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Cellulose fiber extracted from Napier grass in PVA composites

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Cellulose fiber is extracted from Napier grass (*Pennisetum Purpureum Schum*) and used as reinforcement for poly (vinyl alcohol) (PVA) matrix. The extraction of cellulose fibers is carried out with a combination of chemical and mechanical treatment. The effect of amount of fiber in the PVA matrix on the morphological, thermal and mechanical properties of the composite films has been analyzed. Fourier transform spectroscopy, scanning electron microscopy and transmission electron microscopy have been performed on the specimen at different stages during the processing of composite films to evaluate their structural properties. The tensile strength of the composite films is improved with an increase in the fiber content, however, fiber content greater than 8 wt% exhibit problems of aggregation and subsequent decline in the mechanical strength of the composite films. Thermal analysis demonstrate that the presence of Napier fibers do not have a significant effect on the degradation temperature of the composite films.

Keywords: Cellulose fiber, Composites, Napier grass, Poly (vinyl alcohol), Tensile strength

Over the past few decades natural fiber reinforced composites have been undergoing a remarkable transformation. These materials have been developed with a combination of natural fibers in a polymer matrix tailored for specific needs and applications[1-4]. Due to the low cost, renewability, sustainability and low abrasive nature, natural fiber reinforced plastics is fast replacing the synthetic fiber reinforced plastics to make adhesives, create DNA hybrid material, generate hierarchical composites, aerogels, foams etc[5,6]. There has been an increasing interest in the cellulose based composite material mainly due to their availability and biodegradability. Cellulose fibers extracted from plant source are believed to be promising reinforcing fillers in the production of various types of composites. In essence, the principal reason behind using cellulose fibers as potential reinforcing material is their high stiffness, very large surface to volume ratio and excellent mechanical properties[7-9]. In combination with a suitable matrix polymer, cellulose fiber networks hold considerable potential as an effective reinforcement for high quality specialty application of bio-based composites. In this study, cellulose fibers extracted from Napier grass have been evaluated as reinforcing filler for a water soluble polymer PVA which has hydrophilic properties and excellent film forming ability. The main objective of the study is to produce new biopolymer composites with good mechanical properties, thermal stability, maintaining their optical transparency for possible application as packaging material.

Experimental Section

Materials

Napier grass (*Pennisetum Purpureum Schum*) used in the present study was obtained from the neighbouring grounds of Punjab University campus. It was washed several times to remove extraneous impurities and dried in shade. The grass strands were then cut into small pieces of length 0.02 to 0.05 m. Poly (vinyl alcohol) supplied by Otto Chemicals private limited ($\overline{M}_w$= 13,000-23,000) was used as matrix for the composite preparation. Other reagents used in the present study include sodium hydroxide supplied by NICE chemicals, hydrogen peroxide (30%) was procured from EMPLURA Merck and hydrochloric acid (35%) was obtained from Merck.

Proximate analysis was done for the grass samples. The test was repeated 3-4 times and it was found that the grass contains 13-18% moisture content (105±2°C), 72-76% volatile matter 400±15°C) and 5-6% ash content (600±10°C). Analogous results of proximate analysis have been reported by Patel and Gami[10] for Napier grass (elephant grass) which was collected from Ahmadabad district of Gujarat State.

Pretreatment of grass

Washed and dried grass sample was soaked (overnight) in 2% w/v NaOH solution resulting in the swelling of the grass and facilitating further treatments[11,12]. The soaked grass was then treated with 10% w/v NaOH solution in an autoclave (121°C, 15 psi for 2 h) with solid to liquor ratio of 1:10. The washed pulp was then bleached (overnight) with 8% v/v solution of hydrogen peroxide followed by repeated washings. Hydrogen peroxide helps in the oxidation of lignin chromophores thus enhancing the brightness of the isolated fibers. Bleached and washed pulp was then subjected to acidic treatment with 10% (v/v) hydrochloric acid. The acidic treatment assists the breakdown of amorphous moieties of cellulose. The acidic suspension of fibers was sonicated using an ultrasonicator (Saritorius, LAB SONIC) in order to loosen the cellulose fibers and breakdown of agglomerates of cellulose fibers. After repeated washings the suspension was subjected to high shear homogenization (Pro Scientific Inc. USA, Model No. 01- 02250 Pro 250) for 10 min. The shearing force breaks down the fibers into smaller size to produce micro fibers. Subsequently the extracted fibers were obtained as an aqueous suspension.

