Properties of cellulose/*Thespesia Lampas* short fibers bio-composite films

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Abstract

Cellulose was dissolved in pre cooled environment friendly solvent (aq.7% sodium hydroxide+12% urea) and regenerated with $5\% H_2SO_4$ as coagulation bath. Using cellulose as matrix and alkali treated short natural fibers extracted from the newly identified Thespesia Lampas plant as reinforcement, the green composite films were prepared. The effect of fiber loading on the tensile properties and thermal stability was studied. The fractographs indicated better interfacial bonding between the fibers and cellulose. The crystallinity of the composite films was found to be lower than the matrix and decreased with increasing fiber content. In spite of better interfacial bonding, the tensile properties of the composites were found to be lower than those of the matrix and decreased with increasing fiber content and this behavior was attributed to the random orientation of the fibers in the composites. The thermal stability of the composite films was higher than the matrix and increased with fiber content.

Keywords: Regenerated cellulose, Films, Structural analysis, Tensile properties, Thermal analysis

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1. Introduction

There is a mounting interest in upward bio-based polymer materials and pioneering handing out technologies which offer sustainability and improvement of the reliance on fossil fuel (Reddy et al., 2013a). The exertion materials for the production of these polymers may be either renewable or synthetic. There are several types of biopolymer including cellulose, starch, proteins, chitosan, and synthetic (Polylactic acid (PLA), Polypropylene carbonate (PPC), Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate (PHBV) and so on.) materials (Maheswari et al., 2012; Torres et al., 2011; Kumar, 2000; Reddy et al., 2013a). Present and upcoming developments in biodegradable polymers and renewable materials spotlight mostly on the development of product properties but not as an alternative way out to the diffidence of petroleum supplies or to shrink the environmental possibility (Kaplan, 1998). In addition, these are most promising renewable bioresources due to their easy adaptability, lively in price, and applicability to development of novel biomaterials with various uses (Rhim, & Ng, 2007; Kalia, & Averous, 2011). Among those biopolymers, cellulose is the most abundant renewable and biodegradable polymer in the world, that is mainly produced by woody biomass and naturally found with a fibrous structure (Klemm et al., 2005).

Cellulose a linear polysaccharide composed of β-1–4-linked D-glucopyranose repeating units, has drawn much attention due to its unique properties such as higher chemical resistance, mechanical strength, strong hydrophilicity, biodegradability and massive amount of chemical derivations (Heinze, & Liebert, 2001; Klemm et al., 2005). Though, the account of the large network linking hydrogen bonds and partially crystalline structure, cellulose cannot be dissolved in water or nearly all common organic solvents (Soheilmoghaddam et al., 2014). Many of the known solvents for cellulose require long time and the dissolution is a complex process. Some of the solvents for cellulose include lithium chloride/N, N-dimethylacetamide (LiCl/DMAc) (McCormick et al., 1985), N-methylmorpholine-N-oxide (NMMO) [12 Fink et al., 2001], cold LiOH/urea or NaOH/urea (Cai & Zhang, 2005) and ionic liquids (Kosan et al., 2008). The most appropriate solvent for cellulose from among these solvents is NaOH/urea. The ecological safety of this solvent system and its high activity of interaction with cellulose stimulated extensive investigations into the process of cellulose dissolution.

Nowadays, regenerated cellulose composite films are being envisaged as important materials in the packaging industry due to their excellent transparency, mechanical properties, non-toxicity, high biodegradability rate and also low economic cost than synthetic polymers (Takagi & Asano, 2008). Recently, regenerated cellulose with natural fibers or organic or inorganic filler composite films have attracted much attention due to their excellent mechanical, optical, electrical and flame retardancy properties which are widely used in the fields of biomedicine, food packaging and water treatment (Nadhan et al., 2012a; Nadhan et al., 2012b; Han, Yan, Chen, Li, & Bangal, 2011; Delhom et al., 2010; Li et al., 2014). The objective of the present work was to obtain less expensive regenerated composite film materials based on Thespesia Lampas fiber and to evaluate how the addition of cellulose fibers influence the film properties. In an earlier work, the authors reported the structural and physical properties of *Thespesia Lampas* fibers (Reddy et al., 2014). These fibers are biodegradable, renewable and also possess excellent tensile properties and for these reasons were used as reinforcement in this work. In the present paper, the author select to cellulose polymer was used as the matrix material and alkali treated short Thespesia fiber as reinforcing material. The alkali treated short Thespesia fiber reinforced cellulose bio-composite films were prepared by film-casting method. The effect of fiber loadings on the tensile properties and thermal stability of bio-composites films have been studied. The interfacial bonding between the matrix and the fibers was examined using the fractographs. The crystallinity of cellulose/Thespesia composites films was compared with that of neat cellulose film using XRD technique.

