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Preparation and properties of biodegradable films from *Sterculia urens* short fiber/cellulose green composites

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ABSTRACT

The development of commercially viable "green products", based on natural resources for the matrices and reinforcements, in a wide range of applications, is on the rise. The present paper focuses on *Sterculia urens* short fiber reinforced pure cellulose matrix composite films. The morphologies of the untreated and 5% NaOH (alkali) treated *S. urens* fibers were observed by SEM. The effect of 5% NaOH treated *S. urens* fiber (5, 10, 15 and 20% loading) on the mechanical properties and thermal stability of the composites films is discussed. This paper presents the developments made in the area of biodegradable *S. urens* short fiber/cellulose (SUSF/cellulose) composite films, buried in the soil and later investigated by the (POM), before and after biodegradation has taken place. SUSF/cellulose composite films have great potential in food packaging and for medical applications.

1. Introduction

In the past few years, biodegradable polymers have attracted much attention due to the global problems caused by petroleum-based non-degradable (synthetic polymers) materials. However, they also pose serious environmental threats and their raw materials are naturally limited (Kumar, Liu, & Zhang, 2008). The waste from these synthetic polymer-based products are non-biodegradable, resulting in "white pollution" and damaging to wild-life, leading to calls from the "green" movements to return to biologically based (renewable) polymers (Scott, 1999, 2000). Cellulose is the most abundant natural polymer on the earth and it is envisaged that it will become the main chemical resource in the future (Eichhorn, Young, & Davies, 2005; Schurz, 1999). It is considered to be an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products (Klemm, Heublein, Fink, & Bohn, 2005). However, the full potential of cellulose has not yet been exploited because of the lack of an environmentally friendly method and the limited number of common solvents that readily dissolve cellulose (Zhu et al., 2006). Cellophane prepared through the viscose route is transparent, lustrous, durable, flexible and impervious to air, grease, germs, and dirt. However, this method produces serious pollution by the toxic CS_2 solvent used in the preparation.

In recent years, the "green" comprehensive utilization of cellulose resources has drawn a lot of attention from governments and researchers (Fink, Weigel, Purz, & Ganster, 2001; Hyden, 1929). The regenerated cellulose films and fibers prepared from "green" processes have great importance for sustainable development. Today, cellulose offers great opportunities in packaging as well as biodegradable materials, because of its low cost and biodegradability, there by promising an environmental solution to the plastic waste issue (Gindl, Martinschitz, Boesecke, & Keckes, 2006; Grevellec, Marqui'e, Ferry, Crespy, & Vialettes, 2001; Kontturi, Tammelin, & Sterberg, 2006; Rhim & Ng, 2007). Furthermore, a simple route using safe and low-cost chemical reagents has been developed for producing regenerated cellulose materials without producing any hazardous by products. It involves dissolution of cellulose in aqueous NaOH/urea or LiOH/urea solutions at low temperatures, followed by regeneration of cellulose (Cai, Zhang, Chang, et al., 2007; Cai, Zhang, Zhou, et al., 2007; Yang, Qi, et al., 2011). These solvents can readily dissolve even highly crystalline cellulose without significant degradation. New cellulose multifilament fibers (Cai, Zhang, Chang, et al., 2007; Cai, Zhang, Zhou, et al., 2007) and films (Morgado, Frollini, Castellan, Rosa, & Coma, 2011; Yang, Lue, & Zhang, 2010; Yang, Qin, & Zhang, 2011) have been prepared

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from the cellulose dopes. These cellulose materials possess a wide range of mechanical properties, excellent thermal stabilities, and high biodegradabilities because of the nature of cellulose.

Zhang, Cai, and Zhou (2005), and Cai and Zhang (2005) developed a new solvent, 7 wt% NaOH/12 wt% urea aqueous solution pre-cooled to −12 °C, that rapidly dissolving cellulose within 2 min. Interestingly, the quick dissolution of cellulose arises as a result of a dynamic self-assembly process of the solvent molecules (NaOH, urea and water) and cellulose macromolecules through the formation of new hydrogen bonding networks at low temperatures (Cai et al., 2008). The main advantage of this method is its rapid dissolution, relative simplicity and cost-effectiveness and it is an environmentally friendly process.

