




Synthesis and characterization of eco-friendly bioplastic from low-cost plant resources

Akshaya Krishnamurthy¹ · Pavithra Amritkumar¹ 

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Abstract

Alarming rate of environmental pollution caused by single-use plastics has necessitated the search for developing sustainable yet, cost-effective alternatives. This study aimed to develop bioplastic films using combination of jackfruit waste flour and sago as a low-cost starch source. Three composite bioplastic films were developed using starch mix with lemon extract and water but with different cross-linkers: (1) PV (polylactic acid and crude palm oil), (2) AV (glycerol and crude palm oil), (3) PAV (polylactic acid, glycerol and crude palm oil). The formulated films' physical, chemical, mechanical and biological parameters were characterized. PV film showed the best tensile strength (TS) of 5.24 MPa and least elongation at break (EAB) of 3.49%, while PAV film had the least TS of 0.78 MPa with a maximum EAB (73.38%). FTIR analysis of films showed peak at 1736.3–1743.3 cm^{-1} indicating strong interaction of triglycerides (C=O stretching). In thermogravimetric analysis (TGA), all the films displayed gradual desorption occurring between 150 and 220 °C where the volatile compounds started to evaporate and around 300 °C the lower molecular weight compounds like plasticizer, cross-linker and other additives started to release out; pyrolysis of carbonated compounds occurred above 500 °C. PAV film displayed best thermal stability with half decomposition at 330 °C. Biodegradability of films was demonstrated through soil burial method and culturing of pure cultures of microorganisms in minimal media by providing the film as carbon source. Bioplastic films developed in this study using low-cost plant starch sources have displayed properties with potential application in food packaging industry.

Keywords Jackfruit waste flour · Sago · PLA · Bioplastic

1 Introduction

Use of plastics is widespread worldwide because of their versatility and their excellent process ability, thermal and mechanical properties. Most prominent cause of plastic pollution is the single-use plastic/disposable plastic (plastic carry bags, straws, cups, cutlery, water packets, cling wraps, bottles). About 380 million tonnes of plastic is produced and discarded every year throughout the world (<https://ourworldindata.org/plastic-pollution>). Major part of this discard is accumulated in the environment with only 10–13% recycled. Despite their ubiquitous usage, they are non-biodegradable because of stable

carbon–hydrogen bond and very large complex polymeric structure, thus remaining for longer periods of time in the environment causing ocean and land pollution. They usually disintegrate into tiny fragments over long periods of time, which are ingested by smaller eukaryotes, which in turn by higher eukaryotes, affecting the entire food chain, and many species are in endangered situation because of this. Each year, an estimated 8 million tonnes of discarded plastic enters through coastal region into world's ocean. These plastics cause serious threat to coral reefs that are suffocated in plastic bags; turtles, whales and sea birds with plastic stuffed in their bellies and nostrils clogged with straws leading to painful deaths (<https://www.natio>

✉ Pavithra Amritkumar, pavithrashiva@hotmail.com; srikumaripavithra@gmail.com | ¹PG and Research Department of Biotechnology, Women's Christian College, College Road, Chennai, Tamil Nadu 600006, India.



nalgeographic.com/environment/2018/07/ocean-plastic-pollution-solutions/).

Burning of plastics leads to emission of massive amount of carbon dioxide into the environment causing air pollution. They also release toxic chemicals causing hazards to life and environment as a whole [1]. Production of biodegradable alternatives with greater safety and compatibility with the environment is necessary. Bio-based plastics are made from renewable sources like corn, potatoes, wheat and vegetable oil through chemical or biological process which include hydrolysis, acidification, microbial fermentation, etc. [2, 3]. Though there are lot of renewable resources available for production of bioplastic, starch is one of the most important sources utilized by many researchers. Starch is made up of amylose (linear) and amylopectin (branched) and has gelatinization characteristics. The linear structure of amylose in starch usually produces bioplastics with stronger and highly flexible mechanical properties, whereas the branched structure of amylopectin produces bioplastics which show lower resistance to tensile strength and elongation property [4]. Starch in its native state exhibits very limited application because of poor solubility, thermal decomposition, high retrogradation, syneresis and low shear stress resistance [5]. Using starch as a renewable source has several advantages such as low cost, inexhaustible and renewable. According to Kalambur and Rizvi [6], starch in bioplastic manufacturing is not so desirable because of various disadvantages such as brittleness and hydrophilicity. The mechanical properties worsen upon exposure to environmental conditions like humidity leading to hydrolysis. Plasticizers are the additives that increase the plasticity of a material and improve their mechanical property. They play significant role by forming hydrogen bonds with starch by disrupting the strong interaction between intra and intermolecular hydrogen bonds in starch, improving processing properties and flexibility [7]. A variety of plasticizers have been used such as sugars, glycerol, glycol, xylitol, sorbitol and amides, such as urea, formamide and ethylene-bis-formamide [8]. Cross-linking is the process of linking two or more polymeric molecules by a covalent bond. It promotes change in physical properties in the polymers. Vegetable oils such as soybean oil and crude palm oil have been tried as cross-linking agent. Monoglycerides and triglycerides in crude palm oil also act as suitable plasticizer [9]. Addition of crude palm oil (CPO) also improves thermal stability of bioplastic with the mixture becoming highly heat resistant [10]. A recent study on cassava starch bioplastic film with zinc nanofillers and glycerol plasticizer has shown improved mechanical properties [11]. Apart from suitable plasticizers, cross-linking agents and fillers, starch is also blended with other synthetic polymers to improve mechanical properties and to alter the degradation rate

for the purpose of commercial application. PLA (polylactic acid) is the most predominantly used bio-based polymer derived from renewable resources. PLA can be derived from corn starch though fermentation by *Lactobacillus* spp. to produce lactic acid [12].

Research on obtaining starch sources from tropical agricultural wastes is gaining interest. Jackfruit is a tropical fruit having 100 to 500 jackfruit seeds on an average, weighing 8–15% of jackfruit, with high starch content [13]. According to Zawawi et al. [14], sago starch is a natural raw material that contains large amount of amylose, which can easily bond with other compounds, and it undergoes gelatinization at 70 °C when heated. Glycerol as plasticizer can strengthen the bioplastic by improving the chemical bonding leading to higher tensility [14]. The present study aims to synthesize eco-friendly bioplastic from these renewable plant sources and develop an alternative for conventional petrochemical plastic in a cost-effective way and to evaluate systematically its physical, mechanical and biodegradable properties.