PVA composites based on extracted cellulose fibers

Composite films of PVA and the isolated cellulose fibers were then prepared via the solution casting technique. In order to study the effect of amount of fiber on the morphological, thermal and mechanical properties of the composites, specific amount of the aqueous dispersion of fiber was added to aqueous PVA solution. Composite films with PVA/cellulose fiber weight ratios of 96/4, 94/6, 92/8 and 90/10 were casted. The obtained films were 0.1-0.2 mm in thickness.

Characterization of extracted fibers and composite films

Scanning electron microscope (CARL ZEISS SMT Ltd. EVO MA15) was used to analyze the micro structure of cellulose fiber before and after alkali treatment. Images of fiber were taken at 20 kV at different magnifications.

Fourier transform infrared (FTIR) spectroscopy was used to investigate the possible changes in the chemical composition of Napier grass at different stages of treatment in the process of isolation of cellulose fibers. A Perkin-Elmer RZX infrared spectrophotometer was used to obtain the spectra.

Thermo gravimetric analysis was carried out using a Mettler Toledo DSC/TGA/DMA 1 STAR^e system thermo gravimetric analyzer to determine the thermal stability of alkali treated grass and the synthesized composite films.

Tensile strength and strain at break for the composite films was measured according to the ASTM standard method D882 using a Zwick/Roell Z010 universal tensile testing machine. The initial gauge separation and cross speed were set to 0.05 m and 0.025 m min^{-1} respectively. Test specimen with a width of 10 mm was cut from composite sheets. All specimens were equilibrated in a chamber kept at 20°C and 35% relative humidity for 24 h before testing. The tests were conducted at ambient temperature and an average of 3 repeated tests was recorded.

Results and Discussion

Structural and morphological characterization

Isolated cellulose fibers

Autoclaving or steam explosion helps break down the structure of the lingo cellulosic material through hydrothermal treatment[6,13]. The alkaline hydrolysis acts on the ester bonds between the hemicelluloses and lignin leading to the solublisation of lignin[14]. A significant change in the morphology of the grass fibers was observed. Figure 1 shows the scanning electron micrograph of raw Napier grass and alkali treated Napier grass.

In order to study the effect of alkali treatment the grass was treated separately with 5, 8 and 10% w/w

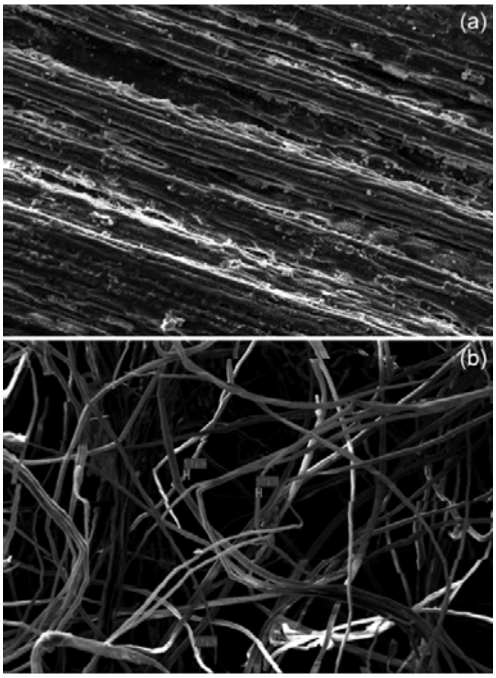

Fig. 1 — Scanning electron micrograph of (a) raw Napier grass and (b) alkali treated Napier grass

