

# Preparation and Characterization of Biodegradable Composite Films from Poly (vinyl alcohol) and Natural Proteins for Food and other Packaging Applications



K. Subramanian, S. Sangeetha, G. Srisugamathi

**Abstract:** Packaging materials provide a means to preserve, protect, merchandise, market and distribute foods. Synthetic polymers are widely and massively used to make packaging materials for diverse applications. The environmental issues due to the non-degradability of the polymer packaging material wastes demands biodegradable and environmental friendly polymers for these applications. Hence increasing research is focussed to manufacture packaging materials from biodegradable synthetic and natural polymers. The present study involves fabrication of biodegradable composite polymer films by solution casting from natural biopolymers such as whey and soy proteins, and synthetic biocompatible polymer such as poly(vinyl alcohol) using UV light, glutaraldehyde etc as crosslinkers, and glycerol as a plasticizers. The prepared films were evaluated for their tensile strength, water vapour permeability, thermal stability, biodegradability, structure, morphology etc. The tensile strength in terms of breaking load and % elongation measured on non standard dimension of the films were in the range 1.6 -4.7 kgf and 75-400 % respectively. Thermogravimetric studies indicated that polymer films were sufficiently thermostable for packaging uses. Soil burial test and X-ray diffraction studies of the films indicated that they were biodegradable and predominantly amorphous respectively. Glutaraldehyde crosslinked composite polymer films were found to have improved antimicrobial properties compared to the uncrosslinked film. The water vapour permeability of the fabricated films were within the acceptable range of values ( $5.208 - 7.81 \text{ g/cm}^2\text{h} * 10^{-5}$ ) reported for typical biopolymer films used in packaging applications. The fabricated composite polymer films may be exploited for commercial packaging applications.

**Keywords:** Biodegradability, Composite film, Cross linking Poly (vinyl alcohol), Whey & soy proteins, Solution casting Tensile strength.

## I. INTRODUCTION

The revolutionary developments in the area of polymers and plastics after World War II has immensely contributed for the comfort of mankind and infrastructure build up in the modern world.

Polymer films and plastics made from petrochemical derived polymers such as poly(ethylene terephthalate), poly(vinylchloride), poly(ethylene), poly(propylene), poly(styrene), poly(amide), ABS copolymer etc by appropriate molding technique [1] are playing vital roles in all the human activities such as food packaging, agricultural mulching, carry bags, hospital bed covers, disposal cups, trays, as scratch proof thin film coatings etc. Polymers are widely used for these applications because of their availability, low cost, good mechanical properties (tensile and tear strength), corrosive resistance etc [2]. But the non-biodegradability of these polymer product waste which are usually disposed randomly accumulates on earth, water, marine and air endangering the health of living beings and pollutes the air. More than 40 % of accumulated plastic wastes (roughly 200 million tons) are from packaging industries and their degradation will take many years (even up to 100 years). Moreover all the plastic waste products are not recyclable and recycling is not economically viable [3,4]. The increase in crude oil price also drives the development of alternatives to synthetic polymers. Hence there is a necessity to develop biodegradable plastic films for packaging uses to bring down the consumption of synthetic plastics from non-renewable petroleum sources. The food manufacturer incorporates food packaging materials that will act as a barrier to gases, water vapour etc to protect the packaged product. Oxygen and water vapour are major concerns in food packaging in relation to shelf life. Presence of oxygen in a packaged food is often a key factor that limits the shelf life of a product. Oxidation can cause changes in flavour, colour, and odour, as well as destroy nutrients and facilitate the growth of aerobic bacteria, moulds, and insects.

Even so, consumer demand for products that are environmentally friendly, safer and nontoxic. The biodegradable polymer films can degrade eco-friendly in the disposed environment. This has promoted applied research to make biodegradable polymer films for packaging applications as well as to bring down the consumption of synthetic polymers and hence the environmental pollution. The use of biopolymers derived from renewable resources contributes to material cycling that is analogous to the natural biogeochemical cycles in nature [5]. Consumers are demanding food packaging materials which are more natural, disposable, potentially biodegradable, as well as recyclable [6].

Manuscript published on November 30, 2019.