2 Materials and methods

2.1 Materials

Sago (Tapioca pearls), pearl corn and crude palm oil were collected from local grocery stores; Jackfruit wastes (seed and core) were collected from local fruit vendor. Glycerol was purchased from Hi-media. Pure bacterial isolates (*Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Streptococcus* spp.) and pure fungal isolates (*Candida albicans*, *Aspergillus flavus* and *Penicillium chrysogenum*) obtained from King's Institute, Chennai, India, were used for this study.

2.1.1 Preparation of starch source

Jack fruit wastes (seed and core) left after the inner pulpy fruit is removed were collected from local fruit market. They were thoroughly cleaned with warm water to remove surface contaminants. Outer seed cover was removed from seed. Core and seeds were cut down into small pieces for enhancing the drying process and were kept for sun drying for 7 days. The dried parts were made into fine flour by dry milling process in local flour mill. Sago and pearl corn were dried in hot air oven for 5 h at 60 °C to remove the moisture content and made into flour by dry milling process in local flour mill (Mill Power Industries, India). The obtained flours were finely sieved and stored in airtight containers in a cool dry place. The flours (sago, jackfruit seed and core) were initially characterized for its composition. Moisture, ash content, carbohydrate, protein and

starch content of flours were determined according to standard procedures in laboratory.

2.1.2 Synthesis of polylactic acid

Lactic acid is prominent source for synthesis of polylactic acid (PLA). In the present study, lactic acid was made through fermentation of pearl corn hydrolysate. Ten g of pearl corn starch was mixed with 95 ml distilled water and 5% concentrated sulfuric acid and autoclaved for hydrolysis. The contents were filtered through filter paper to get a pure hydrolysate and neutralized with NaOH.

Standard contents of MRS broth were mixed with 850 ml of distilled water; 50 ml of pure hydrolysate was added to the broth and pH was adjusted to 6.2 and sterilized. 100 ml of 4% glucose solution was added to the flask through membrane filtration. *Lactobacillus* spores were inoculated and incubated at 37 °C for 84 h. The process was carried out in triplicates. Lactic acid was separated from fermented broth by conventional precipitation method. The broth was first filtered to remove the cells of *Lactobacillus* spp. Excess amount of calcium carbonate was added to neutralize the acid produced in the broth leading to the formation of calcium lactate salt, which was filtered as white precipitate. To the precipitate, 5% concentrated sulfuric acid was added which formed calcium sulfate salt as precipitate and soluble lactic acid into the filtrate. To the filtrate, small amount of activated carbon was added and centrifuged at 6000 rpm for 10 min to separate the remaining impurities from lactic acid. The supernatant was then stored for further usage. Kelling's test was performed using ferric chloride to know the presence of lactic acid. The purity level was quantified through thin layer chromatography using chloroform/butanol/water as a solvent and methylene red–bromophenol blue as indicator. The concentration of lactic acid was determined colorimetrically. Synthesis of PLA in laboratory was done by direct polycondensation method without catalyst [15]. Freshly polymerized lactic acid was immediately used in film formulation.

2.2 Fabrication of composite bioplastic films

In this study, three varying formulations were tried using starch, lemon extract, glycerol, palm oil and PLA for developing bioplastic films. All the films were prepared by conventional casting method. To 97 ml of sterile distilled water, 10 g of starch mix (sago, jackfruit seed and core flours in 9:1:0.5) and 3 ml of lemon extract were added and contents were sonicated for 5 min for proper blending. This was prepared in triplicates. In formulation PV, 2.5% crude polylactic acid (P) and 5% crude palm oil



Fig. 1 Bioplastic films with different formulations

Table 1 Composition of the developed bioplastic films

Contents	Trial I (PV)	Trial II (AV)	Trial III (PAV)
Starch mix (Sago/jackfruit seed/ jackfruit core)	10% (9:1:0.5)	10% (9:1:0.5)	10% (9:1:0.5)
Lemon extract	3%	3%	3%
PLA(P)	2.5%	–	2.5%
Glycerol (A)	–	5%	5%
Crude palm oil (V)	5%	5%	5%

(V) were added; in formulation AV, 5% glycerol (A) and 5% crude palm oil (V) were added, while in PAV, 2.5% crude polylactic acid (P), 5% glycerol (A) and 5% crude palm oil (V) were added and mixed well. Each formulation was heated on hot plate until the thick gelatinized consistency occurred and were poured onto aluminum foil and placed in hot air oven at 45 °C for 2 days. The films were peeled off and processed for further analysis (Fig. 1). Table 1 gives the composition of the three bioplastic films developed in this study.

2.3 Characterization of bioplastic films

2.3.1 Thickness

A handheld screw gauge (ssu 0–25 mm Micrometer Screw Gauge, India) was used for measuring the thickness of the bioplastic films. The bioplastic films produced were cut into 2 cm × 2 cm dimension for testing. At random positions, the thickness of each film samples measured and values were noted. The mean values of thickness were used in the further tests.

2.3.2 Swelling percentage

The swelling percentage was determined by standard ASTM D570. All the bioplastic films were cut into 2 cm × 2 cm dimension and dried at 60 °C in hot air oven. Initial thickness of the samples was measured. The films were kept immersed in water for 24 h. Thickness of the samples after immersion was measured.

$$\text{Swelling\%} = \frac{Th_1 - Th_0}{Th_0} \times 100$$

where Th_0, Th_1 = thickness of the sample before and after immersion in water, respectively.

2.3.3 Water absorption percentage

All the bioplastic films were cut into 2 cm × 4 cm dimension and dried at 60 °C in hot air oven. Initial mass of the films was noted. The films were immersed in the water for 24 h. The mass after immersion was measured.

$$\text{Water absorption \%} = \frac{M_1 - M_0}{M_0} \times 100$$

where M_0, M_1 = mass of the sample before and after immersion of the sample, respectively.

