

ORIGINAL ARTICLE

Bioplastics from Blends of Cellulose Acetate Butyrate and Thermoplastic Starch

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ABSTRACT

The present invention relates to the preparation of bioplastics from a blend of cellulose acetate butyrate and thermoplastic starch (TPS). More particularly application of this prepared bioplastic polymers for application as plastic materials by further processing. This invention relates to a blend of 60-90% w/w cellulose acetate butyrate with 5-10% w/w thermo plastic starch with a plasticizer and other additives to improve its tensile strength, elasticity, thermo stability, UV stability, antimicrobial, antioxidant properties of bioplastics and to enhance the performance of bioplastics. The prepared bioplastics showed advantageous attributes includes enough tensile strength, thermo stability, weight holding capacity, antimicrobial UV stability and antioxidant properties. The prepared biodegradable bioplastic films can be tailored for particular uses. These bioplastic films can be used to manufacture the trays, blister foils and containers used to pack the fruits, vegetables, eggs and meat; bottles for soft drinks and dairy products.

Keywords: Bioplastics, TPS, CAB, Additives.

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INTRODUCTION

Plastics are amorphous organic solid polymers covering a wide range of polymerization products suitable for the manufacture of diversified products. Worldwide annual plastics production is estimated to surpass 300 million tons by 2015 representing trillions of dollars in terms of global economic returns. India is the third largest plastic consumer in the world, with a total consumption of plastics of about four million tons and a resulting waste production of about two million tons. About 1.27 billion people use and dispose plastics almost every day. Additionally both manufacturing and disposing of plastic products by incineration releases vast quantities of toxins that can be damaging to human inhabited ecosystems. Fortunately, advanced technology and the increasing need for eco-friendly products have introduced a sustainable remedy i.e. Bio-Plastics.

Bioplastics are typically derived from renewable raw materials that can contain one or more biopolymeric substances. Improvement in properties of bioplastics especially in their tensile strength, thermal stability, UV stability, weight holding capacity, antimicrobial and anti oxidant properties remains an issue. The additives can be poly lactic acid, ascorbic acid, bees wax, natural rubber, citric acid, casein, ascorbyl palmitate, sodium acrylate and ethyl acrylate or combinations thereof. Additives can enhance the properties of bioplastics. The bioplastics are derived from various renewable raw materials such as cellulose, starch polysaccharides, polylactic acid, casein, etc. These bioplastics degrade in soil within the months, whereas synthetic plastics take prolonged time for the degradation. So, we can protect our global environment from the available natural sources. A blend of cellulose acetate with thermo plastic starch offers the possibility to combine a cheap raw material, starch, with the production of a fiber of the same or better quality and enhanced properties as compared with fibers made of cellulose acetate alone.

The improved quality results from the modification of molecular structure of starch and cellulose. Dry starch is generally a 25/75% mix of linear amylose and branched amylopectin polymer of α -D-glucopyranosyl units. Amylose is a straight, helical, flexible polymer consists of long chains of 1000-2000 glucose units linked by 1,4 glycosidic linkage. Cellulose is a polysaccharide has linear β -D-glucose units linked through β -1,4 linkage, generally obtained from cotton & wood pulp. Cleavage of β -1,6 glycosidic and 1,4 - glycosidic linkage creates a homogenous mass of long, straight polymers. Here the cleavage is

achieved by hydrolysis under the plasticizer at elevated temperature. Cleavage of cellulose is also achieved by organic solvent solubilisation such as benzene and acetone. Cellulose acetate and mixed cellulose esters, such as cellulose diacetate, cellulose triacetate, cellulose acetate propionate, and cellulose acetate butyrate, are all commercially available materials. Chemical modification can also be an effective method of improving the process ability and product performance of TPS. For example, hydroxylation[1], acylation [2] oxidation[3] and acetylation[4] of starch by substituting the ester or ether groups for the hydroxyl were reported to improve the processing behavior, hydrophobicity and mechanical properties. The synthesis of thermoplastic starch acetate with a high degree of substitution through acetylation of starch is one of the common chemical modifications of starch [5]. The starch acetates were shown to have higher thermal stability and hydrophobicity due to the reduction of the hydroxyl group with the acetylation. The invention also reveals that these plastics are degraded in the soil within the 3-4 months. The inventors of the present invention have endeavored to develop a formulation of bioplastics with the blended polymer mixture.