aqueous sodium hydroxide in an autoclave (103.42 kPa, 394.15 K) for 2 hr. FTIR spectra of alkali treated grass fibers showed an increase in the intensity of all peaks with an increase in the alkali concentration from 5% to 10%. The grass fibers treated with 10% alkali treated grass fibers showed the minimum transmittance compared to 5% and 8% alkali treated grass. Consequently, a 10% w/w alkali treatment (sodium hydroxide) in an autoclave for 2 h was invariably used for the isolation of cellulose fibers and in the formation of composite films in this study. Figure 2 illustrates the chemical changes that take place during the alkali treatment. The spectra shows a broad peak at 3365 cm^{-1} attributed to an O-H stretch band of hydrogen bonded hydroxyl group vibrations[15,16]. A high intensity and sharp peak indicated higher hydrophilicity of the fibers compared to untreated grass. Two peaks in the range 2850-3000 cm^{-1} correspond to the aliphatic saturated C-H stretching vibrations in lignin, cellulose and hemicelluloses. The peaks have been modified to a single sharp and strong peak at 2915 cm^{-1} in case of treated fibers suggesting a decrease or modification in the lignin and hemi cellulosic content. A strong peak at 1638 cm^{-1} corresponds to C=C stretching. Absence of peak at 1548 cm^{-1} and shifting of peak from 1462 cm^{-1} to 1430 cm^{-1} in the chemically treated grass is due to partial removal of lignin after alkali treatment of Napier grass. Higher intensities of peaks at 1430, 1336 and 1318 cm^{-1} are attributed to CH_2 bending mode, C-H asymmetric deformation and the CH_2 wagging vibrations in cellulose and hemicelluloses respectively.

The results indicated a high purity of polysaccharides in the treated fibers. The region 1200-1032 cm^{-1} represents the C-O stretch band and deformation in cellulose and residual lignin and hemicelluloses. Elevated peak at 897 cm^{-1} signifies the absorption due to β, 1-4 glycosidic linkages representing a higher content of inter-molecular hydrogen bonds in the cellulose molecules[17]. An increase in the cellulose content upon alkali treatment of Napier grass has been reported by Reddy *et al.*[18] Additionally, dilute acid treatment assisted in the degradation of hemicelluloses and led to the defibrillation of cellulose bundles. Ultrasonication further facilitated the de-agglomeration and size reduction process. Further, mechanical treatment by using a high shear homogenizer assisted the defibrillation of the cellulose fibers to micro scale.

PVA/cellulose fiber composite films

Scanning electron micrograph of the film surface (Fig. 3) demonstrates flat films with some fibril aggregation. All fibrils were found to be uniformly