2.3.4 Film transparency

Film transparency of the film samples was determined according to method determined by Mulyono et al. [16], with minor modification. The bioplastic films were cut into 1 cm × 3 cm in order to match the width and height of cuvette. The films were attached to the side of the cuvette. Synthetic plastic film made from polyethylene was used as control. Absorbance was recorded at 600 nm. Transmittance was calculated using below mentioned equation.

$$\%T = \text{antilog}(2 - \text{absorbance})$$

The transparency was determined using the formula,

$$\text{Transparency} = \frac{\text{Log}\%T}{b}$$

where %T is transmittance at 600 nm and b is the thickness of bioplastic (mm).

2.3.5 Water solubility

Water solubility of the film samples was determined according to method determined by Saberi et al. [17]. All the bioplastic film samples were cut into 2 cm × 2 cm pieces, dried at 60 °C for 2 h and weighed. The dried pieces of films were immersed in 20 ml of distilled water in petri

plate and kept on a rocker for 24 h at room temperature. After 24 h, the films were observed for solubility. The residues were dried at 110 °C for an hour and then weighed to calculate the percentage of the solubility of the films.

$$\text{Solubility \%} = \frac{W_0 - W_1}{W_0} \times 100$$

where W_0 = initial dry weight, W_1 = final dry weight

2.3.6 Tensile strength and elongation at break

Tensile strength was measured with GOTECH Universal Testing Machine (UTM), Taiwan, using standard ASTM D882-02 with mild modification. The film samples were cut into 100 mm × 25 mm in dumbbell shape and gauge of 50 mm, and fixed onto loading unit. The test was conducted with the speed of 2 mm/min.

Elongation at break is the ratio between the initial length and changed length of specimen after breakage when an external stress is applied. The values were measured and results documented.

2.3.7 Chemical resistance

The bioplastic films were immersed in different solvents (0.1 N HCl, 0.1 N NaOH, NaCl solution and 50% Ethanol) for 48 h, and their resistance was ascertained by measuring change in appearance [18].

2.3.8 Fourier transform infrared spectroscopy analysis (FTIR)

FTIR spectra for the film samples were recorded using an infrared spectrometer FT/IR4700 type A, JASCO, Japan. The spectra were obtained in the frequency range between 4000 and 600 cm^{-1} at a resolution of 4 cm^{-1} . Data analysis of each film was performed using FTIR Spectrum Software.

2.3.9 Thermogravimetric Analysis (TGA)

The three bioplastic films (PV, AV, PAV) were subjected to TGA using thermal analyzer—Universal V4.4A, TA Instruments, USA. The temperature was gradually raised from room temperature to 800 °C at the rate of 10 °C/min and flow rate of 20 ml/min. The mass loss within the differential thermal analysis profile was recorded as a function of temperature.

2.3.10 Scanning electron microscope analysis (SEM)

The developed bioplastic films were studied at 30 s of acquisition time and accelerating voltage of 15 kV using

Instrument Quanta 500, Thermo Fisher Scientific, USA. Molecular structure of each film was analyzed in TM3030 Plus Hitachi Electron Microscope and compared.

2.4 Biological parameters

2.4.1 Soil burial biodegradation

The bioplastic films (PV, AV, PAV) and synthetic polyethylene film (control) were cut into small strips. The films were buried under the soil for assessing natural landfill degradation at different intervals of time (15, 30, 45, 60 days). Biodegradation of bioplastic films and synthetic polyethylene films was compared.

2.4.2 Laboratory culture-based Biodegradation

Minimal medium was used for this test keeping our bioplastic film as carbon source for the organisms used. All the essential components of minimal media broth were thoroughly mixed with distilled water and pH adjusted to 7.0 (optimal for bacterial growth) and 5.5 ± 2 (optimal for fungal growth) and poured into the boiling tubes. Cocktail of bacterial (*Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Streptococcus* spp.) and fungal (*Aspergillus flavus*, *Penicillium chrysogenum*, *Candida albicans*) cultures were inoculated aseptically in sterilized tubes separately. Bioplastic films (PV, AV, PAV) and synthetic polythene film of dimensions 3 cm \times 1 cm were introduced separately with the mixture of bacterial and fungal cultures. The tubes were then incubated at 37 °C (bacterial mix) and 25 °C (fungal mix). The growth of organisms and degradation of the samples were checked at regular intervals (7, 15, 30, 45 days) and noted.

3 Results and discussion

3.1 Testing of lactic acid

In Kelling's test, canary yellow color was observed due to the formation of iron lactate. In water, orange coloration was observed. Purity of lactic acid using TLC showed half of the purity level of standard lactic acid (88%). The concentration of the lactic acid colorimetrically was found to be 0.65 g/g of product tested.

3.2 Bioplastic films and their properties

External features of the three bioplastic films developed in this study were compared (Table 2).

3.2.1 Thickness swelling percentage and water absorption

Table 3 presents the thickness and swelling percentage of the three films. PV film took up thrice the amount of water content than AV film, and PAV had swollen twice the amount of that of AV. The crystalline nature of starch is destroyed in the presence of heat and excess water during melting process that makes the amylose and the branched chains of amylopectin to break and form hydrogen bonding. Additionally, there may be some exposed hydroxyl groups of amylose and amylopectin not involved in cross-linking with plasticizers, which react with water when exposed leading to swelling of the film [17]. Polylactic acid-based starch film (PV) may have less cross-linking with starch; PLA easily takes up moisture content; hence, a higher swelling is observed. Glycerol with starch (AV) has formed very strong interaction leaving little space for the film to take up water with least swelling. PLA starch with

Table 2 Physical properties of bioplastic films

Properties	PV film	AV film	PAV film
Brittleness	High, when exposed to temperature above 50 °C	Moderate when exposed to temperatures above 80–90 °C	Moderate when exposed to temperatures above 70–80 °C
Ductility	Low (when absorbs moisture)	Moderate	High
Recasting ability	Yes	Yes	Yes
Texture	Smooth surface and less flexible	Slightly rough and flexible	Soft and flexible with even surface