In the present paper, we collected *Sterculia urens* locally in Nallamala forest area located near Sresailam and Atmakur Taluk, Kurnool district's of Andhra Pradesh, India. During this search, some trees bearing uniaxial fabrics were identified. It has also been observed that these fabrics are thin and have fibers arranged in uniaxial directions. As uniaxial fabrics are rare in occurrence, the authors used these unique fabrics as reinforcement for the preparation of green composites. The plant *S. urens* (Roxb) from which the fabric was extracted from the branches belongs to the *Sterculiacea* family and exists in large quantity in the local area.

In the present study, the morphologies of the untreated and 5% NaOH (alkali) treated *S. urens* fabrics have been studied by SEM. The effects of pure cellulose, untreated and 5% NaOH treated *S. urens* fiber at different loadings on the mechanical properties of composites films have been investigated. In addition, the thermal stabilities of the pure cellulose, 5% NaOH treated *S. urens* fiber composite films were studied. Finally, the biodegradability of matrix films and their *S. urens* short fiber (SUSF) composites were studied by using the soil burial test.

2. Materials and methods

2.1. Materials

Cotton linters were obtained from China while analytical grade sodium hydroxide (NaOH) and urea were purchased from MERCK Chemicals, India.

2.2. Extraction and modification of S. urens fabric

The naturally occurring fabric *S. urens* was extracted from the branches of its tree as described elsewhere (Jayaramudu, Guduri, & Varada Rajulu, 2009). It was washed thoroughly with distilled water and allowed to dry in the sun for one week to ensure the removal of moisture. Some of the fabric samples were dipped in 5% aq. NaOH solution for 1 h and washed thoroughly with distilled water and then dried in the oven.

2.3. Preparation of short fiber reinforced cellulose composites

Composites with cellulose as matrix and SUSF as reinforcement were prepared. Here the cellulose was taken from cotton linters. To prepare the cellulose films, 7% NaOH + 12% urea solution was prepared and pre-cooled to −12 °C. To this pre-cooled solvent, cellulose linters were added and stirred in order to dissolve rapidly the cellulose within 2 min. The concentration of cellulose was maintained at 4% as good films could be formed at this concentration. The cellulose solution was subjected to centrifugation at 7200 rpm for 20 min at 5 °C and the precipitate containing any undissolved cellulose was rejected and only decant was used for further work.

Transparent solution of cellulose was taken in a beaker and short fibers of *S. urens* (average length ∼2 mm) were added. The effect of alkali treatment on the tensile properties of SUSF/cellulose composites was also studied. The fiber content was varied from 5 to 20% (w/w of cellulose) and mixed with a mechanical stirrer for uniform distribution of the fibers in the cellulose matrix. Then, the solution was poured on a glass plate and spread by using a glass tube with spacers in order to get uniform films. The films were subsequently regenerated in 5% H_2SO_4 solution for 5 min. Then, the films were kept in deionized water for a day. Finally, the films were fixed on a PVC sheet in order to avoid the wrinkles and subsequently dried at ambient temperature. Then the films were peeled off from the PVC sheet and used for further testing.

2.4. Morphology analysis

The scanning electron micrographs of the fabrics under various conditions of treatment were recorded on a JOEL JSM 820 microscope (Akishima, Japan). The surface morphology of the films, before and after biodegradation, was investigated with Polarized optical micrographs (POM) (BHA-1, Olympus). The surface of the untreated and alkali treated *S. urens* fabric was examined by the scanning electron microscope (SEM) (AMRAV, USA) operating at 10 kV. The samples were coated with gold before their micrographs were recorded.

2.5. Soil burial test

Biodegradation of pure cellulose (matrix), SUSF/cellulose composite films were studied by the soil burial method as per the procedure reported by Potts, Clendinning, and Ackart (1972), with a slight modification. The garden pots with an approximate capacity of 10 L were filled with compost, taken from municipal waste. Rectangular film samples 30 mm × 10 mm (in triplicate) of about 0.2 g weight were placed in the compost at a depth of about 5 cm. The compost was kept moist by sprinkling water at regular time intervals to maintain 40 ± 2% humidity. The excess water was drained through the hole at the bottom of the container. The containers were stored at about 30 ± 2 °C. The degradation of the samples was studied at regular time intervals (5 days) for a total of 40 days by carefully removing the samples from the soil and washing them gently with distilled water to remove the soil adhering on the surface. The samples were dried at 60 °C under vacuum until a constant weight was obtained. Matrix experiments were carried out by using sterilized compost. Percent weight loss of the samples with respect to time of burial in the soil was recorded as a measure of degradation.