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# Preparation and Characterization of Biodegradable Composite Films from Poly (vinyl alcohol) and Natural Proteins for Food and other Packaging Applications

Hence increased research interest has been focused globally to fabricate eco-friendly biodegradable plastic and films from the natural polymers and synthetic biopolymers for wide spectrum of applications [7] by tailoring the physicochemical properties of the existing commercially available natural polymer by appropriate modification via blending, grafting, cross linking, plasticizing, adding fillers etc with appropriate chemical reagents and additives [8].

The global market for biodegradable polymers exceeds 114 million pounds and is expected to rise at an average annual growth rate of 12.6% [4]. Natural polymers or polymers derived from natural products, like food protein, offer the greatest opportunities since their biodegradability and environmental compatibility are assured. In addition, films made from protein can supplement the nutritional value of the food [9,10]. Poly(vinyl alcohol) (PVA) a synthetic, water soluble polymer prepared by hydrolysis of poly (vinyl acetate) has excellent film forming, emulsifying, and adhesive properties. It also has good tensile strength and biodegradability and has been used in various biomaterial applications. It has also been approved for use in packaging meat and poultry products by the USDA [1,11]. PVA is a semicrystalline polymer whose crystallinity index depends on the synthesis process and on physical aging. Hydrogen bonds bind the polymer chains together, even in the amorphous phase, and the glass transition and melting temperature of PVA are 85 and 240 °C, respectively [12]. Over the last years, PVA has gained interest due to its biodegradability and non toxicity. It is excellently miscible with other compounds and it has good film forming characteristics, which involves acceptable strength and good resistance to pH-variability. The transparency of PVA film is usually close to 100%, which means that they allow UV-Vis irradiation easily to pass through, reducing at the same time their application possibilities. Attempts were made by many authors to improve the mechanical properties of the PVA matrix by adding some fillers and some liquid phase that were miscible and compatible with PVA solution [13,14]. Whey an abundant byproduct of cheese industry and soy protein isolates are potential biopolymers having engineering applications. The film forming and barrier properties of whey protein are nearer to those of petroderived polymers. Soy protein isolate (SPI) and whey protein isolate (WPI) are widely used as edible films and as films for other low stress uses. The poor mechanical properties of SPI and WPI can be improved by blending with suitable ecofriendly compatible polymers like PVA. WPI is an edible and biodegradable biopolymer, which can be obtained from the whey generated by cheese industries, and can be used as polymeric matrix for packaging film. Here the biodegradable WPI and SPI were chosen as constituent additives to be solution blended with PVA for making food grade packaging films. WPI based films present desirable properties of transparency and good oxygen barrier, since the film forming includes the proteins heating, inducing their denaturation above 50°C, and thus the proteins become insoluble and aggregated [23,24]. Predominant amino acids present in whey were leucine, isoleucine, lysine, tyrosine, cysteine, valine, threonine, tryptophan and histidine [23]. SPI a cheap plant protein of renewable resource, is safe and has good film-forming

ability, and biocompatibility [25]. It is widely used as food ingredients owing to their high nutritional and excellent functional properties [26]. Soybean proteins are composed of two major components, glycinin (11S globulin of about 360 kDa) and  $\beta$ -conglycinin (7S globulin of 180 kDa). Different treatments, including physical (such as high pressure, heat, and mild alkali), chemical (such as deamidation, phosphorylation, and acylation), and enzymatic extraction methods, could affect the structural and physicochemical properties of soybean proteins. Its surface composition, morphology, and physical properties of powders can affect particle-water interactions, particle-particle interactions, and particle-air interactions in food processes [27]. Predominant amino acids present in soy protein were leucine, isoleucine, lysine, phenyl alanine, methionine, valine, threonine, tryptophan and histidine [28]. The present investigation involves the fabrication of the eco-friendly polymer films using PVA a synthetic biocompatible polymer along with WPI and SPI extracted from dairy waste and soy bean respectively along with processing additives like glycerol, citric acid etc and cross linkers like glutaraldehyde, UV light and evaluation of their properties like tensile and tear strength, elongation, thickness, moisture pickup, water vapour permeability, thermal stability, biodegradability, antimicrobial activity, morphology (by X-ray diffraction (XRD), chemical structure by attenuated total reflection -Fourier Transform Infrared spectroscopy (ATR- FTIR) etc.