Table 3 Thickness and swelling properties of films

Bioplastic film type	Thickness before immersion (mm)	Thickness after immersion (mm)	Percentage
PV (PLA and crude palm oil)	0.28 \pm 1	0.39 \pm 1	39.3
AV (glycerol and crude palm oil)	0.34 \pm 1	0.35 \pm 1	2.94
PAV (PLA, glycerol and crude palm oil)	0.27 \pm 1	0.35 \pm 1	29.6

Table 4 Water absorption property of bioplastic films

Bioplastic film type	Mass before immersion (g)	Mass after immersion (g)	Percentage
PV (PLA and crude palm oil)	0.28 ± 1	1.08 ± 1	285.7
AV (glycerol and crude palm oil)	0.30 ± 1	0.40 ± 1	33.3
PAV (PLA, glycerol and crude palm oil)	0.28 ± 1	0.78 ± 1	178.6

Table 5 Transparency analysis of bioplastic films

Film type	Absorbance	Transmissi- on%	Thickness	Transparency
Polyeth- ylene (control)	0.398	39.99	0.12	13.34
PV	0.440	36.30	0.28	5.57
AV	0.450	35.48	0.34	4.56
PAV	0.420	38.30	0.27	5.86

glycerol (PAV) showed intermediate property with moderate swelling. Table 4 shows percentage of water absorption with respect to mass gained, by the three films, and the trend was similar to swelling percentage.

3.2.2 Film transparency

Bioplastic films showed lower transparency than synthetic polythene (Table 5), which could be due to the fillers used in the making of bioplastic and thickness. Despite this, PAV bioplastic had better transparency when compared to other studies. Mulyono et al. [16] achieved maximum transparency value of 3.13 for tapioca film, while the bioplastic films produced in our study had better transparency (5.86).

3.2.3 Water solubility

The solubility of the films is an indicator of the presence of hydrophilic compounds in the film. PV film had higher solubility because of the water absorbing nature of PLA. Films with glycerol were less soluble because of high level of intermolecular attractions within the matrix and cross-linking bringing about lower capability to interact with water. Hence, AV film had least solubility in water, while PAV had a moderate solubility percentage (Table 6).

3.2.4 Tensile strength and elongation at break

Tensile strength (TS) and elongation at break (EAB) show the ability of film's integrity under stress and hence are important to determine their application. TS value of PV film (polylactic acid–crude palm oil) was 5.24 MPa, and EAB value was 3.49%. The increased tensile strength

Table 6 Solubility percentage displayed by bioplastic films

Bioplastic film type	Initial dry weight (g)	Final dry weight (g)	Solubility percentage
PV	0.20	0.06	70
AV	0.25	0.22	12
PAV	0.22	0.12	45.45

value was because of palm oil which enhanced interaction with PLA in the starch blend and jackfruit core acted as a filler providing strength and toughness to the film, but in contrast elongation strength was low due to low ductility of PLA. TS value of AV film was 1.45 MPa, and EAB was 32.45%. Addition of glycerol improved the mechanical property of the film, making the film flexible and palm oil enhanced cross-linking; thus, EAB value increased with moderate TS value. TS value of PAV film was 0.78 MPa, and EAB was 73.38%. Brittleness was lowered by glycerol that gelatinized with the starch; palm oil enhanced cross-linking with PLA, increasing the ductility with higher elongation. However, the film was softer and more flexible compared to other two formulations with low tensile strength (Fig. 2a, b). Addition of plasticizer varies inversely with the addition of fillers and decreases the value of tensile strength. Plasticizer lowers the density of the structure of the polymeric chains leading to decrease in tensile strength [19].

3.2.5 Chemical resistance

All the three bioplastic films were exposed to different chemical solvents, and their effect on the films was observed according to the parameters given in Table 7. All the formulated films were affected by strong acid. They absorbed the solvent and got softened in alkali which could be due to the presence of acid in the film which reacted and neutralized. PV and PAV films became soft in all the solvents, while AV film showed brittleness when exposed to 50% ethanol. Similar kind of results was observed by Jack et al. [18] for their bioplastic film in acid and alkali.

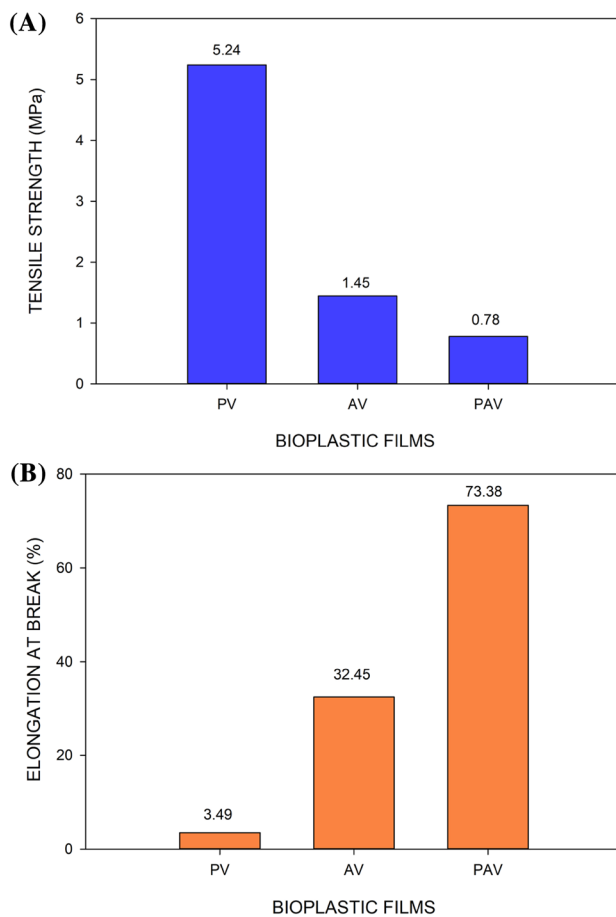


Fig. 2 a Tensile strength of the films, b elongation at break of the films

Table 7 Chemical parameter displayed by the bioplastic films

Solvent	Reaction of bioplastic film*		
	PV	AV	PAV
0.1 M HCl	a, c, e, h	b, d, e	a, c, e, h
0.1M NaOH	b, d, e, h	b, d, e, h	b, d, e, h
NaCl solution (saturated)	b, d, e, h	b, d, e	b, d, e, h
Ethanol (50%)	b, d, e, h	a, d, e, g, i	b, d, e, h