2.6. Thermal properties

The thermogravimetric analyses (TGA) of pure cellulose and SUSF/cellulose film samples were carried out using TGA Q500, TA instrument under a nitrogen atmosphere. The samples were scanned from 30 °C to 600 °C, at a heating rate of 10 °C/min.

2.7. Tensile properties

The tensile properties of SUSF/cellulose composite films were determined as per ASTM D 882-02 standard method. Specimens with dimensions of 100 mm × 10 mm × 0.03 mm were selected. Tensile properties, such as: maximum stress, Young's modulus and % elongation at break were determined using an INSTRON 3369 Universal Testing Machine, at a crosshead speed of 5 mm/min and a gauge length of 50 mm. In each case, five samples were tested at 50% RH and 23 °C and the average values are reported.

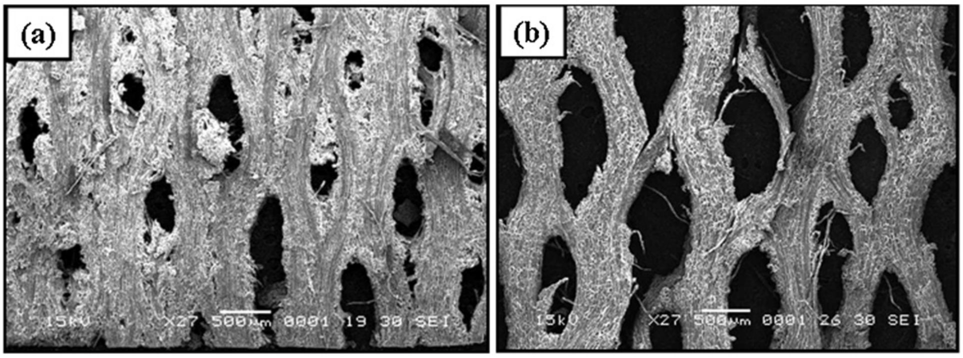

Fig. 1. Scanning electron microscope of *Sterculia urens* fabric: (a) untreated and (b) 5% NaOH (alkali) treated fabric same magnifications.

3. Results and discussion

3.1. Morphology analysis

Tree of *S. urens* from which the fabric was extracted belongs to the family of *Sterculiacea*. The SEM images of surface of the untreated and the alkali-treated fabrics are shown in Fig. 1(a) and (b), respectively, at a same magnification. From these micrographs, it is evident that the fabric is roughly made up of uniaxial parallel fibers. Furthermore, at higher magnification, the void regions present in the fabric are clearly visible. The micrographs also reveal a white layer on the untreated fabric, which may be due to the hemicellulose component. On alkali treatment, the white layer content is found to decrease. This may be attributed to the reduction in the hemicellulose content following alkali treatment. Further, the surface of the fabric is found to become rough with alkali treatment (Jayaramudu et al., 2009; Jayaramudu, Gudur, & Varada Rajulu, 2010; Jayaramudu et al., 2011). Photographs of the cellulose and SUSF/cellulose composite films with different fiber content are shown in Fig. 2.

3.2. Biodegradation in soil

Polarized optical micrographs of the pure cellulose and SUSF/cellulose composite films, before and after degradation in soil, along with a graph depicting the variation of weight loss with time are shown in Fig. 3. Studies on the biodegradation behavior of biocomposites are important because of its implication on the environment. In this work, soil burial experiments were performed on composite films with pure cellulose film as reference. From Fig. 3, it can be observed that the degradation behavior is approximately linear. Pure cellulose film (matrix) and the SUSF/cellulose films weight losses, show approximately linear relation with degradation time over 5 days soil burial duration. The degradation behavior of the crystalline regions appears, to be rather, complicated. The potential of films to degrade depends extensively on physicochemical uniqueness of the substrate, such as the degree of crystallinity and the extent of polymerization of cellulose, of which the crystallinity degree of cellulose is the main structural parameter. However, porous structure with fungal mycelia on the surface of the decomposed film was observed. An average of 70% weight decrease was observed over 25 days soil burial duration for all the composite films. It is clear that after 25 days of test time the film surface began to show increased roughness and found more cracks. As confirmed by the weight loss in Fig. 3, the microbes digested away parts of the matrix and increased fiber loading, breaking it into pieces. This led to increased surface roughness and formation of crevices increased fiber loading in the composites. It indicated the fact that the biodegradation of the films was caused by the bacteria mycelia, and this occurred gradually. Following the burial of composites in soil for 40 days, there is the degradation of the matrix which led to the exposure of the fibers, in it due to the removal of matrix (pure cellulose) as an eusol of the biodegradation process. Only broken fragments of the composite films were observed, and after 45 days, no remains of the composite films were found in the soil. The results indicated that the bacteria in the soil directly attacked and metabolized the matrix and SUSF composite films. Therefore, the matrix