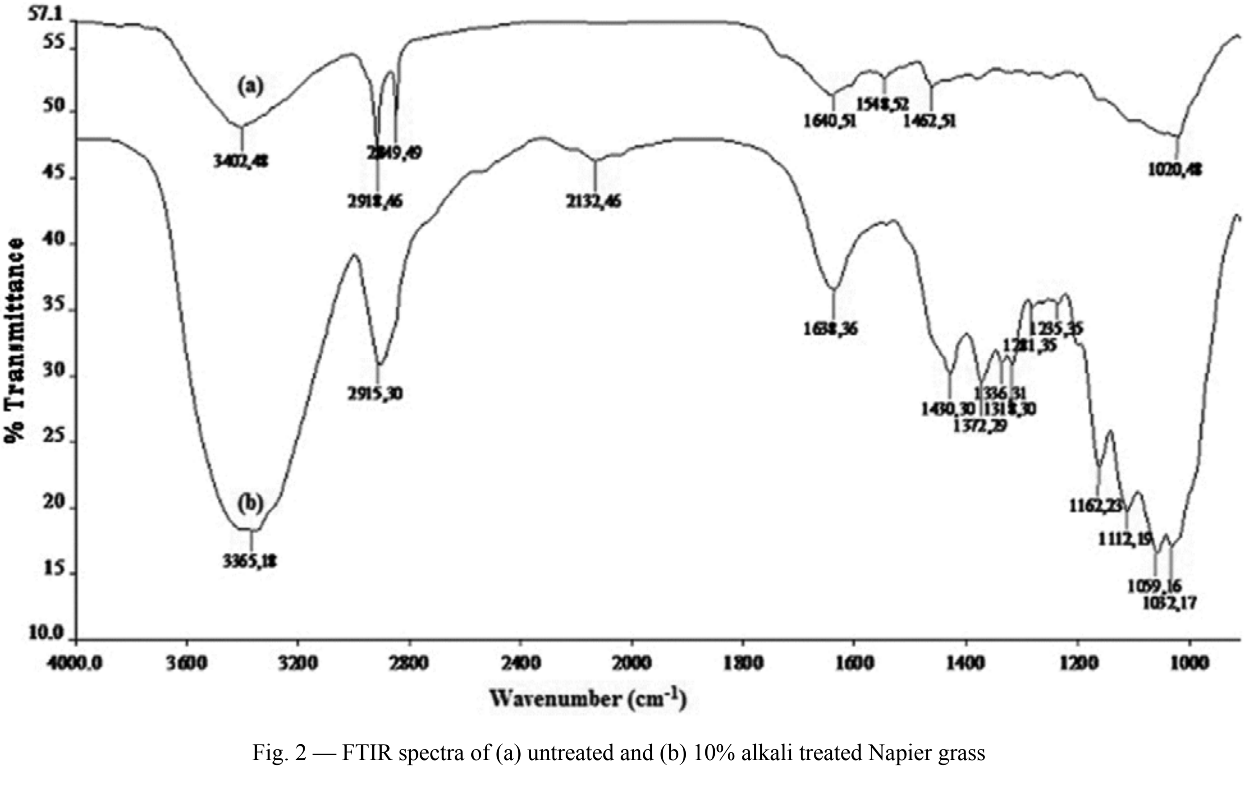

Fig. 2 — FTIR spectra of (a) untreated and (b) 10% alkali treated Napier grass

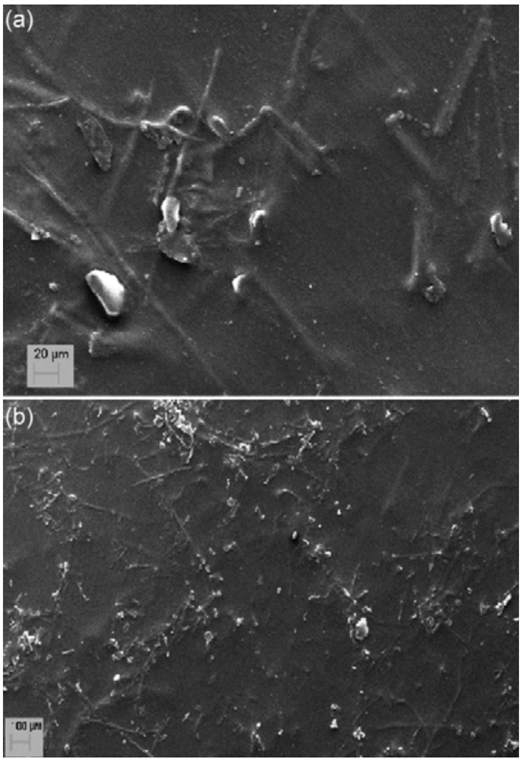

Fig. 3 — Scanning electron micrographs for (a) 96/4 and (b) 90/10 PVA/cellulose fiber film composites

coated with the polymeric material. The fibers were randomly distributed throughout the PVA matrix.

