



Synthesis, characterization and antibacterial activity of biodegradable starch/PVA composite films reinforced with cellulosic fibre



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ABSTRACT

Cellulosic fibres reinforced composite blend films of starch/poly(vinyl alcohol) (PVA) were prepared by using citric acid as plasticizer and glutaraldehyde as the cross-linker. The mechanical properties of cellulosic fibres reinforced composite blend were compared with starch/PVA cross linked blend films. The increase in the tensile strength, elongation percentage, degree of swelling and biodegradability of blend films was evaluated as compared to starch/PVA crosslinked blend films. The value of different evaluated parameters such as citric acid, glutaraldehyde and reinforced fibre to starch/PVA (5:5) was found to be 25 wt.%, 0.100 wt.% and 20 wt.%, respectively. The blend films were characterized using Fourier transform-infrared spectrophotometry (FTIR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA/DTA/DTG). Scanning electron microscopy illustrated a good adhesion between starch/PVA blend and fibres. The blend films were also explored for antimicrobial activities against pathogenic bacteria like *Staphylococcus aureus* and *Escherichia coli*. The results confirmed that the blended films may be used as exceptional material for food packaging.

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1. Introduction

In the latest years, industries have been working to decrease the dependence on petroleum based fuels and products due to the increase in environmental consciousness. This leads to investigate the environmentally friendly sustainable materials to replace the existing ones. The tremendous increase in production and use of plastics in our life resulted in generation of huge plastic wastes. Due to disposal problems, as well as strong regulations and criteria for cleaner and safer environment, have directed great part of the scientific research towards eco-composite materials (Bledzki & Gassan, 1999). In order to solve the problems generated by plastic waste, many efforts have been made to obtain the environmental friendly materials. Many researchers are working on the substitution of the petro-based plastics by biodegradable materials with similar properties and low in cost. Several studies have been reported the use of biodegradable starches from different sources to prepare films and coatings with different properties (Bertuzzi, Armada, & Gottifredi, 2007; Larotonda, Matsui, Sobral, & Laurindo,

2005; Mali, Grossmann, Garcia, Martino, & Zaritzky, 2005; Mali, Sakanaka, Yamashita, & Grossmann, 2005). Starch is the most important polysaccharide polymer used to develop biodegradable films, as it has potential to form a continuous matrix. Starch exhibits some disadvantages such as a strong hydrophilic character and poor mechanical properties as compared to conventional synthetic polymers, which make it inadequate for some packaging purposes (Alves et al., 2006; John & Thomas, 2008). Poly(vinyl alcohol) is an important synthetic biodegradable polymer having excellent gas barrier properties, high strength, tear and flexibility. However, it has poor dimensional stability due to high moisture absorption. Moreover, it has relatively high price compared to other commercial polymers. Therefore, blended with renewable and abundant agro-resource based such as polysaccharides, particularly starch can be utilized to reduce the manufacturing cost. Blending with starch resulted in improved moisture resistance and accelerated degradation (Han, Chen, & Hu, 2009; Russo et al., 2009). However, the properties of the blends deteriorated as starch content in the blend formulation increased, owing to poor compatibility between the two components and phase separation during blend preparation. Many techniques have been reported to improve the compatibility between PVA and starch such as addition of suitable plasticizers, cross-linking agents, fillers

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Table 1

Composition of St/PVA blend films and fibres reinforced St/PVA composite blend films.

Sample	Starch (%)	PVA (%)	CA (wt.%)	GLU (wt.%)	Fibre loading (wt.%)
St/PVA	5	5	–	–	–
St/PVA/CA	5	5	5	–	–
St/PVA/CA	5	5	10	–	–
St/PVA/CA	5	5	15	–	–
St/PVA/CA	5	5	20	–	–
St/PVA/CA	5	5	25	–	–
St/PVA/CA	5	5	30	–	–
St/PVA/CA/GLU	5	5	25	0.050	–
St/PVA/CA/GLU	5	5	25	0.100	–
St/PVA/CA/GLU	5	5	25	0.150	–
St/PVA/CA/GLU	5	5	25	0.250	–
St/PVA/CA/GLU	5	5	25	0.300	–
St/PVA/CA/GLU/fibre	5	5	25	0.100	5
St/PVA/CA/GLU/fibre	5	5	25	0.100	10
St/PVA/CA/GLU/fibre	5	5	25	0.100	15
St/PVA/CA/GLU/fibre	5	5	25	0.100	20
St/PVA/CA/GLU/fibre	5	5	25	0.100	25
St/PVA/CA/GLU/fibre	5	5	25	0.100	30

and compatibilizers (Dean & Petinakis, 2008; Jia, Cheng, Zhang, & Zhang, 200; Krumova, Lopez, Benavente, Mijangus, & Perena, 2000; Nath, Gupta, Yu, Blackburn, & White, 2010; Peng, Kaishuen, Wei, & Lui, 2005; Sanghavi, Mobin, Mathur, Lahiri, & Srivastava, 2013; Sanghavi, Sitaula, et al., 2013; Sanghavi & Srivastava, 2013; Siddaramaiah & Somashekar, 2004; Sin, Rahman, Rahmat, & Samad, 2010; Sreedhar, Sairam, Chattopadhyay, Rathnam, & Mohan, 2005; Yoon, Chough, & Park, 2006; Zhu, Zhang, Lai, & Zhang, 2007). However, some of these cross-linking agents always display toxicity and thus their potential applications as biomaterials have been limited. To overcome these disadvantages, certain nontoxic functional additives and simple modification techniques are required to improve the mechanical properties and water resistibility of the St/PVA films. Citric acid (CA) with one hydroxyl and three carboxyl groups exists widely in citrus fruits as main organic acid. Due to its multi-carboxylic structure, interaction could take place between the carboxyl groups of CA and the hydroxyl groups on the starch. It resulted in improved water resistibility (Borredon, Bikiaris, Prinos, & Panayiotou, 1997), prevent recrystallization and retrogradation and enhance the mechanical properties (Imam, Cinelli, Gordon, & Chiellini, 2005; Park, Choughy, Yun, & Yoon, 2005; Raddy & Yang, 2010; Shi et al., 2007, 2008; Yoon et al., 2006). CA is non-toxic metabolic product of the body (Krebs or citric acid cycle) and has been approved by FDA for using in food formulations (Ghanbarzadeh, Almasi, & Entezami, 2011). It has been reported that sorbitol, glycerol, urea are used as the plasticizer blend films but citric acid showed improved properties (Imam et al., 2005; Park, Chough, Yun, & Yoon, 2005). Several studies has been reported on the development of composite blends of starch with polyethylene of low and high density (LDPE, HDPE), starch and poly(vinyl alcohol) (PVA), poly(3-hydroxybutyrate co-3-hydroxyvalerate) (PHBV) and poly(lactic acid) (PLA), poly(butylene succinate) (PBS) with cellulosic fibres such as banana, pineapple leaf, sisal, jute, ramie and bamboo fibres (Avella, Martuscelli, & Raimo, 2000; Averous & Boquillon, 2004; Cao, Shibata, & Fukumoto, 2006; Carvalho, Curvelo, & Agnelli, 2001; Chen et al., 2006; Choi et al., 2004; Cunha, Liu, Feng, Yi, & Bernardo, 2001; Digabel, Boquillon, Dole, Monties, & Averous, 2004; Fang & Fowler, 2003; Gadhari, Sanghavi, & Srivastava, 2011; Godbole, Gote, Latkar, & Chakrabarti, 2003; Guimaraes, Wypych, Saul, & Ramos, 2010; Kunanopparat, Menut, Morel, & Guilbert, 2008; Lee & Wang, 2006; Luo & Netravali, 1999; Ma, Yu, & Kennedy, 2005; Misra, Misra, Tripathy, Nayak, & Mohanty, 2002; Pinto, Carbajal, Satyanarayana, Fernando, & Ramos, 2009; Rodriguez, Ramsay, & Favis, 2003; Sanghavi & Srivastava, 2010; Sanghavi, Kalambate, Karna, & Srivastava, 2014; Tripathi, Mehrotra, & Dutta, 2009; Zobel, 1988). Globally, efforts have been made to