MATERIALS AND METHODS

Materials:

Corn starch, Cellulose acetate butyrate, Bees wax, Sorbitol, polylactic acid, quercetin, Ascorbic acid, Methanol, Benzene were collected from Qualigens Fine chemicals Mumbai.

Equipment: Autoclave (OSWAL)

Procedure for Bioplastic Preparation:

The preparation of bioplastics comprising of cellulose acetate butyrate and TPS and one or more rate controlling polymers comprises the following steps: Predetermined quantity of corn starch was taken and added the specified quantity of water and plasticizer, i.e. sorbitol (Table:1). This mixture was heated together to melt in an autoclave at 121°C for 45 min to prepare a thermoplastic starch. Cellulose acetate butyrate was dissolved in the mixture of organic solvents in a minimal volume of benzene and methanol by mixing the components thoroughly with constant stirring under closed conditions for 3 h. The solutions of thermoplastic starch and cellulose acetate butyrate were mixed for another 1 h. Then specified quantities of additives such as polylactic acid, bees wax, quercetin and ascorbic acid were added and mixed. Then the melt was processed into desired shapes depending on the requirement by pouring into the glass moulds having specific diameter to achieve desired thickness. The moulds were placed in a dryer at 45°C for 48 h and the dried films were removed from the moulds and kept in a desiccator for 24 h. Suitable rate controlling polymers are used in accordance with the present invention are plastic forming polymer i.e. cellulose acetate butyrate and thermoplastic starch. Add the suitable additives (Table:1) to the above prepared bioplastics to improve its characteristics..

Table I: Compositions of Bioplastics

Composition	Purpose of use	Trial 1	Trial 2	Trial 3
Cellulose acetate butyrate	Film former	2 g	2.5 g	3 g
Methanol	Solvent	15 cm ³	15 cm ³	15 cm ³
Benzene	Solvent	10 cm ³	10 cm ³	10 cm ³
Thermoplastic starch (TPS)	Film former	0.5 g	2 g	2.5 g
Sorbitol	Plasticizer	2.5 g	2.5 g	2.5 g
Polylactic acid	Antioxidant, hydrophobic agent, antimicrobial agent, thermo stabilizer, UV stabilizer and elasticizer	2 mg	4 mg	5 mg
Bees wax	UV stabilizer	5 mg	10 mg	15 mg
Quercetin	Antioxidant, UV stabilizer	0.1 mg	0.2 mg	0.5 mg
Ascorbic acid	Antioxidant	10 mg	10 mg	10 mg
Distilled water	Solvent	25 cm ³	25 cm ³	27 cm ³

RESULT AND DISCUSSION

The above prepared bioplastics were evaluated for tensile strength, elasticity, thermo stability, UV Stability, antioxidant, antimicrobial, weight holding capacity and biodegradation capacity. The bioplastics portrayed in this revelation can contain littler measures of different fixings without ruining the coveted properties of the bioplastic. Cases of such fixings incorporate plasticizers, hostile to oxidants, hydrophobic operators, antimicrobial additives, warm stabilizers, UV light stabilizers and elasticizers.

Thickness: The thickness of bioplastics described in this disclosure, was measured at five positions on the perimeter and at the center of the film by a dial type micrometer (model 2050-08, Mitutoyo, Japan) to obtain an average value (Table:1).

Percentage moisture loss: Percentage moisture loss of bioplastics described in this disclosure was determined by keeping the weighed strips in a desiccator containing anhydrous calcium chloride. After three days, the strips were taken out and reweighed (Table:II). The percentage moisture loss was calculated [6].

Folding Endurance: Folding Endurance of bioplastics described in this disclosure, was evaluated by repeatedly folding a small strip of film of 2 cm×2 cm size at the same place till it broke. The number of times (n), the strip was folded at the same place, without breaking, gave the value of folding endurance(Table:II).