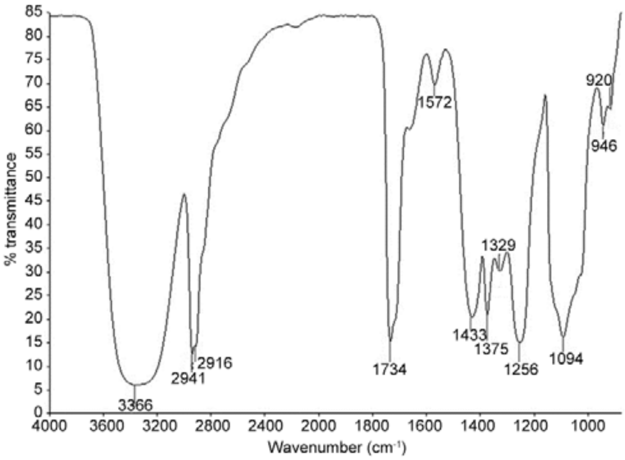

Fig. 4 — FTIR spectra of PVA film

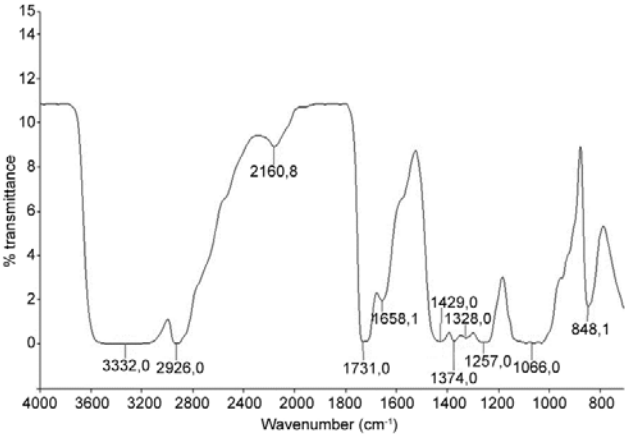

Fig. 5 — FTIR spectra of PVA/cellulose fiber (96/4) composite film

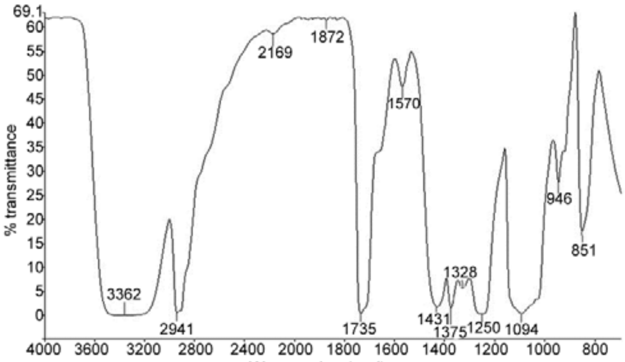

Fig. 6 — FTIR spectra of PVA/cellulose fiber (90/10) composite film

Figure 4 depicts the FTIR spectra of pure PVA film. The major characteristic peaks at 3366 cm^{-1} corresponding to the O-H stretching and the H-bonding interactions, at 2941cm^{-1} and 2916 cm^{-1} corresponding to C-H stretching, at 1734 cm^{-1} and 1572 cm^{-1} corresponding to the aromatic C=O (residual acetate in PVA) and C=C stretching respectively[19]. Peaks at 1433, 1375 cm^{-1} correspond to the CH$_2$ bending vibrations in the PVA molecules while the peak at 1329 cm^{-1} corresponds to the combination frequency of C-H and O-H bonds and a peak at 1256 cm^{-1} corresponds to the C-H wagging. A significant peak at 1094 cm^{-1} signifies the C-O stretching in the C-O-H bond. And the peaks at 946 and 926 cm^{-1} represent the O-H bending vibrations[20]. The FTIR spectra obtained for PVA/ cellulose fiber reinforced composite films is shown in Fig. 5 and Fig. 6. It was observed that the peak at 1734 cm^{-1} which is a characteristic absorption of PVA was also present in the FTIR of composite films. Also, the peak around 897 cm^{-1} which is a characteristic of β,1-4 glycosidic linkages absent in pure PVA film now appeared in the composite films. The two peaks existed together in the FTIR spectra of composite films indicating the success of blending of PVA and cellulose fibers. However, a small shift of this peak to lower frequencies was observed for the composite films and the shift increased with the increasing concentration of fibers in the composite films. It is worth noting that the location of the main peaks in the composite films is closer to PVA. This suggests that the interaction between the PVA-PVA molecules is stronger than PVA-cellulose fiber molecule.