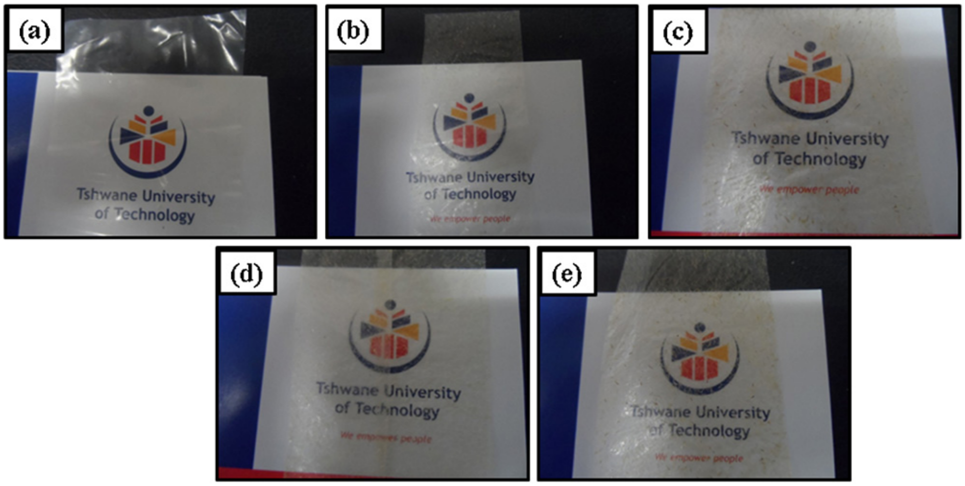

Fig. 2. Photographs of pure cellulose and SUSF/cellulose composite films: (a) pure cellulose (matrix), (b) SUSF5% + cellulose, (c) SUSF10% + cellulose, (d) SUSF15% + cellulose, and (e) SUSF20% + cellulose.