Tensile strength: The bioplastic formulation can be advantageously used in various applications due to their increased tensile strength. The increase in tensile strength is due to natural sources like cellulose and starch and they are biodegradable. Tensile strength is the force per unit area that can be applied to a material. Tensile properties of the samples of bioplastics described in this disclosure were examined according to ASTM D882 standard test method. The tensile strength of the films was determined by universal strength testing machine. The sample films were cut into a rectangular shape (15 cm × 2.5 cm) and conditioned in a closed chamber containing saturated sodium nitrite solution at 25 ° C (65% RH) for 3 days prior to testing. The sensitivity of the machine is 1 g. It consists of two load cell grips. The lower one is fixed and the upper one is movable. The test film of specific size was fixed between these cell grips and force was gradually applied till the film breaks. The tensile strength of the film was taken directly from the dial reading in kilograms (Table: II).

Thermo stability: Thermo stability of bioplastics described in this disclosure, was determined by weighing the measured quantity of prepared bioplastic material and focusing it to the different temperature conditions such as 20, 30, 40 and 50 °C. Based on the weight difference of plastic at different temperatures conditions the thermal stability can be determined(Table: II). Here the bioplastics described in this disclosure maintains the similar weight at different temperature conditions. Therefore, the bioplastics described in this disclosure was found to possess significant thermal stability.

UV Stability: UV Stability of bioplastics described in this disclosure was determined by weighing the measured quantity of bioplastic and by focusing it to the UV radiations at different time intervals from 5-45 min in an UV chamber. The average of weighted difference was for every 15 min time interval and checked the UV stability. The bioplastics described in this disclosure has maintained the similar weight on prolonged UV exposure. Therefore, the bioplastics described in this disclosure were found to have enough UV stability (Table: II).

Anti-oxidant property: Evaluation of antioxidant activity of bioplastics described in this disclosure was determined according to the method of Oyaizu [7]. A sample (1 mg) was added to a mixture of phosphate buffer (2.5 cm³) and potassium ferricyanide (1% w/v, 2.5 cm³) and then heated to 50 °C for 20 min. After cooling to ambient temperature, this was mixed with trichloroacetic acid (10% w/v, 2.5 cm³) and centrifuged at 9000 rpm for 10 min. The supernatant (2.5 cm³) was then mixed with distilled water (2.5 cm³) and freshly prepared ferric chloride solution (0.1% w/v, 0.5 cm³). The absorbance at 700 nm of the mixture was recorded as a function of time 72 h (Table: II).

Antimicrobial strength: To assess the antimicrobial property of the bioplastics described in this disclosure, the bacterial cultures of *Bacillus subtilis* (Gram +ve) and *Escherichia coli* (Gram -ve) were employed as test organisms (Indian Pharmacopoeia 1996). The results after 24 h showed no observation of growth of these test cultures on bioplastics described in this disclosure(Table: II).

Weight holding capacity: To measure the weight holding capacity of the bioplastics described in this disclosure, a 1 cm × 10 cm strip of bioplastics was taken. The films were hanged at one end and the other end a hanging tray (10g) was fixed with the help of a plastic strip which is pasted using Quick Fix® adhesive. The weight holding capacity of bioplastics was measured by placing different weights ranging from with an increment of 10 g until the film breaks(Table: II).

Biodegradation capacity: Biodegradation capacity of bioplastics described in this disclosure was determined by weighing the measured quantity of bioplastic and by burying them under the soil at 0.2 m depth for up to 3 months (modified methods of ISO 16929 and ISO 14855-1). The test was performed at ambient tropical conditions (temperature 25-35°C and RH 40% to 65%) during the study period. Visual observation for any degradation of the bioplastics was done. The weight difference was measured at every 15 days time interval and observed the degradation level of bioplastics. The results showed that, there was a significant and drastic weight depreciation for every 15 days, and it was also found that the complete degradation of bioplastics in about 55-60 days (Table: II).