2. Materials and methods

2.1. Materials

Extracted Thespesia fibers, Cotton linter pulp (degree of polymerization 620) was supplied by Hubei Chemical fiber Co. Ltd (Xiangfar, China). Acetic acid, sodium hydroxide (NaOH), sulfuric acid and urea were supplied by Shanghai Chemical Reagent Co. Ltd;, China and used as received.

2.2. Fiber extraction and treatment

Thespesia fibers were extracted from the stems of the plant. First, the stems were cut from the plant and immersed in water for 24 h for debarking, then the bark was removed from the stem manually. This combined water and mechanical retting process was adopted for extraction of fibers from the bark. The separated fiber strands were washed thoroughly using water and then sun dried for one week to ensure maximum moisture removal. After the extracted fibers were treated with 5% (w/v) sodium hydroxide solution for 1 h at room temperature, maintaining a liquor ratio of 25:1 to remove the hemicellulose and surface impurities. Finally, the fibers were neutralized using 1% (w/v) acetic acid solution followed by water and then the fibers were dried at 100 °C for 24 h to remove moisture. Treated fibers were cut manually into length of ~1mm.

2.3. Dissolution of Cellulose

An aqueous solution having 7wt.% NaOH and 12 wt.% urea was cooled to -12 °C and cellulose was added (4 wt.%) to it and stirred vigorously at room temperature as described elsewhere. The obtained clear solution (within 2 minutes of stirring) was centrifuged at 5 °C at a speed of 7200 rpm for 15 minutes to separate any undissolved cellulose and impurities. The stock solution was stored at 5 °C till it was used. The above procedure of regeneration of cellulose was adopted from (Nadhan et al., 2012a).

2.4. Preparation of cellulose/Thespesia composite films

To the cellulose solution, alkali treated ~1mm short Thespesia fibers were added in 1 to 5 wt.% of cellulose separately , stirred well and degassed. The solutions were cast on glass plates using a spreader and regenerated using aq.5% H_2SO_4 as coagulation bath. The gel films were thoroughly washed in water several times and dried at room temperature. Transparent films with ~30 µm thickness were obtained.

2.5. Microscopic analysis

Composite film samples for SEM observation were sputter-coated with a thin layer of gold. Then the coated samples were observed by JSM 6700 F scanning electron microscope with 5 kV accelerating voltage in secondary electron mode. The magnification was 2000 X in SEM images.

2.6. Tensile testing

The rectangular composite film strips of 100 mm X 10 mm were tested for tensile properties using an Instron 3369 Universal Testing Machine, maintaining a gauge length of 50 mm at a crosshead speed of 5 mm/min. For each test, ten specimens were tested and the average values reported.

2.7. Thermogravimetric analysis

Primary thermograms of composite film samples were recorded using a thermogravimetric analyzer (Perkin Elmer TGA-7) in the temperature range of 30 ºC to 800 ºC at a heating rate of 10 ºC/min under nitrogen atmosphere.