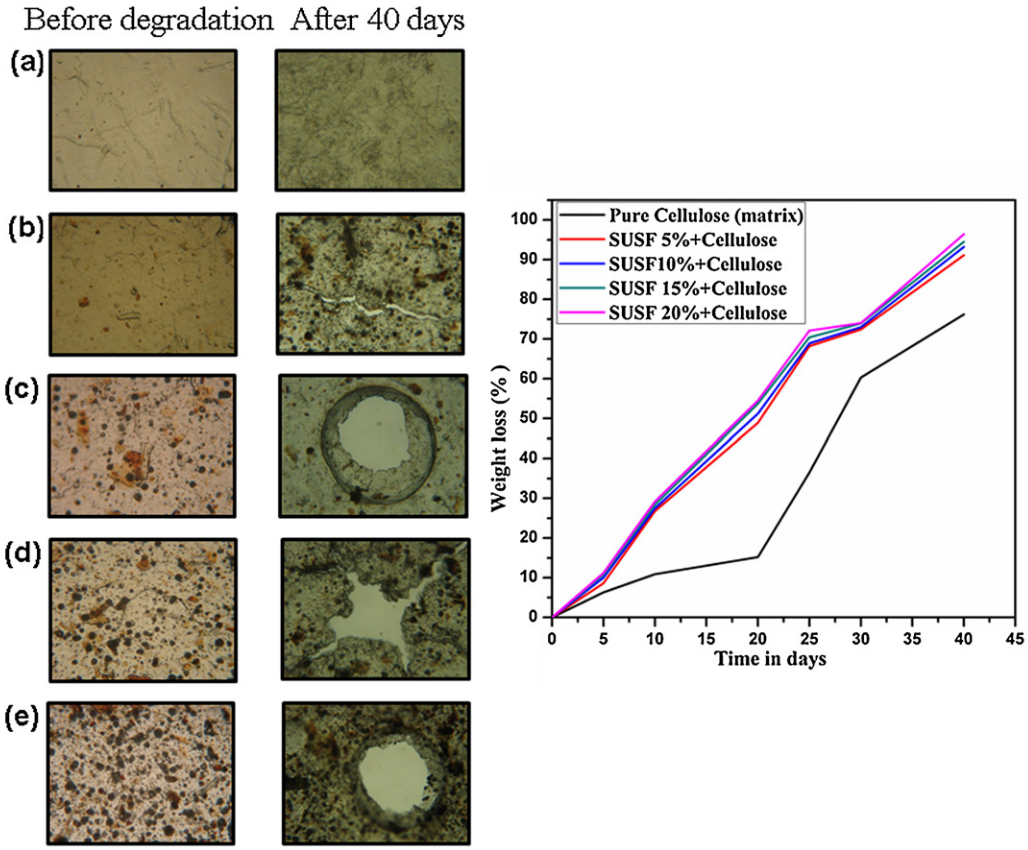

Fig. 3. Polarized optical microscope of pure cellulose with SUSF/Cellulose composite films before and after 40 days degradation in soil: (a) pure cellulose (matrix), (b) SUSF5% + cellulose, (c) SUSF10% + cellulose, (d) SUSF15% + cellulose and (e) SUSF20% + cellulose at same magnifications and including weight loss graph also.

and SUSF composites films were completely biodegrade in the soil.

3.3. *Thermal properties*

In order to verify the thermal stability of the composite films, in this study, their thermal properties were evaluated by thermogravimetric analysis (TGA). The primary thermograms of pure cellulose and the SUSF/cellulose composite films are presented in Fig. 4. From the thermograms, it can be seen that the pure cellulose started decomposition at 263 °C and SUSF/cellulose composite films started to decompose at 280 °C. The temperature at the maximum degradation rate for pure cellulose is about 361 °C, which is but higher than that of SUSF/cellulose composite films with different fiber loading (353–349 °C). All SUSF/cellulose composite samples are thermally stable up to 340 °C, which is the same for pure cellulose. For a given heating rate, the temperature at the maximum degradation rate is slightly shifted to higher values for the *S. urens* composite films, which may be due to the increased fiber loading in the composites.

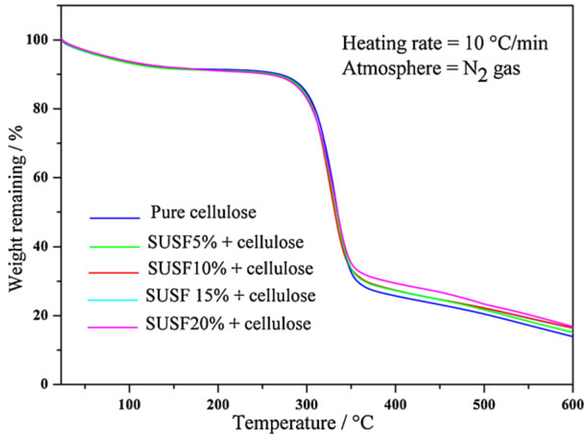

Fig. 4. Thermograms of pure cellulose and composites with different *Sterculia urens* fiber loading.

3.4. *Tensile properties of SUSF/cellulose composite film*

Tensile strength and modulus of SUSF/cellulose composite films are presented in Fig. 5(a) and (b), respectively. The average tensile strength (MPa) obtained, and Young's modulus of the composite films with different SUSF/cellulose composite films content are presented in Table 1. From Fig. 5(a) and (b), it is clear that the tensile strength and modulus of cellulose composite films are lower than that of the matrix. This is due to the fact that fibers were randomly oriented and, as a result, the stress was not being transferred uniformly. Furthermore, the tensile properties are found to improve in the case of the alkali treated fiber composite films, but the properties of these composite films are still lower than that of the matrix. On alkali treatment, the hemicelluloses and other waxy materials are removed and the surface of the fabric has become rough there by facilitating improved bonding between the fiber and matrix. However, the SUSF/cellulose composites have exhibited tensile properties comparable to the conventional packaging films such as polypropylene.