develop bioplastics from renewable polymers for use as mulch film, materials for green-house construction, packaging, and aids for transporting and transplanting plants/seedlings and antimicrobial properties which improve the food safety and shelf-life. Antimicrobial packaging has one of the most promising active packaging systems. Antimicrobial packaging has been used for the inhibition of certain bacteria in foods, but barriers to their commercial implementation continue to exist (Tripathi et al., 2009).

This paper describes the preparation of cellulosic *Grewia optiva* fibre reinforced composite cast films from blends of corn starch and PVA. Citric acid and glutaraldehyde have been used as plasticizer and crosslinker, respectively. The effect of citric acid and glutaraldehyde on mechanical properties and degree of swelling were also attempted. Further, the composite blend films were characterized with Fourier transform infrared spectrophotometer (FTIR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The antibacterial activity of St/PVA crosslinked blend films and composite blend films were explored on food pathogenic bacteria such as *Escherichia coli* and *Staphylococcus aureus*.

2. Experimental

2.1. Materials and methods

Starch (corn starch) (St), glutaraldehyde (GLU) and polyvinyl alcohol (PVA) were obtained from CDH India and used without any further purification. Citric acid (CA) was obtained from Aldrich Company India. PVA was 99% hydrolysed with average molecular weight of 99,000–1,000,000. The weighing of the samples has been done on Libror AEG-220 (Shimadzu, Japan) electronic balance. Bacterial strain, *S. aureus* ATCC 43300 and *E. coli* MTCC 739 were used by Bio Tech. Research Laboratory Shoolini University, Solan, Himachal Pradesh, India. Antibiotic discs (amoxicillin 25 µg/disc) and nutrient agar were obtained from Himedia Laboratories Limited.

2.2. Preparation of St/PVA blend films

St/PVA blend films were prepared by casting method. In this method, 5 g of PVA was dissolved in hot water (90 °C). The gelatinized starch was mixed to form homogeneously gel solution. The mixture was continuous stirring for 5 min on a mechanical stirrer (1500 rpm) at room temperature. CA (5–30%) and GLU (0.05–0.250%) were added to above mixture with continuous stirring. The total amount of polymeric mixture was 100 g. The mixing compositions of different additives were shown in Table 1. The

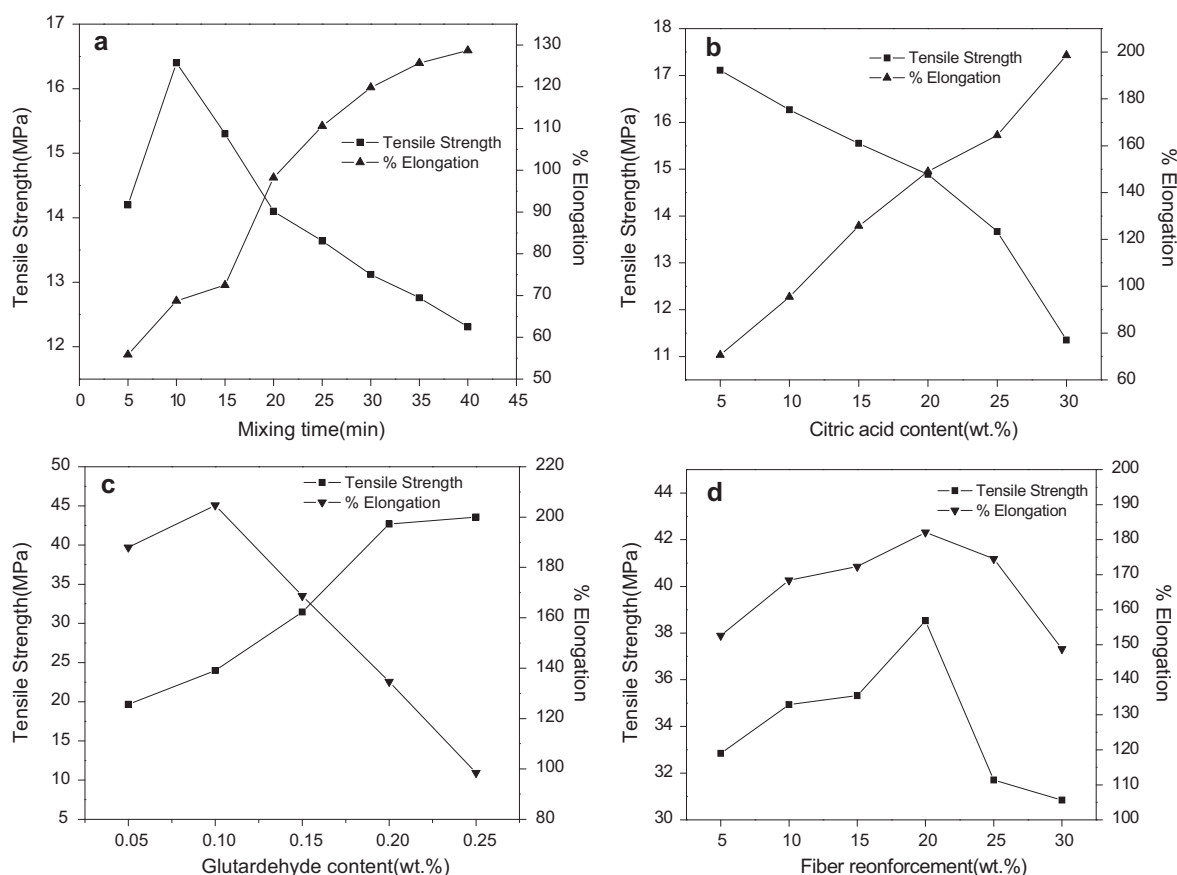


Fig. 1. Tensile strength (TS) and % elongation (%E) of (a) St/PVA, (b) St/PVA/CA, (c) St/PVA/CA/GLU and (d) St/PVA/CA/GLU/*Grewia optiva* fibre.