3. Results and discussion

All the cellulose/Thespesia composite films were found to be transparent with uniform distribution of randomly oriented short fibers. Figure 1 shows the photograph of a flower wrapped with cellulose/5wt.% Thespesia composite film. The film had good transparency and can be used for package purpose. In order to probe the chemical interactions between the fibers and the matrix, the FTIR spectra of cellulose and cellulose/Thespesia composite films were recorded and are presented in Figure 2. From Figure 2, it is evident that the spectra of cellulose and the composite films are similar. It is understandable as both regenerated cellulose and fibers are cellulosic. However, the intensity of the bands in the spectra of composites was higher than the matrix and increased with increasing fiber content. The broad band at ~3330 cm⁻¹ was assigned to H-bonded OH groups and the other one at around 2910 cm⁻¹ to the CH stretching vibrations (Reddy et al., 2013b). The band at 1460 cm⁻¹ was assigned to the aromatic C=C ring stretching of lignin (Maheswari et al., 2012). This band is almost absent in the spectrum of cellulose. Another prominent broad band at around 1240 cm⁻¹ was attributed to the –COO vibration of acetyl groups in hemicelluloses (Maheswari et al., 2012). The intensity of this band is very low in the matrix compared to the composites. Another sharp absorption band at around 895 cm⁻¹ was attributed to the ring valence vibration, characteristic of β-glycosidic linkages between the sugar units (Sain and Panthapulakkal 2006). For all the bands observed for both the matrix and the composite films, the band positions remained the same whereas their intensities

increased with increasing fiber content indicating uniform distribution of the fibers in the composites.

In a composite, the interfacial bonding between the reinforcement and the matrix is a crucial factor that judges the mechanical properties. In this direction, the fractographs of the brittle fractured composite films were recorded. The fractographs of cellulose/Thespesia composites having 2wt.% and 5 wt.% fibers are shown in Figure 3. From the figure, it is evident that matrix skin was formed on the fibers. Further, a narrow interface was observed besides breaking of the fibers instead of pulling. These observations indicate the existence of good interfacial bonding between Thespesia fibers and the cellulose matrix. Such a bonding is expected in the present case as both the matrix and the fibers are lingo-cellulosic in nature.

Crystallinity is another factor which influences the mechanical properties of polymers and their composites. In order to probe the effect of fiber loading on the crystallinity of the composites, the X-ray diffractograms of cellulose and the composite films were recorded and are presented in Figure 4. Two main peaks observed at $2\theta=12.2^{\circ}$ and $2\theta=23.1^{\circ}$ were assigned to result from (11-0) and (200) planes respectively (Oh et al., 2005). The presence of the peak at $2\theta=12.2^{\circ}$ indicates partial transformation of Cellulose–I ($2\theta=23.1^{\circ}$) to Cellulose–II by chemical treatments (Oh et al., 2005). From Figure 4, it is also evident that the intensity of both these peaks was lower for the composite films than for cellulose and decreased with increasing fiber content. This clearly indicates the lowering of crystallinity of the composites due to the presence of the Thespesia fibers. This is understandable as the alkali treated Thespesia fibers still had amorphous components - hemicelluloses (20.8%) and lignin (14.98%) (Reddy et al., 2014).

The tensile properties of the composite materials, which can provide significant information in sequence concerning the internal structure of materials, are strongly influenced by the microstructure. Stress–strain curves of all the composite films are shown in Figure 5. From Figure 5, it is evident that the Thespesia short fiber reinforced composite films followed brittle fracture than the pure cellulose film. The average tensile strength, tensile modulus and elongation at break of all the composites films are presented Table 1and corresponding graphs

are shown in Figure 6 (a-c). From Figure 6 and Table 1, it can be observed that the Thespesia short fiber reinforced composite films had lower tensile properties than the matrix and decreased with increasing fiber content. Evidently, the presence of the amorphous lignin and hemicellulose (as impurities) in the fiber led to the weakening of the materials, indicating that those components had negative effect on tensile properties (Abdulkhani et al., 2013). In addition to this, random orientation of fibers in the composite films with respect to stress direction was also responsible for the decrease in tensile properties of the composites over the matrix. It is already established that tensile properties of a composite is a function of orientation of fibers and has maximum value when the fibers are aligned and reduces to 1/3 when the fibers are randomly oriented (Seymour and Carraher 1984). However, even with random oriented fibers, the tensile properties of cellulose/Thespesia composite films are better than those of conventional polymer films like polyethylene and polypropylene (Tesarikova et a., 2014) and are compared in Table 1.