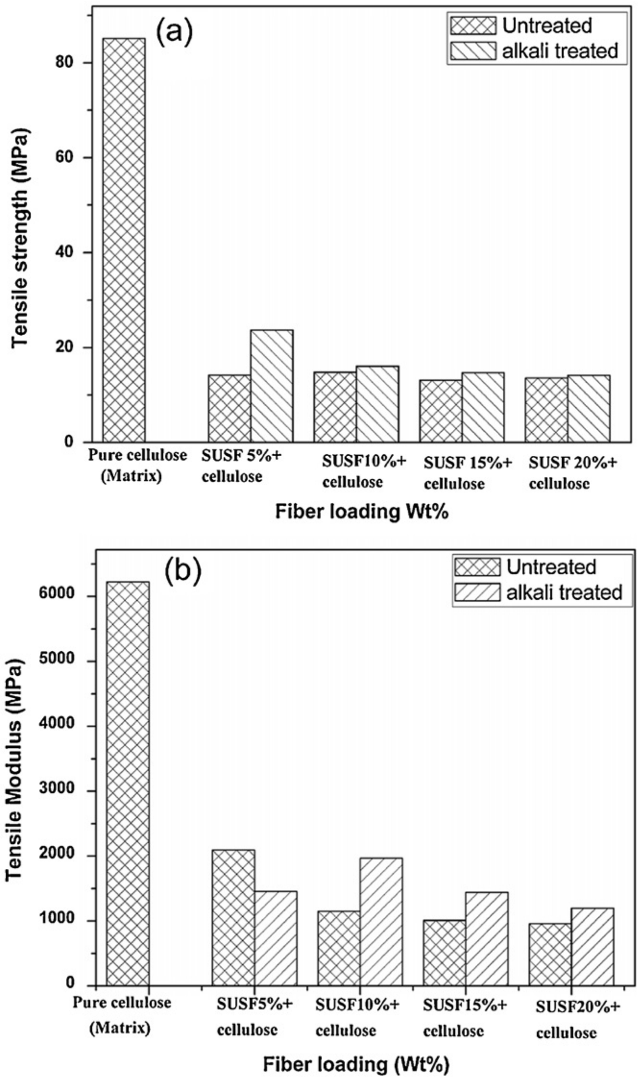

Fig. 5. (a) Tensile strength and (b) tensile modulus of pure cellulose and *Sterculia urens* fiber loading composites films (untreated and NaOH (alkali) treated).

Table 1
Tensile properties of cellulose (matrix) and *Sterculia urens* short fiber reinforced composite films.

Fiber loading (%)	Tensile strength (MPa)		Tensile modulus (MPa)	
	Untreated	Treated	Untreated	Treated
SUSF5% + cellulose (SD)[a]	16.4 (1.23)	26.9 (2.35)	3124 (101.6)	4820 (128.4)
SUSF10% + cellulose (SD)[a]	17.2 (1.54)	18.32 (1.58)	2196 (89.61)	3701 (113.7)
SUSF15% + cellulose (SD)[a]	16.34 (1.22)	17.02 (1.41)	1146 (61.2)	2980 (96.8)
SUSF20% + cellulose (SD)[a]	15.27 (1.13)	17.79 (1.52)	1002 (58.7)	2093 (86.07)
Cellulose (matrix) (SD)[a]	85.1 (32.71)		6223 (151.6)	

[a] Standard deviation.

4. Conclusion

The preparation and properties of biodegradable films from *S. urens* short fiber/cellulose green composites were studied. The SU/cellulose composite films have been prepared using green process. The whole production route of the matrix, SUSF composite films for packaging and functional materials are from renewable raw materials via an environmentally friendly method. The films are safe, stable and biodegradable. The SEM analysis showed the morphology of the fabrics as less thickness, rough surface with large number of etched striations and uniaxial roughly parallel fibers for 5% NaOH treated due to the removal of amorphous on the surface of the fabrics. The tensile properties of pure cellulose, SUSF with different percentage loading in the composite films are low when compare to matrix. However, the tensile properties of the composite films are comparable to those of the conventional packaging materials, such as polypropylene. The soil burial degradation behavior of the SUSF/cellulose composite films also indicates that the degradation rate of composite is faster than that of the matrix as confirmed by POM, which renders the composite films more advantageous in terms of environmental protection. In addition, this composite is thermally stable up to 340 °C. Finally, these green composites are completely biodegradable and safe for use in packaging applications, anti-counterfeiting and as functional materials.

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