*Interpretation parameters: a change in dimension; b no change in dimension; c dissolved in the liquid; d not dissolved in the liquid; e absorbed the liquid; f not absorbed the liquid; g wrinkle; h softened; i brittle

3.2.6 Fourier transform infrared spectroscopy analysis (FTIR)

FTIR spectroscopy was used to ascertain the possible chemical interactions in the three composite films. (a) Only three peaks were formed in PV Film. The initial broad peak at 3296.71 cm^{-1} indicated the presence of carboxylic acid

O–H stretch, confirming the interaction of different –OH groups in the starch and polylactic acid blends; peak at 1735.62 cm^{-1} (C=O stretching) and peak at 997.017 cm^{-1} indicated the presence of (R-CH=CH2) in the sample. (b) AV film and (c) and PAV films had more or less similar peaks in which the first broad peak at 3280.32 cm^{-1} (AV) and 3292.86 cm^{-1} (PAV) indicated the presence of carboxylic acid O–H stretch; a small peak at 2921.63 cm^{-1} in both the films showed good C–H stretch, while a sharp peak at 1743.3 cm^{-1} in PAV indicated triglyceride ester linkage [11]; other peaks of AV films 1647.88 cm^{-1} , 1362.46 cm^{-1} and 1149.37 cm^{-1} showed the presence of substituted alkene, C–H rock with phenolic group and C–H wag with halo compounds, respectively [20]. Other peaks of PAV film— 1454.06 cm^{-1} , 1196.61 cm^{-1} and 1083.81 cm^{-1} —indicated C–H bond stretching with CH₃, halo compounds and secondary alcohol. The strong peak at 1008.59 cm^{-1} in AV and 1012.45 cm^{-1} in PAV was related to strong intramolecular hydrogen bonding of hydroxyl groups. The peaks between 900 and 600 indicated the presence of alkynes, nitro and alkyl halide groups (Fig. 3a–d). From the above results, PV film indicated poor bond formation, and PAV film had very good bond formation compared to AV film possibly due to its composite nature. The peak at $1736.3\text{--}1743.3\text{ cm}^{-1}$ was seen in all the formulation indicating the strong interaction of triglyceride (palm oil). The peak value of 2921.63 cm^{-1} was seen in AV and PAV film but absent in PV film, which could be a C–H interaction of glycerol with starch.

3.2.7 Thermogravimetric analysis (TGA)

From the graph (Fig. 4a), it is clear that initial decomposition of PV film sample occurred at $212\text{ }^{\circ}\text{C}$ where around 9% of sample mass decreased. After that sample underwent single-stage decomposition up to $327\text{ }^{\circ}\text{C}$, with nearly 50% of mass getting reduced. Decomposition continued till $565\text{ }^{\circ}\text{C}$, and only 18% sample remained. At the end of $800\text{ }^{\circ}\text{C}$, 12% of sample was left as residue. After $500\text{ }^{\circ}\text{C}$, PV sample showed slower rate of decomposition, possibly due to palm oil which gave thermal stability to the film. The weight of AV film started to decrease between 120 and $200\text{ }^{\circ}\text{C}$ leading to a loss of 16% of sample weight (Fig. 4b). Nearly half the decomposition occurred at $310\text{ }^{\circ}\text{C}$, and a prolonged decomposition of sample occurred at the end with only 3% of residue. This indicated that starch plasticized along with glycerol underwent faster rate of degradation and mass change. In the PAV film (Fig. 4c), initial decomposition started at $183\text{ }^{\circ}\text{C}$ where 11% of sample mass got reduced. At temperature $329\text{ }^{\circ}\text{C}$, 50% of sample mass got reduced; at $565\text{ }^{\circ}\text{C}$, 10% sample remained. At the end of $800\text{ }^{\circ}\text{C}$, 8% of sample was left as residue possibly because of the filler contents in the film. Starch–polylactic