In order to probe the effect of Thespesia fiber content on the thermal degradation of the cellulose/Thespesia composite films, the primary thermograms of cellulose and the composites were recorded are presented in Figure 7. From Figure 7, it is evident that the composite films had higher thermal stability than the cellulose matrix. Further, the thermal stability of the composite films increased with increasing fiber loading. This behavior is expected as the fibers had 14.98% of lignin (Reddy et al., 2014) that contains phenolic components which in turn increased the thermal stability of the composites.

4. Conclusions
Using cellulose as matrix and alkali treated short fibers of newly identified plant Thespesia Lampas as reinforcement, the green composites were prepared. The cellulose and cellulose/Thespesia composite films were analyzed by FTIR, scanning electron microscopic, XRD, TGA and Tensile tests. The FTIR analysis indicated the presence of minor components of amorphous hemicelluloses and lignin besides the major component of cellulose. The fractographs revealed a good interfacial bonding between the matrix and the composites. The crystallinity of the composites was found to be lower than the cellulose matrix due to the presence of amorphous hemicelluloses and lignin in the fiber reinforcement. In spite of the

similar nature of the matrix and the reinforcement and better interfacial bonding, the tensile properties of the cellulose/Thespesia composite films were lower than cellulose matrix and decreased with increasing fiber loading. This behavior was attributed to the random orientation of the fibers in the composites towards stress direction and lower crystallinity of the fibers. But still the green composite films of cellulose/Thespesia possessed better tensile properties than the conventional polymers like polyolefin's. The thermal stability of the composite films was higher than the matrix and increased with fiber content. The composite films made with cellulose and Thespesia fiber can have an alternative use as packing materials.

Acknowledgements

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Captions for figures

1. Photograph of flower wrapped with Cellulose/Thespesia composite film loaded with 5wt.% fibers.

2. Fractographs of Cellulose/Thespesia composite films – (a) loaded with 2 wt.% fibers and (b) loaded with 5 wt.% fibers.

3. X-Ray diffractograms of Cellulose and Cellulose/Thespesia composite films loaded with 1 to 5 wt.% fibers.

4. Stress-Strain curves of Cellulose and Cellulose/ Thespesia composite films loaded with 1 to 5 wt.% fibers.

5. Variation of Tensile parameters – (a) Tensile modulus, (b) strength and (c) %Elongation at break of Cellulose and Cellulose/Thespesia composite films loaded with 1 to 5 wt.% fibers.

6. Primary thermograms of Cellulose and Cellulose/Thespesia composite films loaded with 1 to 5 wt.% fibers.

Captions for Table

Table 1. Tensile Parameters of Cellulose/Thespesia Lampas fiber composite films compare with Polyethylene and Polypropylene

Figure 1. Photograph of flower wrapped with Cellulose/Thespesia composite film loaded with 5wt.% fibers
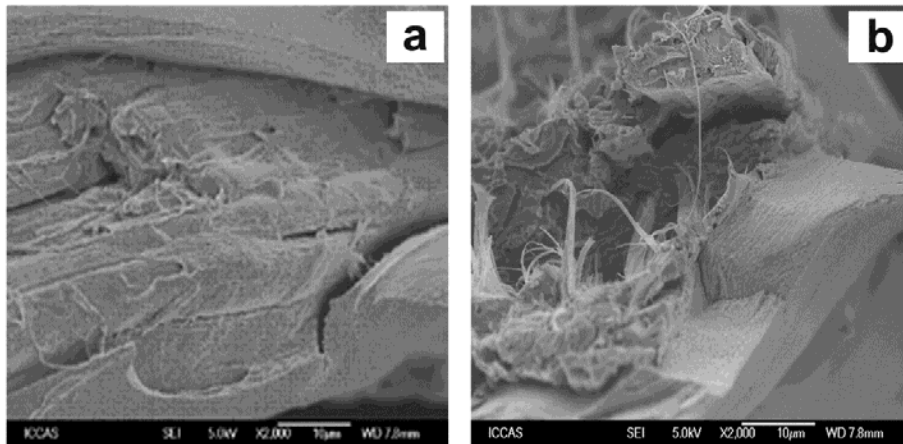