## II. MATERIALS AND METHODS

### A. Polymers and Chemicals

PVA solution (commercial 50% w/w 5.68g/10ml, Molecular Weight 1,25,000), Milk and soy bean seed (Purchased Locally), citric acid (HI-PURE RANKEM), glutaraldehyde (S D Fine-Chem 25% solution), Glycerol (E Merck), recrystallized benzoyl peroxide initiator (Stearic acid coated) were used in the present study. Gram positive and negative cultures were received from the Bio technology department of BIT for antimicrobial test. Bacterial collection from wet soil enriched with cow dung, organic waste of a local cowdung based gohar gas plant was used to test the biodegradability of the polymer film.

### Whey Protein Isolate (WPI) from Milk

Whey is a protein present in the liquid during the production of curd from milk. The liquid in the curd was clarified by membrane filtration and the filtrate is lyophilized (CHRIST Alpha 1-2 LD plus). The solid product thus obtained was vacuum dried and ground to get the powder form. Water is used as solvent for whey and the concentration of whey solution used is 10%

### Soy Protein Isolate (SPI) from Soy Bean Extract

Commercial soya bean was purchased from local market and soaked in water for about 2hrs to remove the hull. It was then blanched in water and ground into a fine paste. To this sodium carbonate solution was added to bring down the pH to 7 and centrifuged.

The supernatant was removed and pH was adjusted to 4.5 using HCl to precipitate soy protein. The precipitated soy protein was lyophilized to get the solid soya protein. This was vacuum dried and ground to get the powder form. For film casting solutions of extracted WPI and SPI at a concentration of 0.1 g/10 ml were used.

## B. Polymer Film Casting and Crosslinking

### PVA Film

Known volume of PVA solution (20ml) was taken and casted as a film on a glass plate (20\*20cm), by evaporating the water at room temperature for 72 hrs followed by heating at 50°C in a hot air oven to peel out the film. Finally it was irradiated with UV light in air at room temperature for 72 hrs.

### PVA- WPI (PW) Pomposite Film

20ml of PVA solution (11.36 g of PVA) was mixed with 10 ml of 0.1% whey solution (2:1 w/w) and homogenized by mechanical stirring for 2 hours followed by at 20 KHz for 1 hr at room temperature. To this citric acid solution (0.5 g / 5 ml) was added and sonication was prolonged for another 15 minutes. Then it was poured on a glass plate (20\*20cm) and dried at room temperature for 72 hrs and subsequently dried at 50°C in a hot air oven to peel it off.

### PVA- SPI (PS) Composite Film

20ml of PVA solution containing 11.36 g of PVA and 10 ml of 0.1 % SPI solution (2:1 w/w) were homogenized by mechanical stirring for 2hrs followed by sonication (20 KHz) at room temperature for 1 hr. To this 0.5 g of citric acid solution (0.5 g / 5 ml) was added and sonication was prolonged for another 15 minutes. Then it was poured on a glass plate (20\*20cm) and dried at room temperature for 72 hrs and subsequently dried at 50°C in a hot air oven to peel out the film.

## C. Crosslinking of PS and PW Films

The above casted films were cross linked using glutaraldehyde by exposing them to the vapours of glutaraldehyde in a desiccator for two days at room temperature. All films prepared were kept in hot air oven (60°C, 5 hrs) to remove the moisture and then used for further characterization. Crosslinked PS and PW with glutaraldehyde are designated as PSG and PSW respectively. Crosslinking was also performed by UV irradiation in air using 18 W UV lamp with BPO as photoinitiator for two to three days. Photocrosslinked PS and PW are designated as PSU and PWU.

## D. Thickness and Tensile Properties of Films

The thickness of individual film samples was determined as a random average of five measurements using screw gauge. The tensile strength (breaking strength) and % elongation of the films were measured on MAG Unistretch tensile machine with non standard samples of dimension 150mm\*20mm\*0.04mm. The grip distance was 60mm initially and the gauge speed was 300mm/min. Average of three replicate measurements were taken as a breaking strength.

