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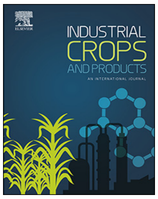

Properties and applications of citric acid crosslinked banana fibre-wheat gluten films

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ABSTRACT

Utilization of agricultural residues for sustainable development and creating products for a better future is gaining importance. Considerable efforts have been done to utilize agricultural residues to develop composites, fibres, films and other commodity products. Similarly, proteins such as wheat gluten, soy protein and casein are obtained as coproducts and considered for food and non-food applications. Fibres extracted from banana stems have been used as reinforcement and wheat gluten as matrix to develop composites. However, banana fibres and gluten are hydrophilic and composites developed do not have adequate mechanical properties. In this study, we have developed films from banana fibres and wheat gluten by solution casting and later compression molding. Further, crosslinking of fibre and gluten with citric acid was done to improve the mechanical properties and decrease water sorption of the bioproducts in comparison to glutaraldehyde (Gtld) as the crosslinker. Films developed were characterized for their water absorption, mechanical properties, effect of ratio of fibre and gluten, effect of the crosslinker type and concentration and changes in morphology. Films without any crosslinker showed maximum water absorption values up to 500% whereas crosslinking reduced water sorption drastically to about 200%. Crosslinking also led to substantial increase in strength of the films from 3.5 MPa to 13 MPa. It was found that citric acid crosslinked films had marginally higher strength compared to Gltd crosslinked films. Thermal studies confirmed that crosslinking increased resistance to thermal degradation. All the films passed the UL-94 V-1 classification requirements for flame retardancy. The films formed could be moulded into various products and used to replace the commercially available plastic based materials. Utilizing banana fibres and wheat gluten to develop bioproducts will assist towards developing a greener and better environment and also add considerable value to agricultural residues and coproducts.

1. Introduction

Recently, much attention has been focused on biobased products from renewable resources for packaging of commodity products, medical devices, automobile parts and other commercial applications. Considerable efforts are made to replace synthetic polymer based materials by natural lignocellulosic materials because of their easy availability, lower processing cost and biodegradability. For instance, straws, husks, stems and leaves generated as residues have been used for production of biofibres and bioproducts. In addition to the residues, renewable materials like plant fibre, extracts from seeds, proteins and carbohydrates from oil meals which are mostly composed of polysaccharides, lipids or proteins have been extensively studied as sources for developing bioproducts (Irissin-Mangata et al., 2001).

Banana fibre is a natural cellulose rich fibre extracted from the stem of the banana plant. Once the bananas are harvested from the plant, pseudostem is mostly considered as a residue and generally disposed by burning or burying. Since large quantities of banana stems are available, it would be a good opportunity to add value to banana stems and utilize the fibres for commercial applications. Natural cellulose fibres have been extracted from the stems of banana plants using mechanical and chemical means. Banana fibres have good tensile properties and excellent appearance. Banana fibres are used for the production of home furnishings, ropes, mats, packaging box, apparel, garments etc. They are also utilised in the production of biocomposites along with various proteins like soy (Kumar et al., 2008), wheat gluten (Guna et al., 2016) and for hybrid composites by combining with other fibres and matrices (Venkatasubramanian et al., 2014; Venkateshwaran and Elayaperumal, 2010; Pujari et al., 2014).

Wheat gluten is a prominent material in the food industry and is one

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of the major proteins that are commercially available for food and non-food applications (Boland et al., 2005; Krishnakumar and Gordon, 1995). Wheat gluten is a protein having two major components known as glutenin and gliadin which are responsible for the physical and chemical properties of wheat gluten (Ewart, 1967; Krull and Inglett, 1971). Several studies have been done to find applications for wheat gluten and most efforts have been towards developing biodegradable packaging films for food wrapping and storage (Guilbert et al., 2002). Wheat gluten films have exceptional oxygen and carbon dioxide barrier properties along with very low water vapour barrier properties in contrast to plastic films (Chinnan and Park, 1995). Conventionally, wheat gluten films are prepared by either solvent casting (Lagrain et al., 2010) or dry processing (Angellier-Coussy et al., 2011; Chen et al., 2012).

Application of wheat gluten in non-food industry includes as binder in paper coating industry (Kersting et al., 1994), as medical bandages, adhesive tapes, cosmetics, biodegradable resins, as encapsulating agents of weed and pest agents (Quimby et al., 1994), in cigarette (Soichiro et al., 1972) and ceramics (Hayes and Roberts, 1994). Researchers have also shown that wheat gluten and gliadin can be converted into regenerated protein fibres for textile and medical applications (Li et al., 2008; Reddy and Yang, 2007).

Since banana fibres and wheat gluten are agricultural residues or coproducts, available in large quantities at relatively low cost, researchers have used banana fibres as reinforcement and wheat gluten as matrix to develop biocomposites for dielectric applications (Bhuvaneswari et al., 2017) and also as printed circuit boards (Guna et al., 2016).