Figure 2. Fractographs of Cellulose/Thespesia composite films – (a) loaded with 2 wt.% fibers and (b) loaded with 5 wt.% fibers
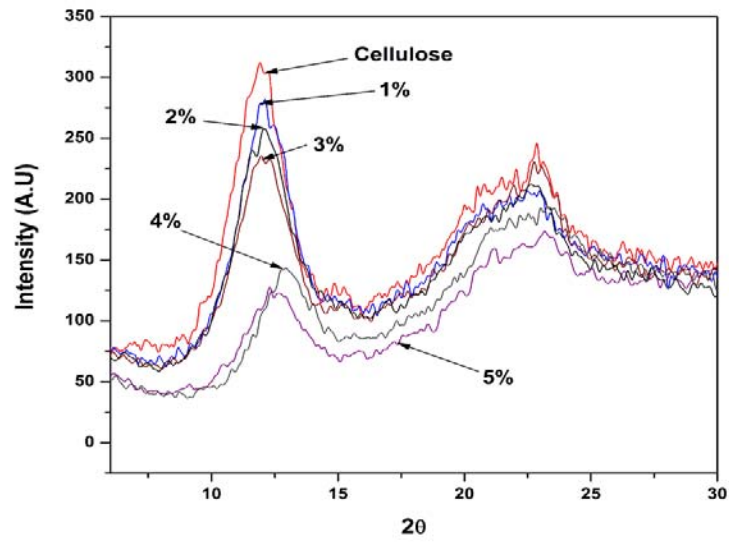
Figure 3. X-Ray diffractograms of Cellulose and Cellulose/Thespesia composite films loaded with 1 to 5 wt.% fibers
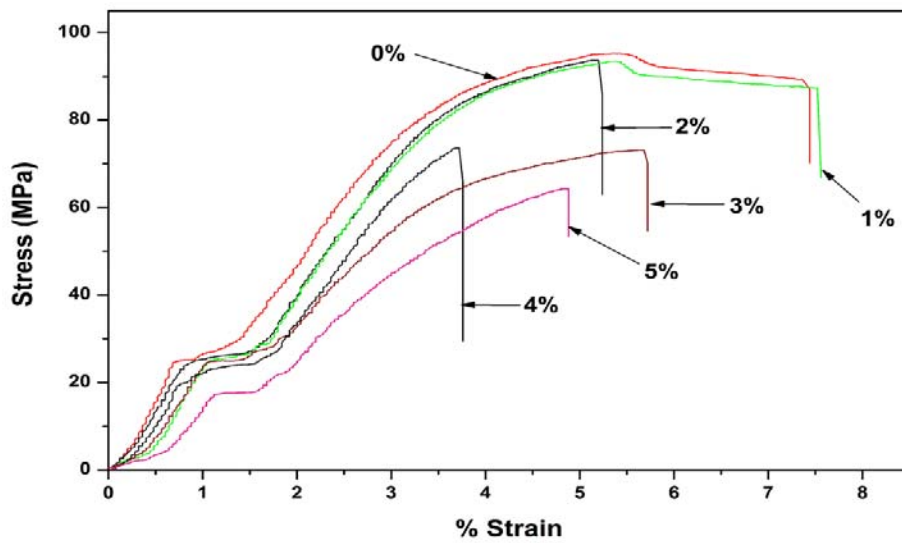