reaction parameters such as mixing time, CA and GLU concentration were optimized. Bubbles formed during the preparation of blend films were removed by using an aspirator. The suspension so formed was poured onto teflon plate to prepare blend film. The blend films were dried at room temperature for 72 h.

2.3. Reinforcing material

In this study *G. optiva* fibres collected from local resources were used as reinforcing material. The fibres were washed with mild detergent to remove the impurities involved during extraction of fibres. The fibres were dried at hot air oven maintained at 80 °C for 12 h. After drying the fibres were converted into fine particle using ball mill (FRITCH Pulbersette-5) of dimension 15–20 μm.

2.4. Synthesis of lignocellulosic fibre reinforced St/PVA blend films

G. optiva fibres of dimension 15–20 μm were mixed thoroughly with St/PVA blend using a mechanical stirrer, at different loadings (5–30% in terms of weight). This mixture was poured into teflon plate and allowed to dry at room temperature. The mixing composition of raw *G. optiva* fibre was shown in Table 1.

2.5. Mechanical properties of St/PVA blend films and fibre reinforced St/PVA blend films

Tensile strength (TS) and elongation percentage (%E) of St/PVA blend films and fibre reinforced St/PVA blend films were performed on a computerized Universal Testing Machine (Hounsfield H25KS). The tensile test was conducted in accordance with the ASTM D

638 method. The specimen average thickness was about 1 mm and operated at a cross-head speed of 20 mm/min at 30 °C.

2.6. Degree of swelling (DS) of St/PVA blend films

In this, dried St/PVA blend films were immersed in distilled water at room temperature (35 °C) and kept for 24 h, moisture on the surface of the film was removed, and the weight of the films was measured. The degree of swelling (DS) of St/PVA blend films was calculated as (Ghanbarzadeh et al., 2011):

$$DS = \frac{W_i - W_f}{W_f} \quad (1)$$

where W_i is the initial weight of St/PVA blend films and W_f is the final weight of St/PVA blend films.

2.7. Fourier transforms infrared (FTIR) spectroscopy

FTIR spectra of St/PVA blend films were recorded on a Perkin Elmer spectrophotometer using KBr pellets. The spectrum was recorded in the range from 4000 to 400 cm⁻¹ with a resolution of 2 cm⁻¹.

2.8. Scanning electron microscopy (SEM)

The scanning electron microscopic analysis of different samples was performed on a Leo Electron Microscopy Machine (No. 435-25-20).

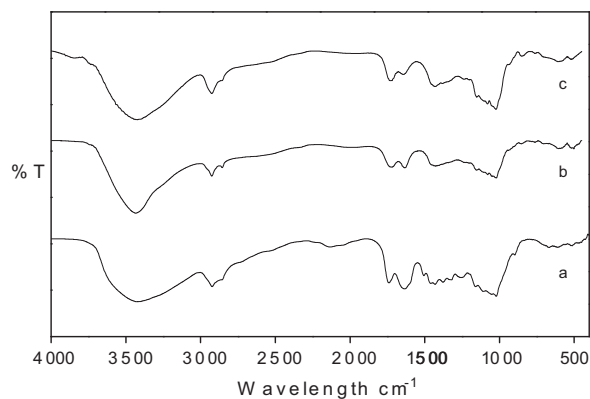


Fig. 2. FTIR of (a) raw *Grewia optiva* fibre, (b) St/PVA crosslinked blend film and (c) fibres reinforced St/PVA composite blend film.

2.9. Thermogravimetric analysis

Thermogravimetric analysis of starch/PVA blend film was performed using EXSTAR TG/DTA 6300 at a heating rate of 10 °C/min under nitrogen atmosphere.

2.10. Antibacterial activity

Antibacterial activities of starch/PVA blend films were measured against Gram negative (*E. coli*) and positive bacteria (*S. aureus*) with disc diffusion method (Vimala et al., 2011).

2.11. Biodegradability in soil

In this method, samples of starch/PVA films, 20 mm × 20 mm × 1 mm small pieces were weighted and placed for 120 days into the agricultural soil in a pot. The pot was covered with a plastic net and exposed to atmospheric conditions for 120 days. Variations in film morphology, the time of films disintegrated