The major peak at 3363 and 3332 cm^{-1} in the composite film spectra correspond to the O-H stretching similar to pure PVA but with a minor shift and peak broadening corresponding to the possible overlapping of bonds and intermolecular and intramolecular hydrogen bonding. The peak at 2941 cm^{-1} in pure PVA was also observed in composite film with peak shifting to 2926 cm^{-1} in case of 90/10 composite films suggesting a decrease in the C-H stretching vibrations and hence brittle film as were observed visibly. In case of 96/4 composites, a weak band at 2169 cm^{-1} correspond to the combination frequency of C-H and C-C bonds which was missing in the 90/10 composites, suggesting that there is a decrease in the molecular interactions with an increasing concentration of the fibers in the composite films. Peak at 1658 cm^{-1} was prominent in case of 90/10 composite films which could be either due to C=C stretching or O-H bending. The analysis suggests a decrease in the polymer filler interaction as the concentration of the filler goes on increasing.

Thermo gravimetric analysis

The thermal decomposition behaviour of the composite films was measured by thermo gravimetric analyzer (TGA). Analysis of the thermal properties of materials is important to determine their processing temperature range and use. The TGA data thermographs obtained for the composite films is shown in Fig. 7.

A two stage degradation thermograph was obtained for the PVA/cellulose fiber reinforced composites. The initial weight loss between 50°C to 140°C is attributed to the moisture loss in the composite films. The second stage degradation between 220°C to 350°C is because of pyrolysis of cellulosic fibers. The third stage weight loss beyond 420°C is due to the decomposition of carbonaceous matter. The 50% weight loss (T_{50}) and 75% weight loss (T_{75}) temperatures for the pure PVA film and PVA/cellulose fiber composite films have been tabulated in Table 1.

Reinforcement with a filler material usually causes a thermal transition depending on the type of interaction that takes place between the base matrix and the filler. From the T_{50} values, it was observed that the presence of cellulosic fibers isolated from Napier grass in the PVA matrix up to a loading of 8 wt% had no significant effect on the thermal stability of the composite films. The marginal temperature change observed might be due to the presence of impurities in the sample. However, there is a significant fall in the onset degradation temperature, T_{10}, T_{50} and T_{75} for the 90/10 composite films. There is a 10% fall in the T_{50} temperature for 90/10 composite compared to pure PVA film. The SEM images of the 90/10 composite films also showed aggregation of the fibers on the surface of the film. FTIR spectra also suggested weak interactions for this composite film.

Mechanical testing

The mechanical properties of the composite films are mainly associated with the amount of filler loading, processing methods, compatibility of the filler with matrix. Good dispersion of fibers in the polymer matrix and good adhesion is an important prerequisite for achieving good mechanical properties of the resulting composites. The PVA/cellulose fiber