## SEM Micrograph

The surface Morphology of the film samples were investigated using SEM FEL- Quanta 250. The film samples (1×1 cm<sup>2</sup>) were cut and mounted onto a bronze stub with double-sided tape. The surface features and cross sectional view of the films were visualized at different magnifications for 20-1000 kV range at a pressure of 60 pa.

## Thermogravimetry

Thermal properties of film and polymers were studied by simultaneous thermogravimetry and differential thermal analysis on NATZSCH STA 2500 (Regulus) at heating rate of 10<sup>0</sup> C per minute in nitrogen at a flow rate of 60 ml/min.

## FT-IR Spectra

FT-IR spectra was recorded on SCHIMADZU IR affinty 1 model under ATR mode for the spectral with 4000 - 400 cm<sup>-1</sup> at a resolution of 2 cm<sup>-1</sup> for 45 number of scans.

## X-Ray Diffraction

X- ray diffractogram was recorded on D8 DISCOVER in reflection mode with CuKα radiation in the range of 5° - 60° to analyze the crystalline/amorphous feature of the films.

## Moisture Pickup

A desiccator containing 250 ml of saturated sodium chloride solution has been taken. The relative humidities (RHs) of these sodium chloride solution at temperature 35°C, 55°C and 65°C were 74-75% respectively. A known weight (0.03-0.09g) of polymer film of dimensions 4cm\*2cm\*0.04cm was placed on the platform inside the desiccator and allowed to equilibrate at each temperature. After equilibration the films were taken out and weighed. The moisture pick-up of the film is calculated using the equation

$$\% \text{ Moisture pick up} = (W_f - W_i) * 100$$

where  $W_f$  is the weight of the film after moisture pick up,  $W_i$  is the initial dry weight of the film.

## Water Vapor Permeability (WVP)

A known weight (0.20g) of self indicating dried silica gel was taken in 50 ml beakless beaker of 1.5 cm diameter. It was covered with the casted polymer film of 1.6 cm diameter of known weight (0.03-0.09g). Then it was kept inside a desiccator containing saturated sodium chloride solution and equilibrated for the temperatures 33, 36 and 39°C for 24 h.. After equilibrium the weight of the silica gel in the beaker was determined using four decimal balance after transferring it to a weighing bottle with a lid for each temperature. From the increase in weight of silica ( $W_g$ ) the water vapor permeability of the film was determined using the formula [21]

$$\text{Water vapor permeability} = W_g / t . A$$

## Biodegradability

A known weight (0.03-0.09g) of the polymer films of dimension 2cm\*2cm\*0.04cm were taken for biodegradability.

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Wet soil enriched with cow dung and organic waste mixed with known amount of water (20ml) and filtered. Then the polymer films were immersed in the filtrate for known intervals of time (1 week, 2 week, 3 week) at room temperature (37°C). For each duration the films from the solution were taken out washed with ethanol and dried under vacuum (50°C). The biodegradable films were evaluated for their structure and thermal stability.

## Antimicrobial Activity

Antimicrobial activities of the prepared films were evaluated by measuring the zone of inhibition using disk diffusion method [29]. Petri dish (9cm in diameter) containing agar medium and nutrient broth were prepared. Gram positive bacteria (*Bacillus subtilis*) and gram negative bacteria (*E.coli*) were inoculated in the medium. Circular films of dia 5mm were from the casted films were placed on the inoculum inside the petridish. The petri dishes were stored at 37°C over night in an incubator for bacterial growth. Then the zone of inhibition was analyzed.

## III. RESULTS AND DISCUSSION

Photos of typical solution casted films of PW and PS blends are shown in Figure 1. The thickness of individual film samples determined as a random average of five measurements was 0.04 mm.