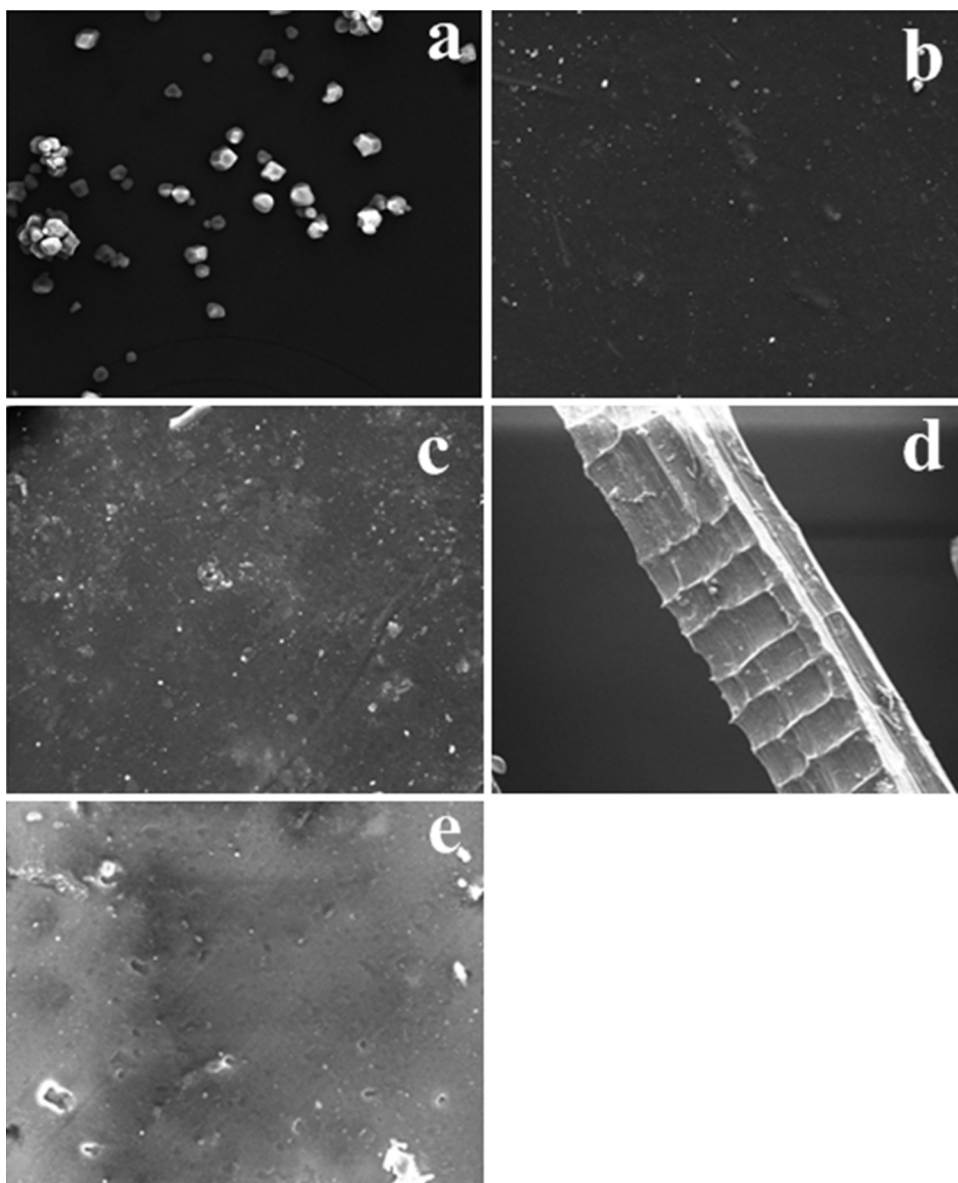


Fig. 3. SEM images of (a) starch, (b) PVA film, (c) St/PVA crosslinked blend film, (d) raw *Grewia optiva* fibre and (e) fibres reinforced St/PVA composite blend film.

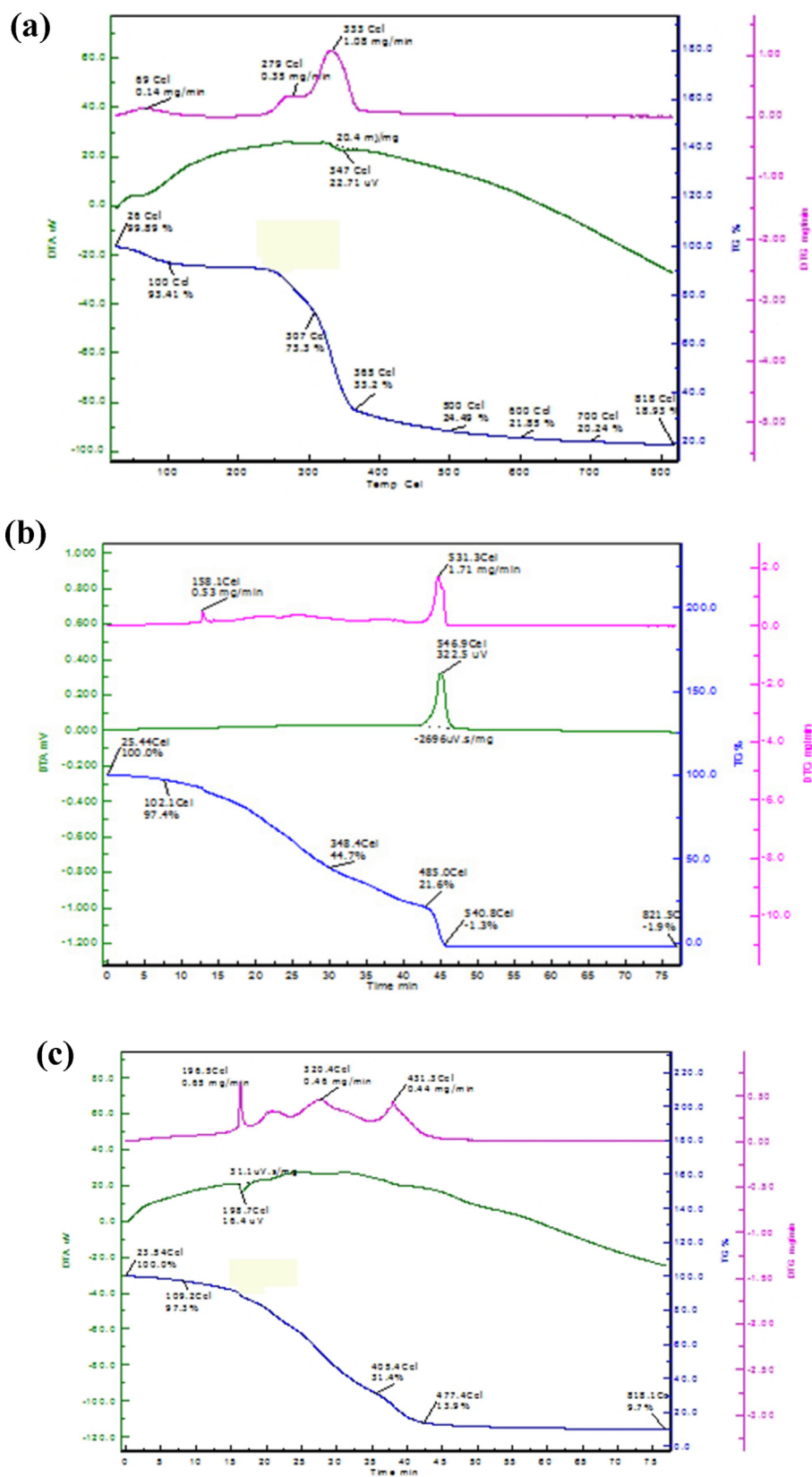


Fig. 4. TGA/DTA of (a) raw *Grewia optiva* fibre, (b) St/PVA crosslinked blend films and (c) fibres reinforced St/PVA composite blend film.

Table 2

Degree of swelling of St/PVA blend films and weight loss in St/PVA crosslinked blend film and fibre reinforced St/PVA composite blend film exposed to soil for 120 days.

Sample	Degree of swelling (DS)	% wt. loss
St/PVA	2.8	–
St/PVA/CA	1.72	–
St/PVA/CA/GLU	0.53	35.54
Fibre reinforced St/PVA blend film	0.74	45.65

and weight loss were recorded. To determine the weight loss the specimen of each sample was quickly washed with cold water and dried in an oven at 70 °C to constant weight. The weights of the sample, before and after washing were recorded (Imam et al., 2005).