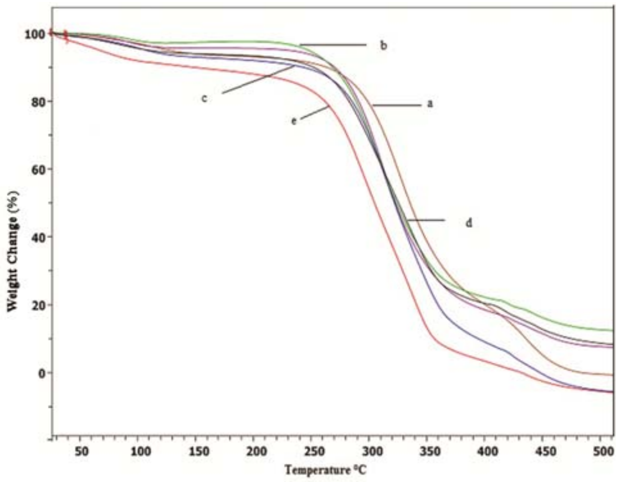

Fig. 7 — TGA data thermograms of PVA and cellulose fiber reinforced PVA films (a) PVA; (b) 4 wt% cellulose fiber; (c) 6 wt% cellulose fiber; (d) 8 wt% cellulose fiber and (e) 10 wt% cellulose fiber

Table 1 — TGA data of cellulose fiber reinforced PVA composite films

System	T_{50} (°C)	T_{75} (°C)
PVA	340	380
PVA/ cellulose (96/4)	330	377
PVA/ cellulose (94/6)	329	367
PVA/ cellulose (92/8)	325	365
PVA/ cellulose (90/10)	305	335

Table 2 — Mechanical properties of composite films

System	Tensile strength (MPa)	Strain at break (%)
PVA	49.3	22
PVA/ cellulose (96/4)	53.7	13
PVA/ cellulose (94/6)	57.4	9.6
PVA/ cellulose (92/8)	67.3	4.1
PVA/ cellulose (90/10)	21.4	2.8

composite films were subjected to mechanical testing on a universal tensile testing machine. The tensile strength and the % strain at break for pure PVA and the composite films are presented in Table 2.

Addition of cellulose fibers to the PVA matrix had a positive effect on the tensile properties, inducing significant increase in the tensile strength. An increment in the tensile strength indicates the effectiveness of the cellulose fibers isolated from Napier grass as reinforcement in the PVA matrix. A 36.5% increase in tensile strength over pure PVA films was observed for 92/8 composite films. However, the tensile strength decreased drastically for the 90/10 composite films. An Increase in the tensile strength with the addition of cellulosic fibers to hydrophilic matrices has been previously reported by different researchers[1,14]. The observed decline in the tensile strength at 10 wt% cellulose fiber loading might be due to the non uniform dispersion of the fibers in the matrix. In case of higher fiber loadings with high density of hydroxyl groups on the surface of cellulose, an intra and inter connected network forms which may decrease the adherence with surrounding matrix. Agglomeration was also observed in the SEM images of the 90/10 composite films. TGA analysis also supported this observation as there was a decline in the degradation temperature of 90/10 composite films.

Conclusion

The extraction of cellulose fibers from the Napier grass has been considered to produce PVA based composites with a maximum cellulose content of 10 wt%., with the objective of studying its compatibility with the polymer matrix and the possible reinforcement effect on the composite. The morphological study revealed a positive interaction between the cellulose fibers and PVA molecule. However, some aggregation of the fibers was observed for higher fiber loadings of 10 wt%. Clusters were observed in the SEM images of the 90/10 composite films. Thermal analysis suggests that addition of cellulose fibers to PVA matrix had no significant effect on the thermal stability of the composite films. A decrease in the temperature for 50% weight loss and 75% weight loss of the samples was observed. However, in case of 90/10 composite films, there are a marked decline in the onset degradation temperature. Mechanical analysis revealed that there is an increase in the tensile strength of the cellulose reinforced PVA composite films. The tensile strength observed for PVA, 4%, 6%, 8% and 10% cellulose reinforced films were 49.3, 53.7, 57.4, 67.3 and 21.4 MPa respectively. However, there is an abrupt fall in the tensile strength of 90/10 composite film which may be due to the aggregation of cellulose fibers creating weak pockets in the films. This observation was supported by the TGA results, where in a fall in the onset degradation temperature was observed. The optimum concentration of cellulose fiber reinforcement is thus proposed to be 8wt% beyond which the system becomes critical.

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