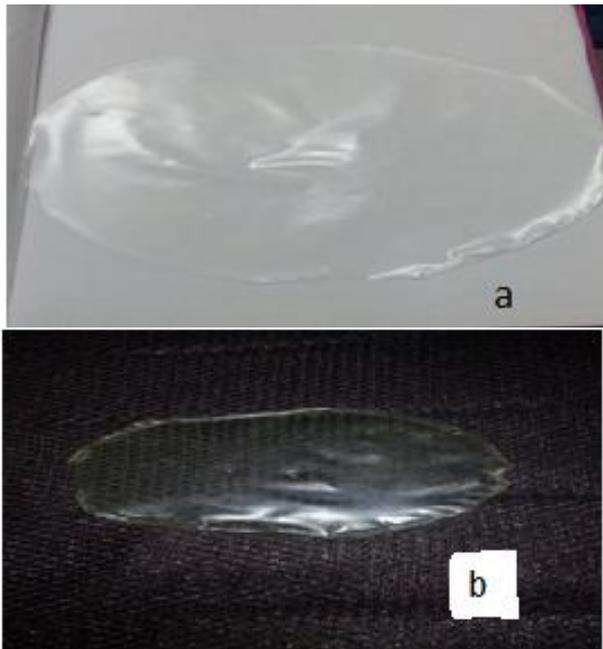


Fig. 1. Composite films of a) PW and b) PS

### A. Tensile Strength and % Elongation

Breaking strengths and % elongations of casted films from PVA, PVA-WPI (PW), PVA- SPI(PS), glutaraldehyde crosslinked PVA-WPI (PWG) and PVA-SPI(PSG), UV irradiated PW (PWU) and PS(PSU) films are furnished in Fig. 2 ( (a)& (b)). These values are within the range reported in literature[7] for packaging

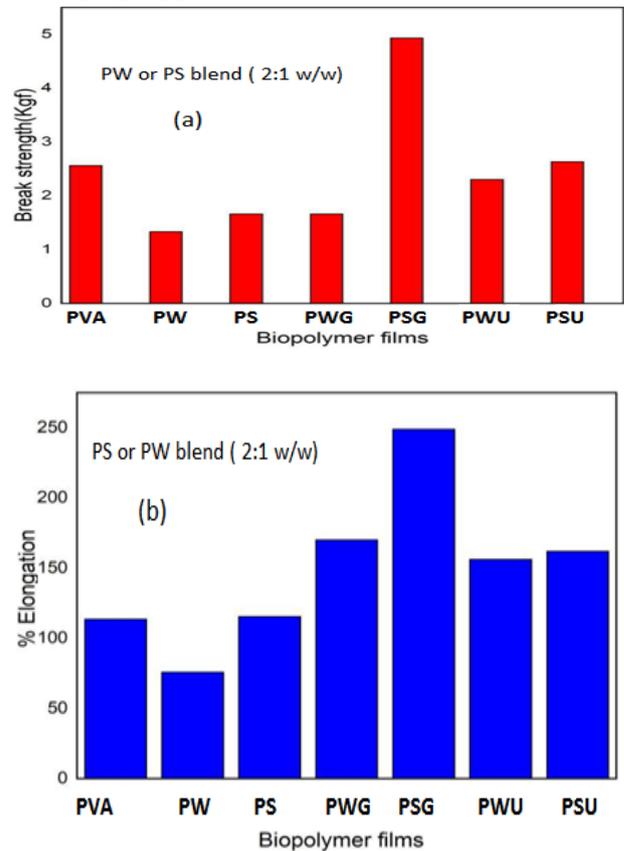
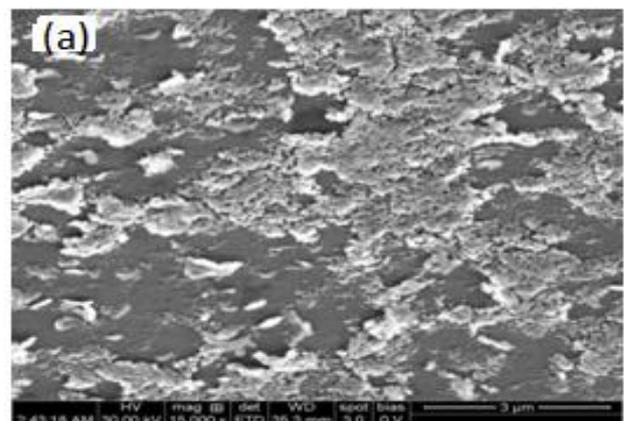


Fig.2. Break strengths(a) and % Elongations(b) of PS, PVA,PW,PWG,PSG,PWU and PSU films

films. Glutaraldehyde crosslinked PS (PSG) appeared to have the highest breaking strength and % elongation among the prepared films.