3. Results and discussion

3.1. Optimization of different parameters on mechanical properties

3.1.1. Effect of mixing time

Fig. 1a shows tensile strength (TS) and elongation (%E) of St/PVA blend film without additives for 40 min at 90 °C. At the mixing time of 10 min, TS and %E were found to be 16.4 MPa and 68.74% respectively. Further, increase in time resulted in change in colour and decrease in TS and %E of blend films.

3.1.2. Effect of citric acid (CA)

Effect of CA on TS and %E of St/PVA blend film was shown in Fig. 1b. The CA as the crosslinker and the plasticizer in the St/PVA blend films. With the initial increase in CA value from 5 to 30 wt.%, value of TS and %E increases. It has been evident that with increase in CA wt.%, the decrease in TS (17.11–11.35 MPa) and increase of the %E (70.65–198.59%) was observed. The residual CA in the blends acted as the plasticizer, which reduced the interactions among the macromolecules. The decrease in the interactions may be due to the presence of hydroxyl group and carboxyl groups present on CA, which form hydrogen bonds between St/PVA and additive molecules (Ghanbarzadeh et al., 2011; Yoon et al., 2006). It has been extensively used to improve the flexibility due to its diplex function (Avella et al., 2000).

3.1.3. Effect of glutaraldehyde as crosslinking agent

Fig. 1c shows the effect of GLU (0.05–0.250%) on TS and %E of St/PVA/CA blend film. The effect of crosslinking of GLU on St/PVA films has been reported (Yoon et al., 2006). It has been found that TS (43.4 MPa) increases and %E (204.23%) decreases with the increased in wt.% of GLU from 0.05 to 0.150%. The blend film so formed was referred as St/PVA crosslinked blend film with remarkable TS and %E.

3.1.4. Effect of fibre loading on St/PVA crosslinked blend films

TS and %E of *G. optiva* fibre loading onto St/PVA crosslinked blend films was shown in Fig. 1d. Fibres were added to crosslinked blend from 5 to 30 wt.%. The result indicated that TS increased on reinforcement with cellulosic fibres. It has been observed that at 20%

loading, TS and %E were found to be 38.53 MPa and 182.1%, respectively. The film so formed was referred as fibre reinforced St/PVA composite blend film.

3.2. Degree of swelling

The swelling behaviour of St/PVA, St/PVA/CA, St/PVA/CA/GLU and fibre reinforced St/PVA composite blend films were shown in Table 2. It was observed that degree of swelling decreased with increase in time. The addition of CA and GLU in St/PVA blend films decreased the DS value which confirmed the superior reactivity of CA and GLU (Krumova et al., 2000). The slight increase in DS value was recorded in fibre reinforced St/PVA composite blend films, which may be due to the greater affinity of water for OH groups present in the fibre reinforced St/PVA blend films.

3.3. FTIR analysis

FTIR spectra of raw *G. optiva* fibre, St/PVA crosslinked blend films and fibre reinforced St/PVA composite blend films were shown in Fig. 2a–c. FTIR spectra of raw *G. optiva* fibre (Fig. 2a) showed a broad peak at 3431.39 cm^{−1} due to bonded OH groups. The absorption peak at 2922.31, 1431.01, and 1021.93 cm^{−1} was due to –CH₂, C–C, and C–O stretching, respectively (Singha & Rana, 2012; Singha, Rana, & Guleria, 2012). Fig. 2b shows the IR spectra of St/PVA crosslinked blend films. The peak at 3434 cm^{−1} was assigned to the stretching vibration of the hydroxyl groups. Broad peak at 1717 cm^{−1} may be due to the C=O stretching vibration and it was probably caused by the ester bond and carboxyl C=O groups in CA (Shi et al., 2008). The peak at 2858.10 cm^{−1} and 2925 cm^{−1} corresponds to C–H stretching of aldehydic group of glutaraldehyde crosslinked to blend (Tudorachi, Cascaval, Rusu, & Pruteanu, 2000). The change in peak intensity at 3434 cm^{−1} in Fig. 2c confirmed the number of the hydroxyl groups rises due the interaction of fibre with St/PVA crosslinked blend.

3.4. Surface morphology

Scanning electron micrographs of corn starch, PVA, St/PVA crosslinked blend film and fibre reinforced St/PVA composite blend film were shown in Fig. 3a–e. The corn starch (Fig. 3a) showed polyhedra or polygon shape granules. Fig. 3b confirmed the smooth surface of PVA film. The St/PVA crosslinked blend film (Fig. 3c) was found to be smooth without any cracks and pores. The SEM images of *G. optiva* fibre confirmed the rough surface (Fig. 3d). Morphological investigations of fibre reinforced St/PVA composite blend film (Fig. 3e) clearly indicate the proper mixing of fibre particles with the St/PVA crosslinked blend.

3.5. Biodegradability in soil

The crosslinked and fibres reinforced St/PVA composite blend films were exposed to soil for 120 days under prevailing environmental conditions. After 120 days of exposure in soil, films eventually diminished in size and appeared hard and fragile. Film deterioration was also accompanied by loss in their total weight

Table 3

Thermogravimetric analysis of *Grewia optiva* fibre, St/PVA crosslinked blend film and fibres reinforced St/PVA composite blend film.

Sample	IDT (°C)	FDT (°C)	DT (°C) at 20% wt. loss	DT (°C) at 40% wt. loss	DT (°C) at 60% wt. loss	Residual left (%) at 800 °C
<i>Grewia optiva</i> fibre	241.18	356.38	287.74	326.35	348.77	18.93
St/PVA/CA/GLU	156.6	490.23	224.93	296.00	371.64	–
Fibres reinforced St/PVA composite blend film	210.43	450.43	240.74	310.17	367.66	9.82