Polymer-additives interactions: Polymer-additive chemical interactions of bioplastics described in this disclosure were determined using Fourier Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC). FTIR performed on samples of cellulose acetate butyrate, thermo plastic

starch, sorbitol, polylactic acid and bioplastic using Bruker Optik GmbH Alpha FTIR Spectrometer, Germany. The samples were dried to constant weight and triturated with an equal quantity of potassium bromide (KBr). Each sample was then compressed to material of DSC supplied by Shimadzu corporation) as reference standard (Table: II).

obtain discs for IR analysis. The spectra of these discs were recorded in the spectral region of 500-4000 cm^{-1} . The experiments were carried out in triplicate. (Table: II).

Thermal analysis of samples of cellulose acetate butyrate, thermo plastic starch, sorbitol, polylactic acid and bioplastic was performed using a DSC Perkin Elmer, USA, DSC 4000 model. Samples of 1-4 mg were sealed hermetically in flat bottomed aluminium cells or pans. Then the samples were heated over a temperature of 30-450°C in an atmosphere of nitrogen ($0.5 \text{ cm}^3/\text{sec}$) at a constant rate of 10°C per min using alumina (standard Plasticizers are the materials that can soften and reduce the viscosity of a polymer structure by reducing the intermolecular forces and by increase intermolecular ability of the polymer. Additives may be included from 1-2%. If the amount of plasticizer is increased the bioplastics becomes more elastic and workable. If the amount of elasticizer is reduced, the bioplastics becomes more rigid and more brittle. Examples of plasticizers included low molecular weight polymers like sorbitol and polylactic acid.

Table II: Summary of characterization of bioplastic films

Trial	Thickness (μ)	Moisture loss (%)	Folding endurance (n)	Tensile strength (Kg/cm^2)	Thermal stability at 50°C (% change in wt.)	UV Stability (% change in wt.)	Antioxidant strength (radical scavenging)	Antimicrobial strength	Weight holding capacity (g/cm^2)
Trial 1	216±15	1.21±0.16	326±14	124±0.6	0.63±0.09	0.22±0.03	21.4±0.9	-ve	55.8±1
Trial 2	238±21	1.46±0.22	361±22	132±0.9	0.71±0.05	0.25±0.05	25.6±1.2	-ve	63.5±3
Trial 3	257±18	1.85±0.11	410±26	135±1.4	0.79±0.07	0.31±0.08	27.1±1.1	-ve	68.2±3

BRIEF DESCRIPTION OF DRAWINGS

1. Biodegraded bioplastic films after (A) 0 day, (b) 15 days and (C) 30 days
2. DSC thermograms of materials and product used in preparation of bioplastics.
3. FTIR spectra of materials and product used in preparation of bioplastics.