Figure 4. Stress-Strain curves of Cellulose and Cellulose/ Thespesia composite films loaded with 1 to 5 wt.% fibers
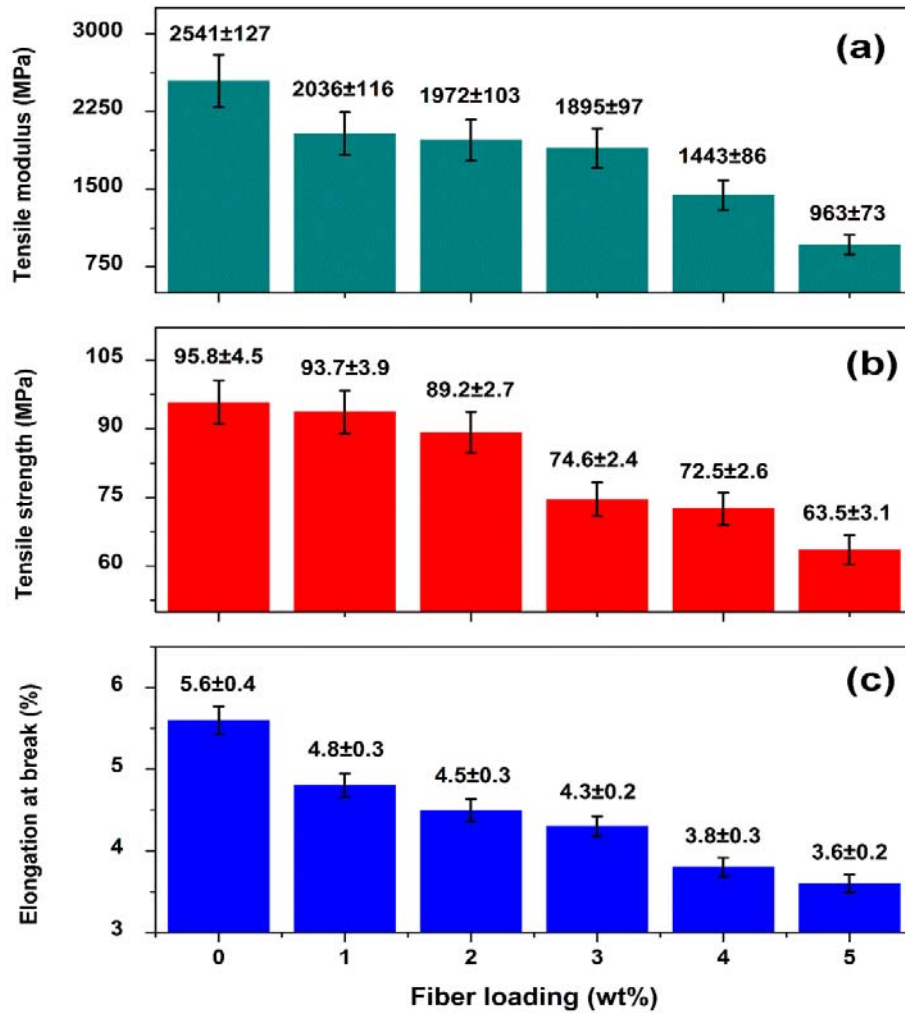
Figure 5. Variation of Tensile parameters – (a) Tensile modulus, (b) strength and (c) %Elongation at break of Cellulose and Cellulose/Thespesia composite films loaded with 1 to 5 wt.% fibers
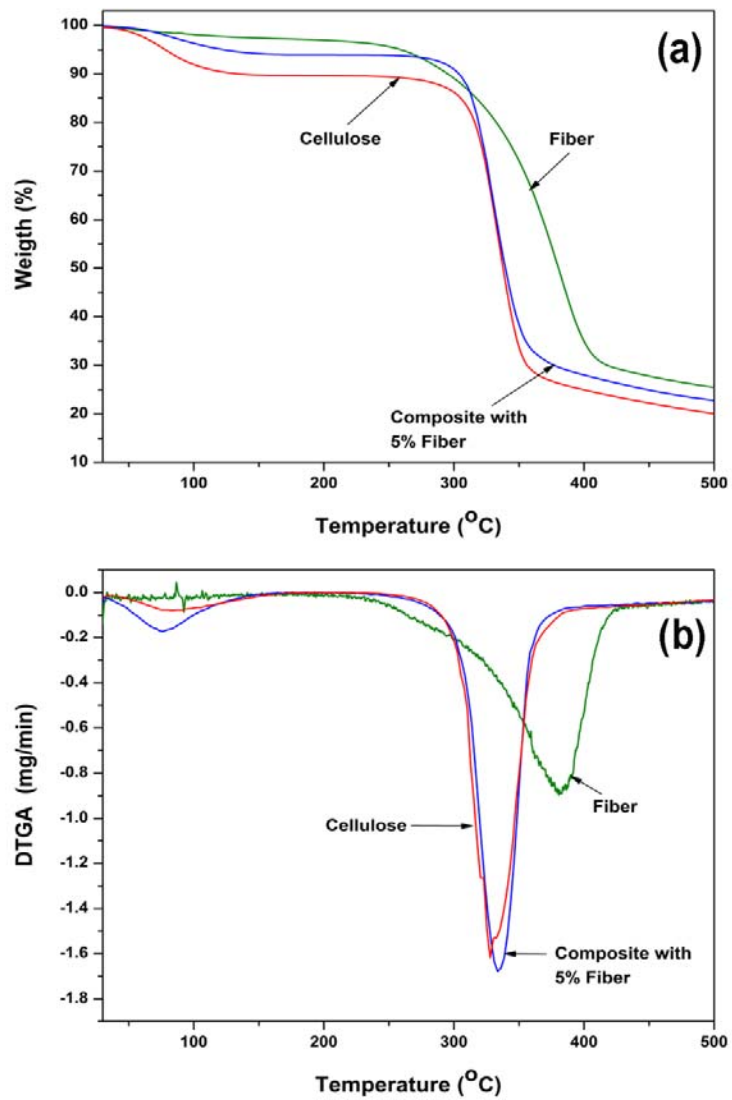
Figure 6. Primary thermograms of Cellulose and Cellulose/Thespesia composite films loaded with 1 to 5 wt.% fibers
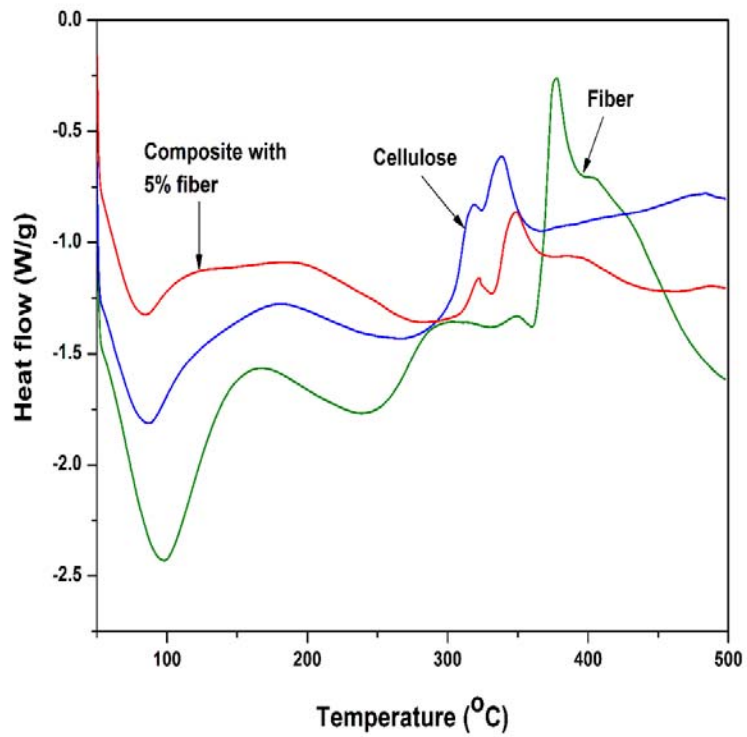
Figure 7. DSC thermograms of Cellulose, alkali treated Thespesia fiber and Cellulose/Thespesia composite films loaded with 5 wt.% fibers

Table 1. Tensile parameters of Cellulose/Thespesia Lampas short fiber composite films compare with polyolefin's

Fiber content in film (Wt%)	Tensile Modulus (MPa)	Maximum Stress (MPa)	Elongation at Break (%)
0	2541±127	95.8±4.5	5.6±0.4
1	2036±116	93.7±3.9	4.8±0.3
2	1972±103	89.2±2.7	4.5±0.3
3	1895±97	74.6±2.4	4.3±0.2
4	1443±86	72.5±2.6	3.8±0.3
5	963±73	63.5±3.1	3.6±0.2
* Low density polyethylene [LDPE]	170 - 700	8.3 - 32.1	50 - 970
* High density polyethylene [HDPE]	1080 - 1100	22.1 - 31.4	10 - 1200
* Polypropylene [PP]	1150 - 1570	31 - 41.9	100 - 600

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