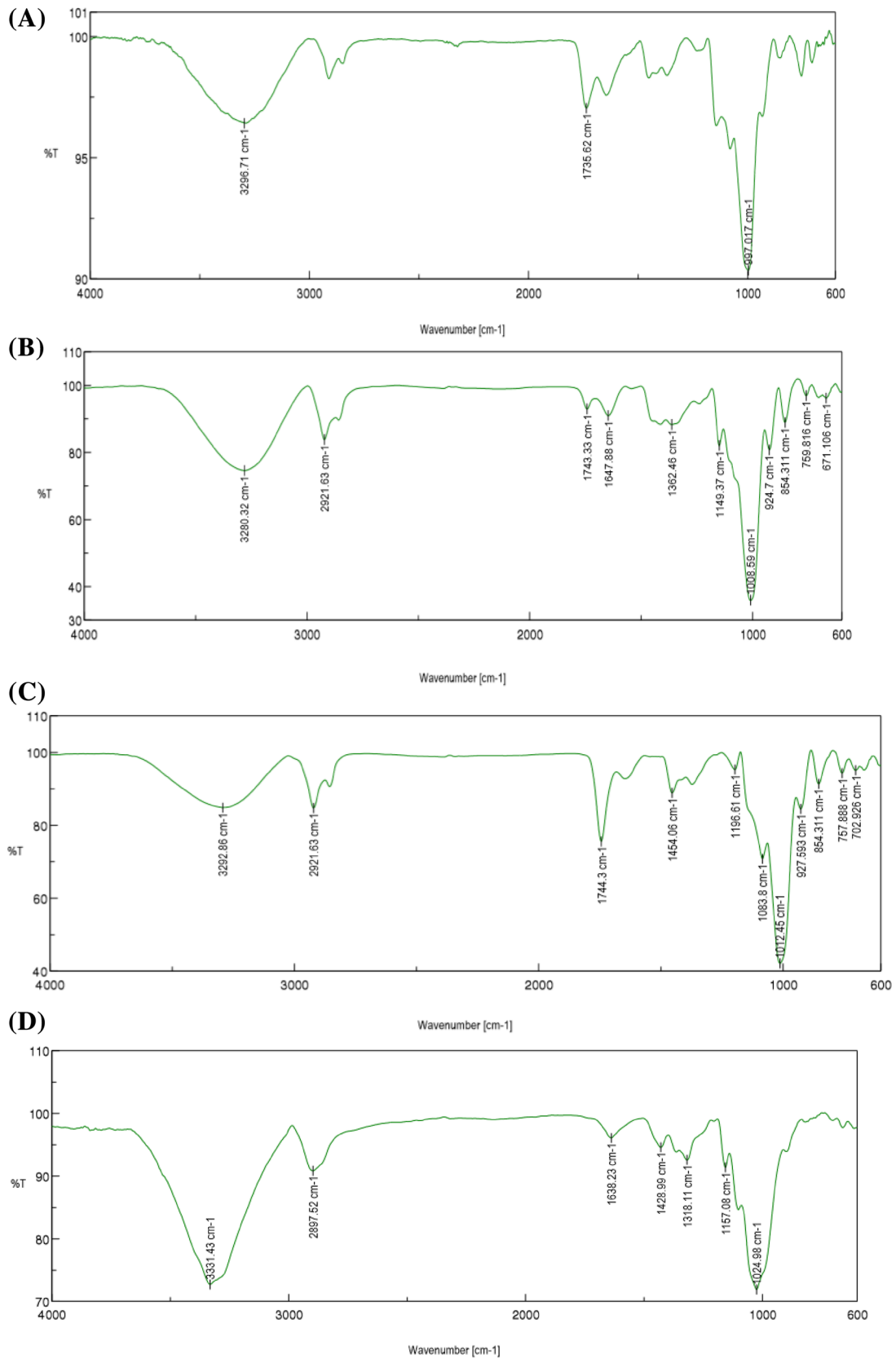


Fig. 3 FTIR spectra of bioplastic films, **a** PV Film, **b** AV film, **c** PAV film, **d** polyethylene control (Iyer and Amritkumar [20])

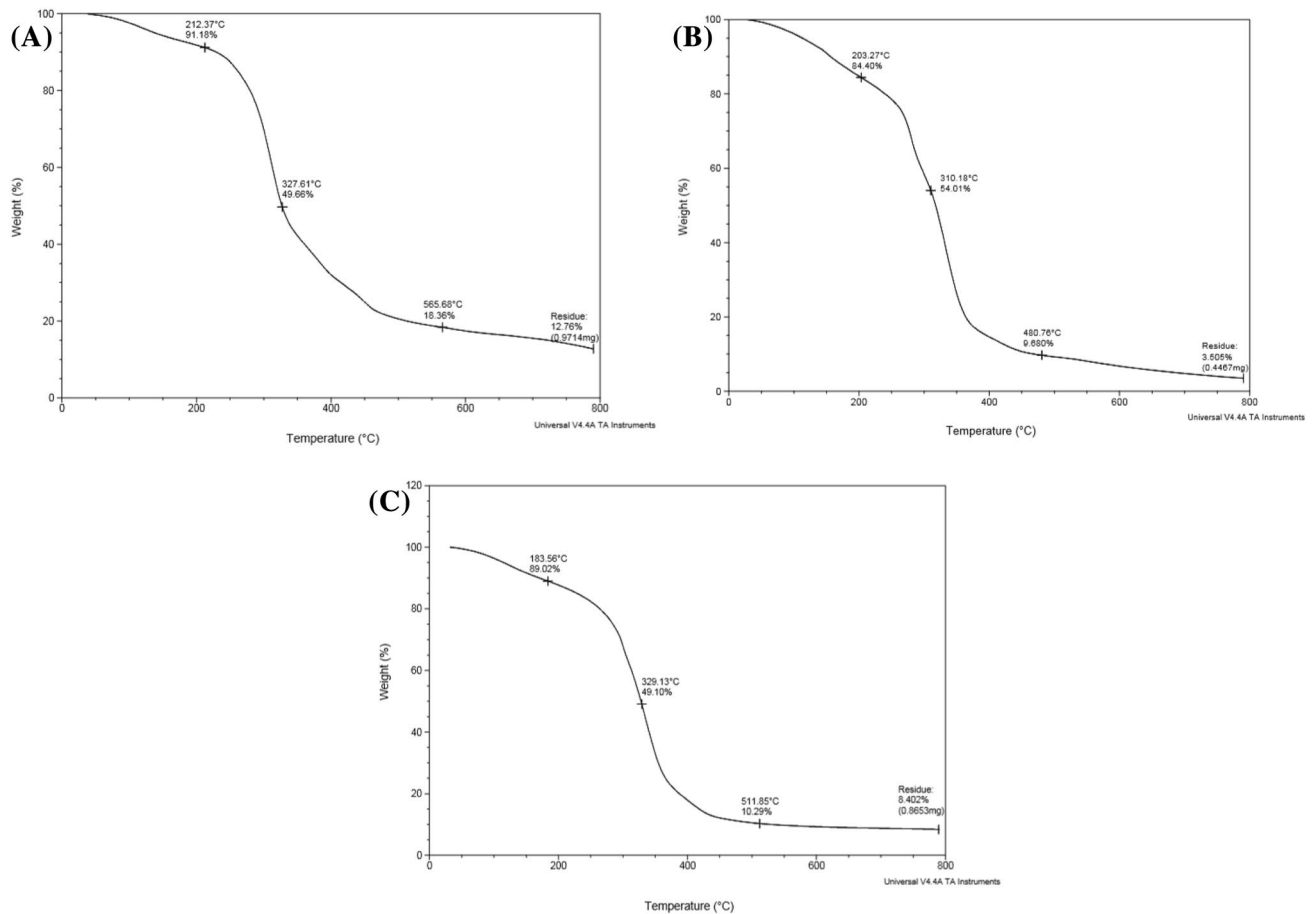


Fig. 4 Thermogravimetric analysis (TGA) of **a** PV film, **b** AV film, **c** PAV film

acid with palm oil (PAV) had better thermal stability. In all the bioplastic films, there was a gradual desorption occurring between 150 and 220 °C where the volatile compounds started to evaporate and around 300 °C the lower molecular weight compounds like plasticizer, cross-linker and other additives started to release out and above 500 °C pyrolysis of carbonated compounds occurred, and the remaining residues were the inorganic materials in the sample. According to Makhtar et al. [11], addition of crude palm oil into the starch film improves the thermal stability. Their glycerol starch film started to decompose at 70–110 °C, and half of the sample weight was lost when the temperature reached 260 °C. But in our study, glycerol with palm oil film (AV) started at 120–180 °C and half decomposition occurred at 310 °C which showed improved thermal stability of the bioplastic film. According to study by Chieng et al. [21], PLA with epoxidized palm oil had half decomposition of sample at 370 °C. In our study, although the amount of PLA was less when compared to starch, half decomposition occurred at around 330 °C indicating good thermal stability.