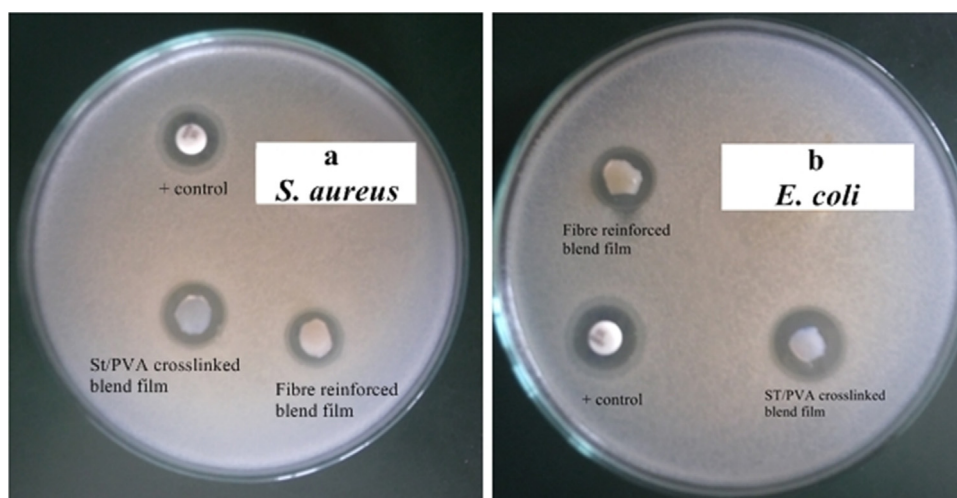


Fig. 5. Inhibitory effect of St/PVA crosslinked blend film and fibres reinforced St/PVA composite blend film against (a) *S. aureus* and (b) *E. coli*.

after soil exposure (Table 2). The weight loss may be due to adhering of soil and debris partial to the film surface (Imam et al., 2005). The decay of 34.54% and 45.65% weight loss were recorded for St/PVA crosslinked film and fibres reinforced St/PVA composite blend films, respectively. Thus, crosslinking results in slow rate of film deterioration in soil.

3.6. TGA analysis

Thermogravimetric analysis of *G. optiva* fibre, St/PVA crosslinked blend films and fibres reinforced St/PVA composite blend films were studied as a function of percentage weight loss with temperature and shown in Fig. 4a–c and Table 3. In case of fibre, depolymerization, dehydration and glucosan formation took place between the temperature range of 26.0–190.0 °C followed by the cleavage of C–H, C–C and C–O bonds (Maiti, Kaith, Jindal, & Jana, 2011; Thakur, Singha, & Thakur, 2013). The initial decomposition temperature (IDT) and final decomposition temperature (FDT) were found to be 241.18 °C (8.04% weight loss) and 356.38 °C (77.11% weight loss). On the other hand, in case of St/PVA crosslinked blend films, two stage decomposition was observed. The IDT and FDT have been found to be 156.06 °C (7.29% weight loss) and 490.29 °C (79.03% weight loss), respectively. The degradation temperatures for fibres reinforced St/PVA composite blend films fall between the degradation temperatures for the blend films and the fibres. It has been observed that for fibres reinforced composite blend films, IDT and FDT were 210.40 °C (13.85% weight loss) and 450.99 °C (82.26% weight loss), respectively. It indicated that the presence of cellulose fibres affect the degradation process. TGA studies were further supported by DTA curve as shown in Fig. 4a–c. Two peaks were observed in the DTA curve of *G. optiva* fibre and St/PVA crosslinked blend films. Fibre reinforced St/PVA composite blend films shows three DTA peaks. The TGA and DTA curves revealed that the *G. optiva* fibre, St/PVA blend films and fibres reinforced St/PVA composite blend films decompose in different stages in the temperature range of 199–500 °C, 150–600 °C and 190–600 °C, respectively. The magnitude and location of peaks found in the derivative thermogravimetric (DTG) curve also provide similar information (Jiang, Qiao, & Sun, 2006; Tudorachi et al., 2000).

3.7. Antibacterial activity

St/PVA crosslinked blend film and fibres reinforced St/PVA composite blend film were screened for their antibacterial activity against Gram-positive (*S. aureus*) and Gram negative (*E. coli*)

bacteria as shown in Fig. 5a and b. Antibiotic amoxicillin (25 µg/disc) was used as a standard (+control). The inhibitory effect was measured based on clear zone surrounding circular film disc. Measurement of clear zone diameter included diameter of film disc, therefore, the values were always higher than the diameter of film disc whenever clearing zone was present. If there is no clear zone surrounding, it suggests that there is no inhibitory zone, and furthermore, the diameter was valued as zero. Films showed fair antibacterial activity against Gram-positive (*S. aureus*) and Gram negative (*E. coli*) bacteria. Inhibitory zone against *S. aureus* and *E. coli* was measured to be 1.5 and 1.2 cm, 1.7 and 1.5 cm for St/PVA crosslinked blend film and fibre reinforced St/PVA composite blend films, respectively (Abdelgawada, Hudsona, & Rojas, 2014; Arora, Lala, Sharma, & Aneja, 2011; Tripathi et al., 2009).

4. Conclusion

St/PVA blend films were prepared by a casting method using citric acid as the plasticizer and glutaraldehyde as crosslinker. Addition of GLU increases the tensile strength and degree of swelling of St/PVA blend films. The mechanical properties of fibre reinforced St/PVA composite blend films were found to be higher than those of the St/PVA crosslinked blend films with 20% of *G. optiva* fibre loading. These properties can make *G. optiva* fibres a potential material for the synthesis of a new class of bio-composites. The composite films were characterized using Fourier transform-infrared spectrophotometry (FTIR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA/DTA/DTG). TGA analysis confirmed the good thermal properties of blend films. The antibacterial experiment indicated that St/PVA blends had good activity against the Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) bacteria. Thermal and antibacterial study reveals that the synthesized blend films might be used as potential materials in food packaging.

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References

- Abdelgawada, A. M., Hudsona, S. M., & Rojas, O. J. (2014). Antimicrobial wound dressing nanofiber mats from multicomponent chitosan/silver-NPs/polyvinyl alcohol systems. *Carbohydrate Polymers*, 16, 166–178.