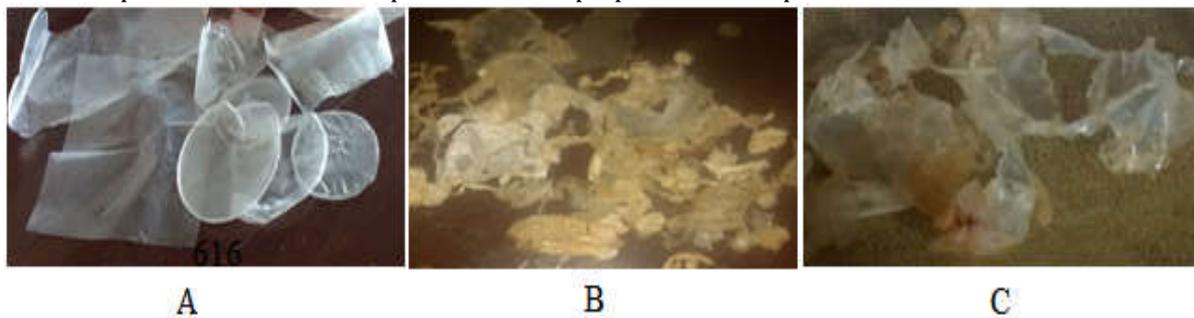


Fig I: Biodegraded bioplastic films after (A) 0 day, (b) 15 days and (C) 30 days

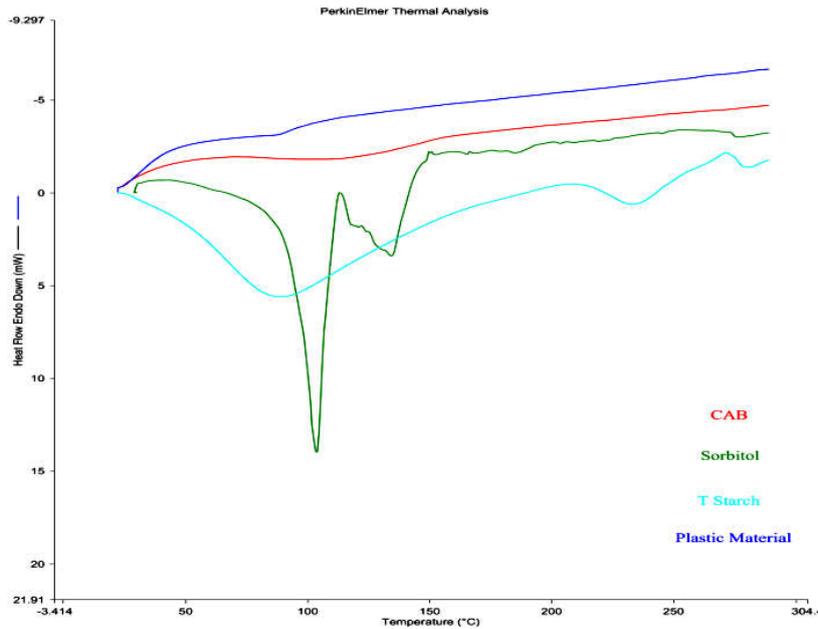


Fig II: DSC thermograms of materials and product used in preparation of bioplastics

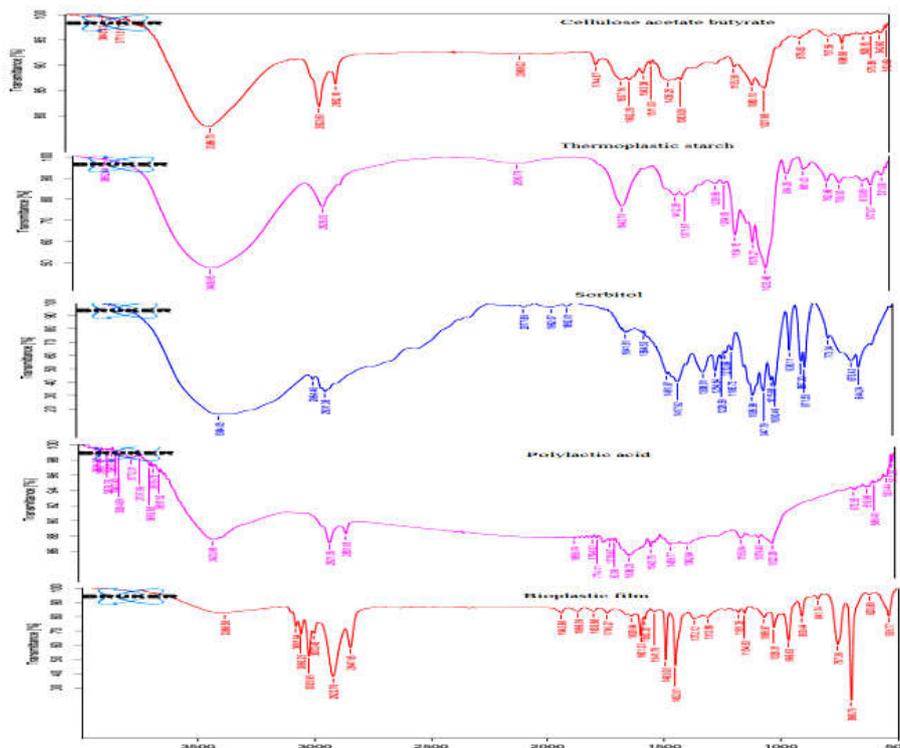


Fig III: FTIR spectra of materials and product used in preparation of bioplastics

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