3.2.8 Scanning electron microscope (SEM) analysis

The surface morphology of bioplastic films was observed under SEM (Fig. 5). PV films showed some cracks on the surface because of their brittle nature (Fig. 5a). AV film had smooth surface, but some microvoids were observed, which may be due to the degree of dispersion of the plasticizer in the polymer matrix (Fig. 5b). The PAV film also has some smaller voids, but displayed good incorporation of plasticizer and cross-linker materials (Fig. 5c). Voids and microvoids are caused when hydrogen bonding in long chains of starch breakdown during gelatinization temperatures, leading to infiltration of water molecules into hydroxyl group of starch molecules [22]. The surface morphology of the bioplastic films had similar morphology as that of recycled polythene plastic material analyzed by Lico et al. [23].

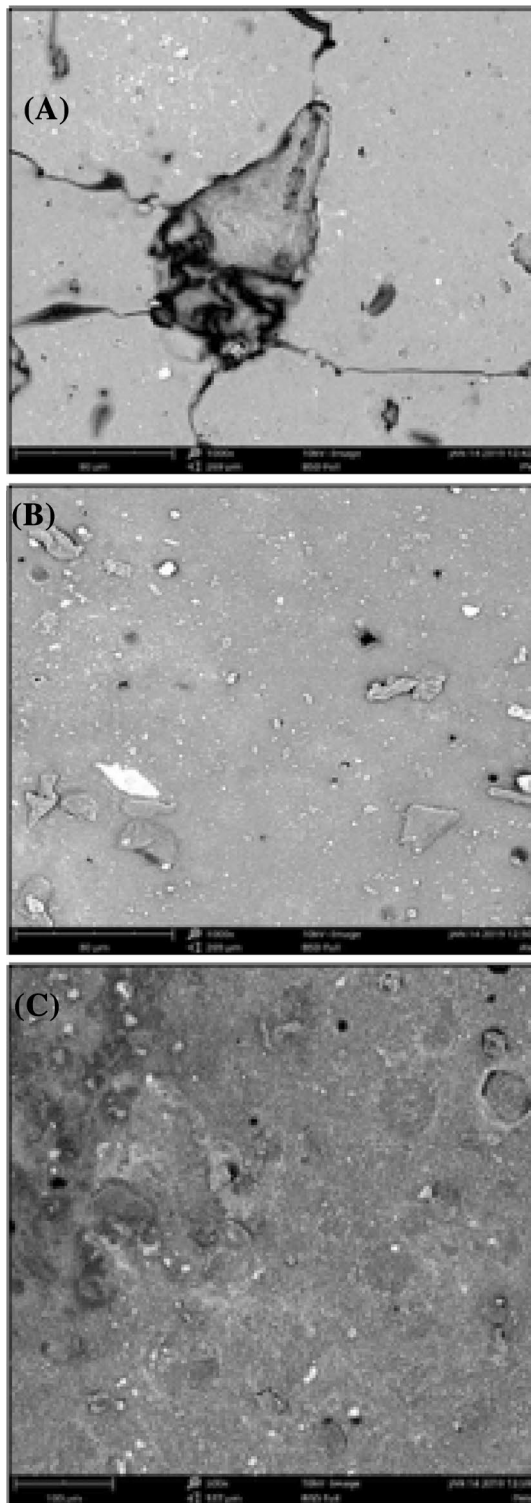


Fig. 5 Surface morphology through SEM of **a** PV film, **b** AV film, **c** PAV film

3.2.9 Biodegradation

3.2.9.1 Soil burial All the soil buried bioplastic samples were taken from the soil at different time intervals. The biodegradation rates were closely observed and compared with the synthetic polythene. On day 15, the size and color the bioplastic films changed and started to degrade slightly. On day 30, the PV film started to disintegrate more when compared to other films. Fungal growth was observed over AV film. PAV film got mixed well with soil and started degrading. On day 45, PV film disintegrated into pieces and half of the sample got degraded, 20% of AV film had degraded, and 35% of PAV film had degraded. On day 60, PV film got completely degraded, 50% of AV film and 80% of PAV film got degraded. No change was observed in synthetic polythene throughout. This study indicated that starch-based bioplastics have the ability to degrade quickly when compared to the synthetic plastics (Fig. 6). Wahyuningtiyas et al. [24] developed bioplastic from Cassava flour with different proportions of glycerol from 1 to 3% and tested its biodegradation by soil burial. The mass of bioplastic got reduced within a week, and complete degradation was attained in 9–12-day interval because of moisture uptake. Compared to their study, our bioplastic films had ability to withstand biodegradation for a longer period.