### B. SEM Micrographs

SEM images of the casted films of PVA, PW, PS and PSG films are shown in Fig. 3. The films were nearly homogeneous in surface features. The white thread like structure seen in PW film (Fig. 3) is due to WPI in the PW blend. The crystal like structure in the SEM micrograph of PSG film may be due to glutaraldehyde crosslinking and it also seems to be more porous compared to uncross linked PS films.



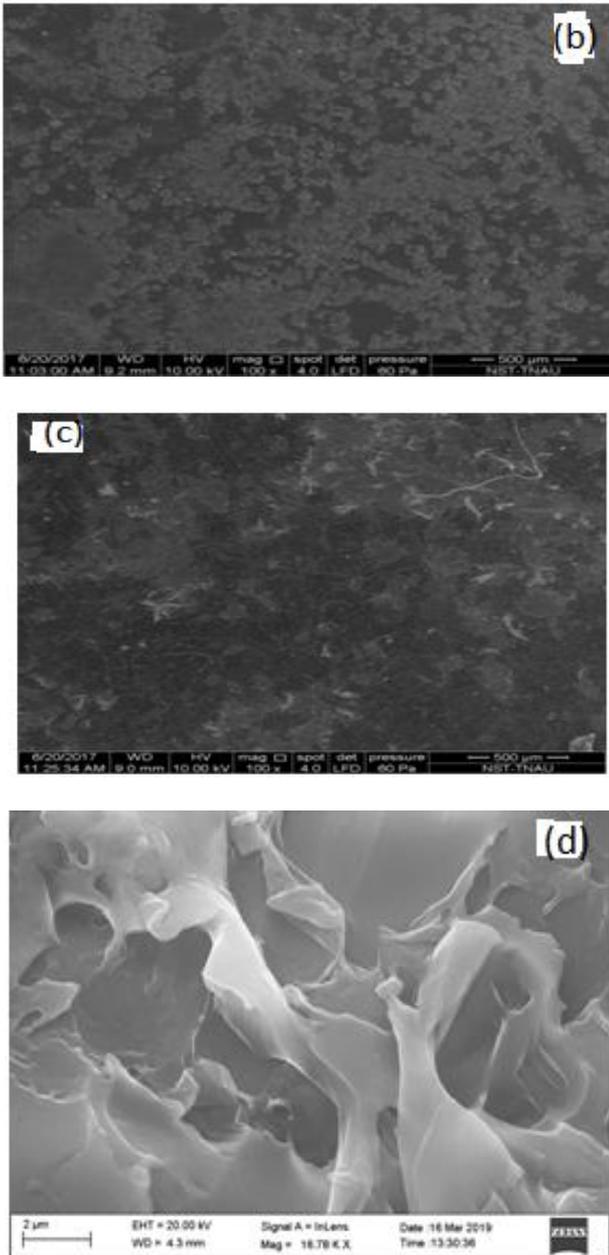


Fig. 3. SEM photos of PVA(a), PS(b), PW(c) and PSG (d) films

C Analysis of Thermograms

TG/DTG

The TGA/DTG and DTA thermograms of i) WPI, SPI and PVA, and those of PW and PS films with and without glutaraldehyde crosslinking are shown in Figure 4. In all the TG/DTG traces(Fig. 4) the weight loss upto 50-125°C were attributed to the removal of traces of free and bound moisture and other volatile impurities if any. Apart from this, PVA showed additional two step gradual weight losses upto 550°C with residual mass of 55% attributed to water elimination and back bone degradation[30]. On set degradation occurred at 185.5°C with a major weight loss at 289 °C . The TGA thermogram of SPI showed two step degradation ( at 200 and 300 °C) after moisture loss. The onset degradation and major weight loss had occurred around 184 and 320 °C respectively .