- Alves, V., Costa, N., Hilliou, L., Larotonda, F., Goncalves, M., & Sereno, A. (2006). Design of biodegradable composite films for food packaging. *Desalination*, 199, 331–333.
- Arora, S., Lala, S., Sharma, C., & Aneja, K. R. (2011). Synthesis thermal and antimicrobial studies of chitosan/starch/polyvinyl alcohol ternary blend films. *Der Chemica Sinica*, 2, 75–86.
- Avella, M., Martuscelli, E., & Raimo, M. (2000). Review – Properties of blends and composites based on poly 3-hydroxy butyrate PHB and poly3-hydroxybutyrate-hydroxyvalerate PHBV copolymers. *Journal of Materials Science*, 35, 523–545.
- Averous, L., & Boquillon, N. (2004). Biocomposites based on plasticized starch: Thermal and mechanical behaviours. *Carbohydrate Polymer*, 56, 111–122.
- Bertuzzi, M. A., Armada, M., & Gottifredi, J. C. (2007). Physicochemical characterization of starch based films. *Journal of Food Engineering*, 82, 17–25.
- Bledzki, A. K., & Gassan, J. (1999). Composites reinforced with cellulose based fibres. *Progress in Polymer Science*, 24, 221–274.
- Borredon, E., Bikiaris, D., Prinos, J., & Panayiotou, C. (1997). Properties of fatty-acid esters of starch and their blends with LDPE. *Journal of Applied Polymer Science*, 65, 705–721.
- Cao, Y., Shibata, S., & Fukumoto, I. (2006). Mechanical properties of biodegradable composites reinforced with bagasse fiber before and after alkali treatments. *Composites Part A: Applied Science and Manufacturing*, 37, 423–429.
- Carvalho, A. J. F., Curvelo, A. A. S., & Agnelli, J. A. M. (2001). A first insight on composites of thermoplastic starch and kaolin. *Carbohydrate Polymers*, 45, 189–195.
- Chen, L., Qiu, X. Y., Xi, Z. G., Hong, Z. K., Sun, J. R., & Chen, X. S. (2006). Poly L-lactide/starch blends compatibilized with poly L-lactide-g-starch copolymer. *Carbohydrate Polymers*, 65, 75–80.
- Choi, J. S., Lim, S. T., Choi, H. J., Mohanty, A. K., Drzal, L. T., & Misra, M. (2004). Preparation and characterization of plasticized cellulose acetate biocomposite with natural fiber. *Journal of Materials Science*, 39, 6631–6633.
- Cunha, A. M., Liu, Z. Q., Feng, Y., Yi, X., & Bernardo, C. A. (2001). Preparation processing and characterization of biodegradable wood flour/starch–cellulose acetate compounds. *Journal of Materials Science*, 36, 4903–4909.
- Dean, K. M. D., & Petinakis, E. (2008). Key interactions in biodegradable thermoplastic starch/polyvinyl alcohol/montmorillonite micro and nanocomposites. *Composite Science and Technology*, 68, 1453–1462.
- Digabe, F., Boquillon, N., Dole, P., Monties, B., & Averous, L. (2004). Properties of thermoplastic composites based on wheat straw lignocellulosic fillers. *Journal of Applied Polymer Science*, 93, 428–436.
- Fang, J., & Fowler, P. (2003). The use of starch and its derivatives as biopolymer sources of packaging materials. *Food Agriculture Environment*, 1, 82–84.
- Gadhari, N. S., Sanghavi, B. J., & Srivastava, A. K. (2011). Potentiometric stripping analysis of antimony based on carbon paste electrode modified with hexathia crown ether and rice husk. *Analytica Chimica Acta*, 703, 31–40.
- Ghanbarzadeh, B., Almasi, H., & Entezami, A. A. (2011). Improving the barrier and mechanical properties of corn starch based edible films: Effect of citric acid and carboxymethyl cellulose. *Industrial Crop and Products*, 33, 229–235.
- Godbole, S., Gote, S., Latkar, M., & Chakrabarti, T. (2003). Preparation and characterization of biodegradable poly-3-hydroxybutyrate–starch blend films. *Bioresources Technology*, 6, 33–37.
- Guimaraes, J. L., Wypych, F., Saul, C. K., Ramos, L. P., & Satyanarayana, K. G. (2010). Studies of the processing and characterization of corn starch and its composites with banana and sugarcane fibres from Brazil. *Carbohydrate Polymers*, 80, 130–138.
- Han, X. Z., Chen, S., & Hu, X. (2009). Controlled-release fertilizer encapsulated by starch/polyvinyl alcohol coating. *Desalination*, 240, 21–26.
- Imam, S. H., Cinelli, P., Gordon, S. H., & Chieffini, E. (2005). Characterization of biodegradable composite films prepared from blends of polyvinyl alcohol cornstarch and lignocellulosic fiber. *Journal of Polymer and Environment*, 13, 47–55.
- Jia, X., Li, Y., Cheng, Q., Zhang, S., & Zhang, B. (2007). Preparation and properties of polyvinyl alcohol/silica nanocomposites derived from copolymerization of vinyl silica nanoparticles and vinyl acetate. *European Polymer Journal*, 43, 1123–1131.
- Jiang, W., Qiao, X., & Sun, K. (2006). Mechanical and thermal properties of thermoplastic acetylated starch/polyethylene-co-vinyl alcohol blends. *Carbohydrate Polymers*, 65, 139–143.
- John, M. J., & Thomas, S. (2008). Biofibres and biocomposites. *Carbohydrate Polymers*, 71, 343–364.
- Krumova, M., Lopez, D., Benavente, R., Mijangus, C., & Perena, J. M. (2000). Effect of crosslinking on the mechanical and thermal properties of polyvinyl alcohol. *Polymer*, 41, 9265–9272.
- Kunanopparat, T., Menut, P., Morel, M. H., & Guilbert, S. (2008). Reinforcement of plasticized wheat gluten with natural fibers from mechanical improvement to plasticizing effect. *Applied Science and Manufacturing*, 39, 777–785.
- Larotonda, F. D. S., Matsui, K. N., Sobral, P. J. A., & Laurindo, J. B. (2005). Hygroscopicity and water vapor permeability of kraft paper impregnated with starch acetate. *Journal of Food Engineering*, 71, 394–402.
- Lee, S. H., & Wang, S. (2006). Biodegradable polymers/bamboo fiber biocomposite with bio-based coupling agent. *Composites: Part A*, 37, 80–91.
- Luo, S., & Netravali, A. N. (1999). Interfacial and mechanical properties of environmental-friendly “green” composites made from pineapple fibers and polyhydroxybutyrate-co-valerate resin. *Journal of Materials Science*, 34, 3709–3719.
- Ma, X., Yu, J., & Kennedy, J. F. (2005). Studies on the properties of natural fibers reinforced thermoplastics starch composites. *Carbohydrate Polymers*, 62, 19–24.
- Maiti, M., Kaith, B. S., Jindal, R., & Jana, A. K. (2011). Microwave-enhanced synthesis of graft copolymer of binary vinyl monomer mixtures onto acetylated *Saccharum spontaneum* L and characterization. *Advances in Polymer Technology*, 30, 122–137.