3.2.9.2 Laboratory culture-based microbial biodegradation On day 7, the mixed bacterial cultures started to utilize the carbon source in the bioplastic film and started to grow, whereas no growth was observed in control minimal media without carbon source and in synthetic polythene. On day 15, 50% of PV films and 25% of PAV were degraded, whereas 5% of AV film got degraded. At day 30, maximum amount of degradation was observed in PV films, 15% of AV film and 75% of PAV film. On day 45, 10% of PV film, 45% of AV film and 20% of PV films were left. No growth was observed in synthetic polythene and in control. The change in color of the media was because of the metabolites/by-products released by the microbes. The biodegradation of the bioplastic films and synthetic polythene by a consortium of fungal cultures (*Aspergillus flavus* and *Penicillium chrysogenum*, *Candida albicans*) were observed at regular interval of time. On day 7, fungal species started utilizing the bioplastic film as carbon source and growth was observed in all tubes. On day 30, maximum degradation of bioplastic films was observed while no change in the synthetic polythene film. PLA mixed with starch (PV) attained faster degradation when compared to glycerol mixed films. This could be due to higher attraction of moisture by PLA and starch than glycerol–palm oil starch film, which can hasten the biodegradation process. Compared to laboratory culture-based degradation, soil burial took a little longer time for

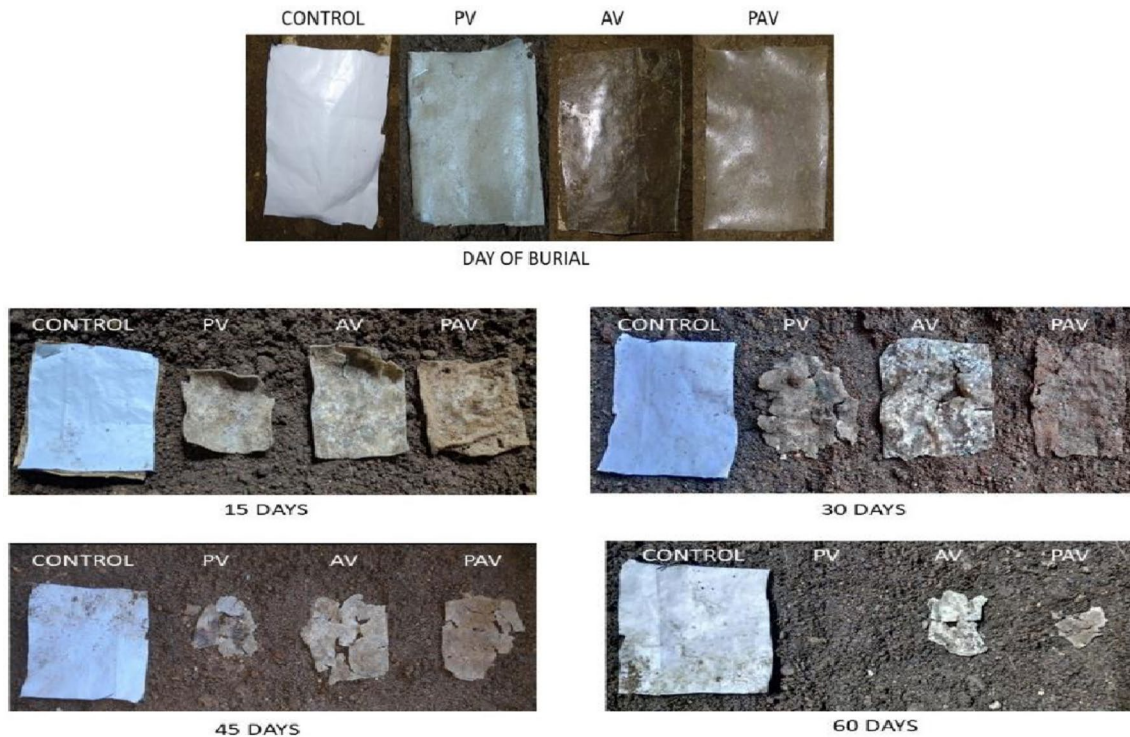


Fig. 6 Biodegradation of bioplastic films by soil burial method

biodegradation of the starch-based bioplastic because all the appropriate conditions were provided for the microbial growth in laboratory for biodegradation along with high load of inoculum, while in natural environment, the atmospheric condition and soil pH vary which make the microbes to grow at slower rate and with slower biodegradation of the sample. The study also observed that mixed colonies showed enhanced biodegradation than individual colonies.

This study has thus conducted extensive analysis of physical, chemical and biological properties on the three films synthesized (PV, AV and PAV) and compared the outcome. The three bioplastic formulations displayed good range of tensile strength, EAB, thermal stability and biodegradability than the jackfruit seed flour-based biofilms developed by previous studies [22, 25]. The ratio of composite flour, cross-linkers and plasticizers used in this study has improved the properties of the biofilms considerably. The previous studies [22, 25] did not conduct extensive analysis of all the parameters like ours, thus making our approach significant and beneficial for judging the potential of the films for future application.

4 Conclusions

This study was conducted with an aim to synthesize eco-friendly and cost-effective bioplastic from plant resources. This study formulated three bioplastic films using same starch source with lemon extract and water but with different cross-linkers: (1) PV (polylactic acid and crude palm oil with starch) (2) AV (glycerol and crude palm oil with starch) (3) PAV (polylactic acid, glycerol and crude palm oil). Each film displayed different properties with respect to hardness and tensility. The formulated films' physical, chemical, mechanical and biological parameters were characterized. PV film showed the best tensile strength (TS) of 5.24 MPa and least elongation at break (EAB) of 3.49%, while PAV film had the least TS of 0.78 MPa with a maximum EAB (73.38%). FTIR analysis of films showed spectral similarity with synthetic polyethylene plastics. In thermogravimetric analysis (TGA), all the films displayed gradual desorption occurring between 150 and 220 °C where the volatile compounds started



Fig. 7 Bioplastic straws and handmade paper without (left) and with bioplastic coating

to evaporate and around 300 °C the lower molecular weight compounds like plasticizer, cross-linker and other additives started to release out; pyrolysis of carbonated compounds occurred above 500 °C. PAV film displayed best thermal stability with half decomposition at 330 °C. Biodegradability of films was demonstrated through soil burial method and culturing of pure cultures of microorganisms in minimal media by providing the film as carbon source. Each of the three bioplastic films formulated displayed different mechanical properties and hence has potential application in different areas according to the needs.

Based on the properties displayed by the bioplastic films developed in this study, two products were tried in the laboratory for potential application. Bioplastic straws (Fig. 7) were made from renewable starch (PV formulation) as a safe and eco-friendly alternative, and handmade paper coated with AV film, which was also checked for water resistance. Paper without coating absorbed water immediately, whereas the paper coated with AV bioplastic held water even after 2 h.

The results of this study showed that sago–jackfruit waste flour along with the polymer polylactic acid (PLA) can be used to make bioplastic which can serve as a safe and cost-effective alternative to synthetic single-use polythene plastics.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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