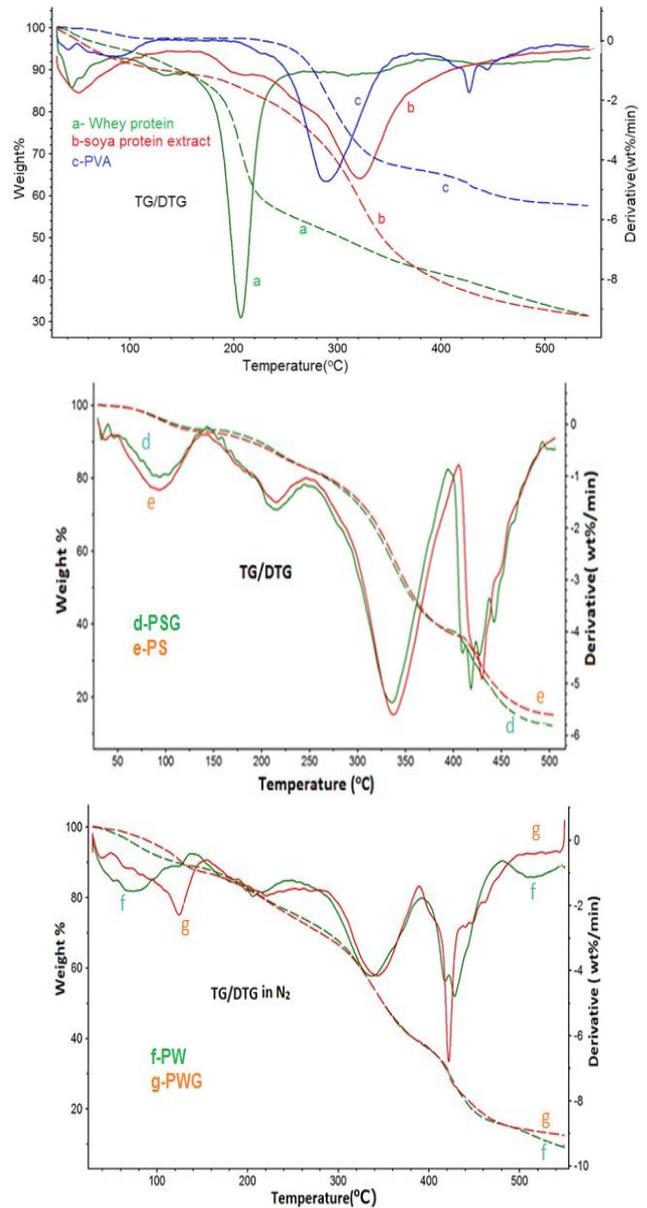


Fig.4. TG/DTG traces (in N<sub>2</sub>) of the polymer films a)WPI, b) SPI, c) PVA, d) PSG, e) PS, f) PW and g) PWG

The onset degradation is attributed to the cleavage of peptide bonds of amino acids. The second and third step degradations in the temperature range 220-320°C were more likely attributed to the breaking of backbone bonds, disulphide linkage, C-O bonds etc leading to the formation of CO, CO<sub>2</sub>,NH<sub>3</sub>,H<sub>2</sub>S etc . The TGA revealed a percent residue of 32.7% at 500 °C.This may be attributed to the formation of stable products through elimination, cyclisation etc reactions [11,25,30, 31,32]. The onset degradation temperatures for these polymers indicated that their thermal stabilities decreased in the order PVA>SPI>WPI and these temperatures were greater than 150°C (Fig. 4) . Hence these polymers are sufficiently thermally stable for packaging uses with other thermally stable polymers as blend . The weight loss around 130° C in WPI protein may be attributed to the loss of bound water and other low molecular weight compounds in the extracted whey protein.

