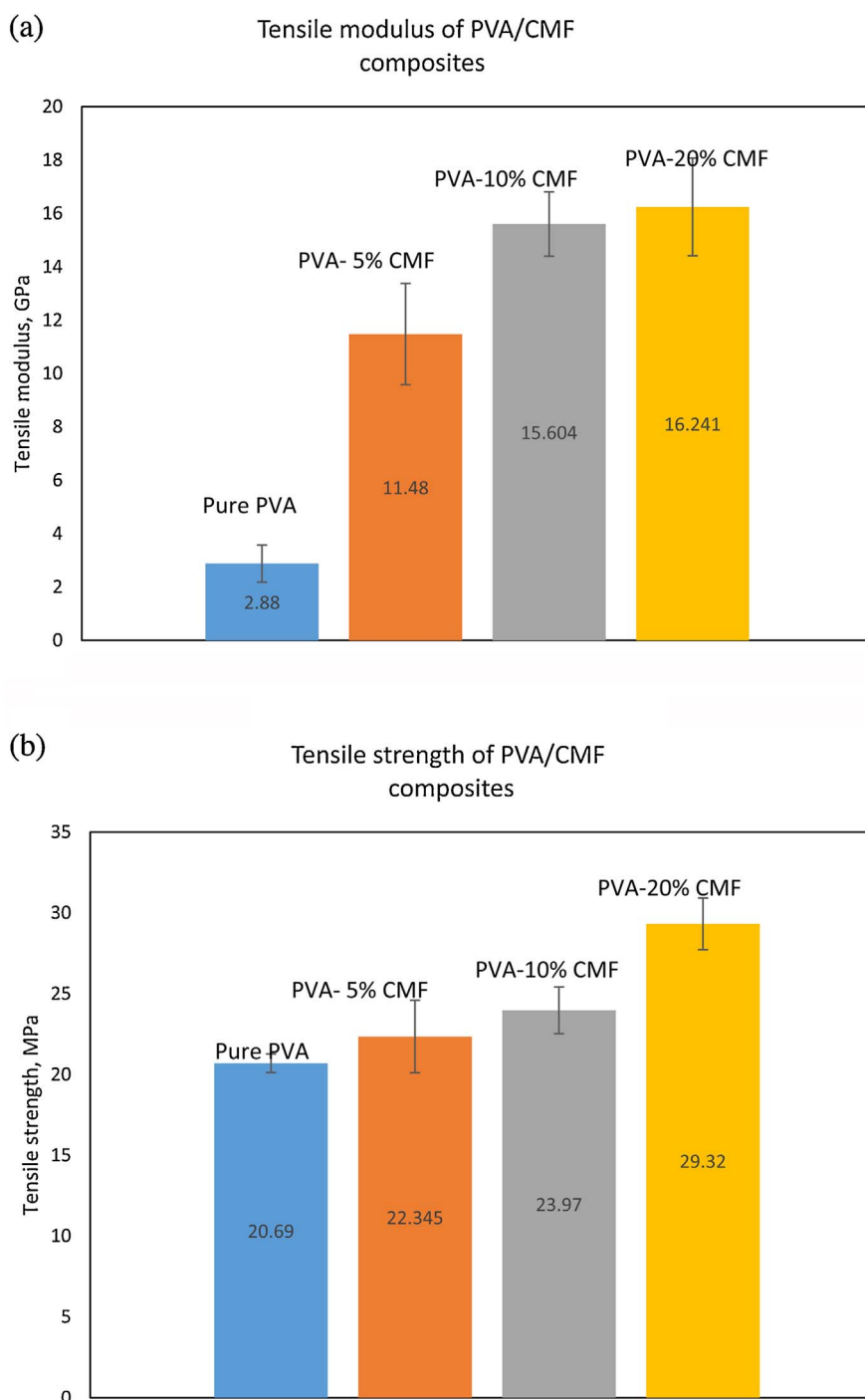


Fig. 7. a. Tensile modulus of pure PVA and cellulose microfibr reinforced PVA. b. Tensile strength of pure PVA and cellulose microfibr reinforced PVA.

Thus, the cellulose fibers isolated from JC seed shell can find potential utilization in packaging field. Since the cellulose microfibrs are being reinforced in PVA, these biocomposites could find application in industries for packaging detergents, dyes, and in polarizer industries [52].

4. Conclusion

JC seed shell can be used as alternative source for the production of

cellulose microfibrs. The chlorination treatment technique proved to be effective in isolation of cellulose microfibrs. Cellulose microfibr's crystallinity increased by 21%. Similarly, thermal stability increased on treatment and was above 200 °C, which makes it a potential source for biocomposites thermoplastics application where the processing temperature is generally above 200 °C. It also finds application in high temperature packaging. Biocomposites reinforced with 5, 10 and 20 wt percent of cellulose microfibrs showed enhanced mechanical properties and thermal stability. This work unveils the potentiality of *Jatropha*

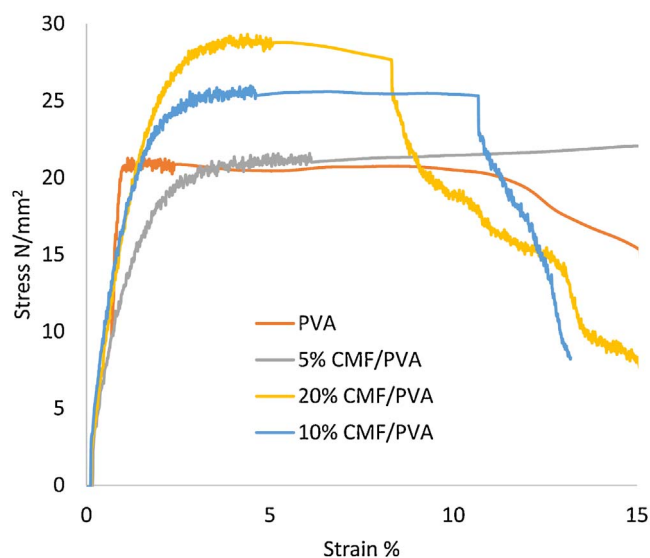


Fig. 8. Stress and strain behavior of PVA and cellulose microfiber reinforced PVA.

Curcas L. seeds shells as source for cellulose microfibrils and feasibility of preparation of cellulose-PVA high performance composites, thus broadening their field of application as biocomposites.

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