- Mali, S., Grossmann, M. V. E., Garcia, M. A., Martino, M. N., & Zaritzky, N. E. (2005). Mechanical and thermal properties of yam starch films. *Food Hydrocolloids*, 19, 157–164.
- Mali, S., Sakanaka, L. S., Yamashita, F., & Grossmann, M. V. E. (2005). Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect. *Carbohydrate Polymers*, 60, 283–289.
- Misra, S., Misra, M., Tripathy, S. S., Nayak, S. K., & Mohanty, A. K. (2002). Novel ecofriendly biocomposites – Fabrication and processing evaluation. *Journal of Reinforced Plastics Composites*, 21, 55–70.
- Nath, D. C. D., Bandyopadhyay, S., Gupta, S., Yu, A., Blackburn, D., & White, C. (2010). Surface-coated fly ash used as filler in biodegradable polyvinyl alcohol composite films: Part 1 – The modification process. *Applied Surface Science*, 256, 2759–2763.
- Park, H., Choughy, S., Yun, Y., & Yoon, S. (2005). Properties of St/PVA blend films containing as citric acid as additive. *Journal of Polymer and Environment*, 13, 375–382.
- Peng, J., Kaishuen, Wei, K., & Lui, W. B. (2005). Response surface optimization of the feed compositions of biodegradable packaging foams. *Packaging Technology and Science*, 18, 321–330.
- Pinto, C. E. S., Carbajal, G. G. A., Satyanarayana, K. G., Fernando, W., & Ramos, L. P. (2009). Studies on the effect of pressure and incorporation of sugarcane bagasse fibers on the structure and properties of poly(hydroxybutyrate). *Composites: Part A*, 40, 573–582.
- Raddy, N., & Yang, Y. (2010). Citric acid crosslinking of starch films. *Food Chemistry*, 118, 702–711.
- Rodriguez, F. J., Ramsay, B. A., & Favis, B. D. (2003). High performance LDPE/thermoplastic starch blends: A sustainable alternate to pure polyethylene. *Polymer*, 44, 1517–1526.
- Russo, M. A. L., O’Sullivan, C., Rounsefell, B., Halley, P. J., Truss, R., & Clarke, W. P. (2009). The anaerobic degradability of thermoplastic starch:polyvinyl alcohol blends: Potential biodegradable food packaging materials. *Bioresource Technology*, 100, 1705–1710.
- Sanghavi, B. J., Mobin, S. M., Mathur, P., Lahiri, G. K., & Srivastava, A. K. (2013). Biomimetic sensor for certain catecholamines employing copper(II) complex and silver nanoparticles modified glassy carbon paste electrode. *Biosensors and Bioelectronics*, 39, 124–132.
- Sanghavi, B. J., & Srivastava, A. K. (2010). Simultaneous voltammetric determination of acetaminophen, aspirin and caffeine using an in situ surfactant-modified multi-walled carbon nanotube paste electrode. *Electrochimica Acta*, 55, 8638–8648.
- Sanghavi, B. J., & Srivastava, A. K. (2013). Adsorptive stripping voltammetric determination of imipramine, trimipramine and desipramine employing titanium dioxide nanoparticles and an Amberlite XRD-2 modified glassy carbon paste electrode. *Analyst*, 138, 1395–1404.
- Sanghavi, B. J., Kalambate, P. K., Karna, S. P., & Srivastava, A. K. (2014). Voltammetric determination of sumatriptan based on a graphene/gold nanoparticles/Nafion composite modified glassy carbon electrode. *Talanta*, 120, 1–9.
- Sanghavi, B. J., Sitaula, S., Griep, M. H., Karna, S. P., Ali, M. F., & Swami, N. S. (2013). Real-time electrochemical monitoring of adenosine triphosphate in the picomolar to micromolar range using graphene-modified electrodes. *Analytical Chemistry*, 85, 8158–8165.
- Shi, R., Bi, J., Zhang, Z., Zhu, A., Chen, D., Zhou, X., et al. (2008). The effect of citric acid on the structural properties and cytotoxicity of the polyvinyl alcohol/starch films when molding at high temperature. *Carbohydrate Polymers*, 74, 763–770.
- Shi, R., Zhang, Z. Z., Liu, Q. Y., Han, Y. M., Zhang, L. Q., & Chen, D. F. (2007). Characterization of citric acid/glycerol co-plasticized thermoplastic starch prepared by melt blending. *Carbohydrate Polymer*, 69, 748–755.
- Siddaramaiah, R. B., & Somashekar, R. (2004). Structure–property relation in polyvinyl alcohol/starch composites. *Journal of Applied Polymer Science*, 91, 630–635.
- Sin, L. T., Rahman, W. A. W. A., Rahmat, A. R., & Samad, A. A. (2010). Computational modelling and experimental infrared spectroscopy of hydrogen bonding interactions in polyvinyl alcohol–starch blends. *Polymer*, 51, 1206–1211.
- Singha, A. S., & Rana, A. K. (2012). A comparative study on functionalization of cellulosic biofibers by graft copolymerization of acrylic acid in air and microwave radiation. *Bioresource*, 7, 2019–2037.
- Singha, A. S., Rana, R. K., & Guleria, A. (2012). Functional polymers from graft copolymerization of binary monomer mixtures onto lignocellulosic biomass: Synthesis, characterization, and properties evaluation. *Lignocellulose*, 1, 129–152.
- Sreedhar, B., Sairam, M., Chattopadhyay, D. K., Rathnam, P. A. S., & Mohan, D. V. (2005). Thermal mechanical and surface characterization of starch/polyvinyl alcohol blends and borax-crosslinked films. *Journal of Applied Polymer Science*, 96, 1313–1322.
- Thakur, V. K., Singha, A. S., & Thakur, M. K. (2013). Pressure induced synthesis of EA grafted saccarum cillare fibers. *International Journal of Polymeric Materials and Polymeric Biomaterials*, 63, 17–22.
- Tripathi, S., Mehrotra, G. K., & Dutta, P. K. (2009). Physicochemical and bioactivity of cross-linked chitosan-PVA film for food packaging applications. *International Journal of Biological Macromolecules*, 45, 372–376.
- Tudorachi, N., Cascaval, C. N., Rusu, M., & Pruteanu, M. (2000). Testing of polyvinyl alcohol and starch mixtures as biodegradable polymeric materials. *Polymer Testing*, 19, 785–799.

- Vimala, K., Yallapu, M. M., Varaprasad, K., Reddy, N. N., Ravindra, S., Naidu, N. S., et al. (2011). Fabrication of curcumin encapsulated chitosan–PVA silver nanocomposite films for improved antimicrobial activity. *Journal of Biomaterials and Nanobiotechnology*, 2, 55–64.
- Yoon, S. D., Chough, S. H., & Park, H. R. (2006). Properties of starch-based blend films using citric acid as additive II. *Journal of Applied Polymer Science*, 100, 2554–2560.
- Zhu, J. F., Zhang, G. H., Lai, Z. C., & Zhang, G. H. (2007). Synthesis and characterization of maize starch acetates and its biodegradable films. *Polymer – Plastic Technology and Engineering*, 46, 1135–1141.
- Zobel, H. F. (1988). Starch crystal transformations and their industrial importance. *Starch*, 40, 1–7.