However, using a hydrophilic protein such as wheat gluten as binder increases moisture sorption and reduces mechanical properties. Hence, the properties of banana fibre wheat gluten composites are not satisfactory. One of the approaches to improve the performance properties of polymeric materials is through crosslinking. Carboxylic acids like citric acid are used to crosslink various biopolymers and also to improve their water resistance and mechanical properties. Gliadin fibres were crosslinked using citric acid which improved tensile strength and elongation (Reddy et al., 2008a). Citric acid crosslinking showed similar effects with zein fibres and zein nanoparticles (Xu et al., 2015; Yang et al., 1996), silk (Yang and Li, 1993), camelina films (Zhao et al., 2014) and also with casein fibres (Yang and Reddy, 2012). Citric acid is a tricarboxylic acid which is weak and organic in nature. Also it is certified as nontoxic by FDA of United States (Gyawali et al., 2010). Citric acid has COOH and OH functional groups which help in binding various biomolecules and allows us to control the extent of crosslinking (Tran et al., 2010). The carboxylic acids are highly reactive and can form ester bonds with wheat gluten along with better functionality (Reddy et al., 2015). Based on the application required, citric acid can be used to increase water sorption like in the case of chitosan or decrease water sorption.

In this study, we have prepared films using banana fibre and wheat gluten and the prepared films were crosslinked with citric acid to improve the mechanical properties and reduce water sorption abilities. Changes in FTIR spectra, XRD patterns and thermal behaviour of the films were investigated. Finally, the films were moulded into specific shapes which can be used as bioproducts for various commercial applications.

2. Materials and methods

2.1. Materials

Banana fibres were obtained from Tamilnadu Agricultural University, Coimbatore, India. Wheat gluten was procured from P.D. Navakar Bio-chem private limited, Bengaluru, India which had a protein content of 80%. The gluten purchased was used without any further treatment or modifications. Citric acid was procured from HiMedia laboratories pvt. Ltd. Sodium hydroxide and Gltd was obtained from nice chemicals (P) ltd. The chemicals used were of reagent grade and purity was 99 ± 1%.

2.2. Methods

We prepared 3 ratios (30/70, 50/50, 70/30 (w/w%)) of banana fibre – wheat gluten films. The prepared films were in situ crosslinked using 2 different crosslinkers namely Gltd and citric acid. The percentage of the above mentioned crosslinkers added was varied (5%, 10%, 20%) to study their effect on water sorption and mechanical properties of the films. Control films without any crosslinker were prepared at different ratios (30/70, 50/50, 70/30) of banana fibres/gluten.

2.2.1. Preparation of citric acid crosslinked banana fibre – wheat gluten films

Banana fibre was cooked in 50 ml of distilled water for 30 min at 80 °C to soften the fibres prior to blending with wheat gluten. In a separate beaker, 100 ml of 0.2 N NaOH solution was heated to 50 °C and wheat gluten was added to this solution with continuous stirring for 20 min. Once the protein had dispersed completely, citric acid was added and stirring was continued for 15 more minutes. Next, both banana fibre and wheat gluten solution were mixed and heated for 30 min with occasional stirring. This mixture was cast on metal plate covered with a plastic wrap and were placed in an oven at 50 °C until dry. Films were later compressed to obtain a crosslinked film. Similar to the above procedure crosslinked films of varied ratios and crosslinker percentages were prepared. Fig. 1 shows the procedure followed for film preparation.

2.2.2. Water sorption studies

All the prepared banana fibre-wheat gluten films were cut into smaller pieces (1 × 1 cm) whose initial weights (I) were determined. These films were then dipped in water for 10 min for the sorption process to take place and later centrifuged for 10 min at 5000 rpm to remove excess water from the films. The final weights (F) of the films were noted and the percentage water absorption of the films were calculated using the formula:

$$\%\,\text{Water sorption} = \frac{F - I}{I} \times 100$$

2.2.3. Determination of mechanical properties

The tensile properties of the films were determined in dry state according to ASTM standards D 882-02 on a universal tensile tester (Model UTM- G-312C, Shantha engineering, Mumbai). A total of 15 specimens were considered for each condition and three replications were done. Samples were cut into specific dimensions of 10 cm × 1 cm. Prior to measurement the samples were conditioned at room temperature. A 500 N load cell was used and the crosshead speed during measurement was 30 mm/min. Average and ± one standard deviations of the tensile properties were calculated.

2.2.4. Flame resistance

Crosslinked films were cut into pieces measuring 125 mm × 13 mm. The flame resistance of the samples were determined according to UL-94 standard test method. Briefly, pre conditioned samples were placed below an igniter vertically for 10 s and the duration required for the flame to self-extinguish was noted. Also, any dripping of the film onto the cotton kept below the sample was observed. For each ratio and % of crosslinker a minimum of five samples were tested and based on the time taken by the flame to self extinguish, the flammability ratings were decided.

2.2.5. Fourier transform infrared spectroscopy

The FTIR spectra of the samples were obtained using Shimadzu IR