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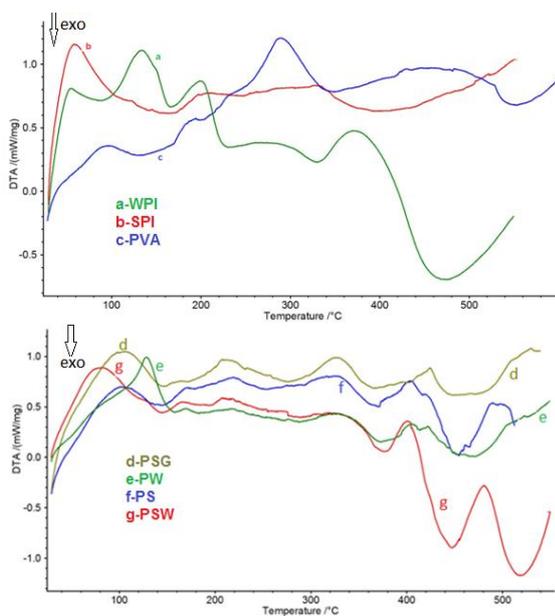
The weight losses observed around 200, 300 and 400<sup>0</sup> C were attributed to the glycerol loss and protein degradation via a multi step mechanism involving peptide bond scission [33-34]. In WPI The percentage residue observed at 500 °C was 34.10%. These may be attributed due the formation of stable products through elimination, cyclisation etc reactions.

The TGA thermogram of PS blend (Figure 4) showed multi step degradation. The weight loss around 180-220°C was due to the loss of citric acid/glycerol plasticizer. The major weight loss occurred at 340 °C . The TGA revealed a percent residue of 12.29% at 500 °C.

In the TGA thermogram of PSG (Fig. 4) the initial weight loss upto 120°C was attributed to a moisture and other volatiles. It showed multi step degradation. Degradation at 155-200°C was attributed to the loss of citric acid/ glycerol plasticizer. The major weight loss occurred at 340 °C due to polymer back bone degradation [30,32,34]. The TGA revealed a percent residue of 15.23% at 500 °C.

## DTA

The DTA thermograms of PVA, SPI and WPI, and PS and PW without and with glutaraldehyde crosslinking are



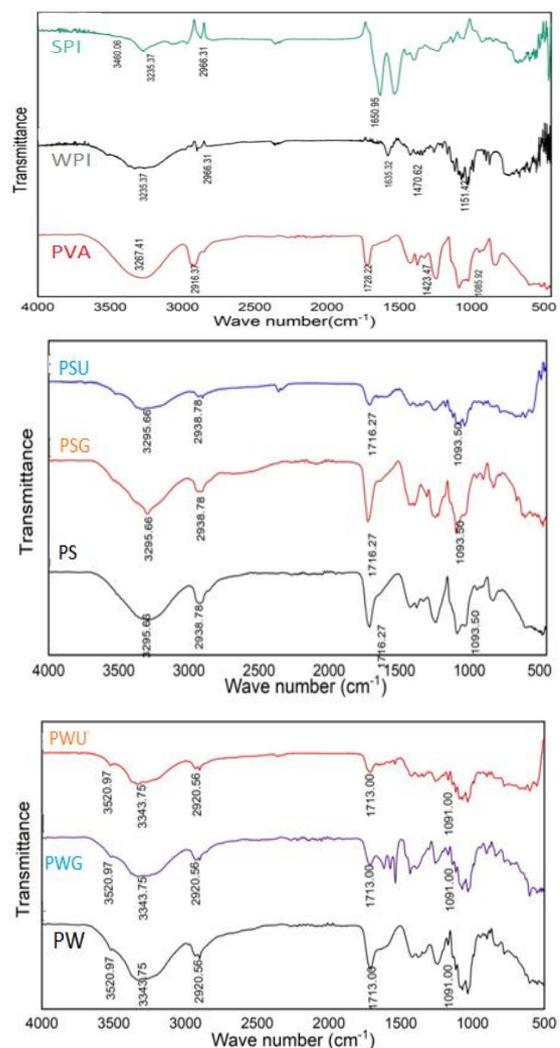
**Fig. 5. DTA thermograms (in N<sub>2</sub>) of WPI(a), SPI(b), PVA(c), PSG(d), PW(e), PS(f) and PSW(g)**

furnished in Figure5 (a-g). The initial broad endotherm upto 120<sup>0</sup>C in DTA of SPI ( Fig. 5 (b)) is due to the loss of moisture (10-15%), volatile matters and denaturation of protein. The endotherms around 200 and 340°C were attributed the plasticizer loss, peptide bond cleavage and breaking of other covalent bonds of backbone and pendant groups followed by formation of stable products through elimination, cyclisation etc reactions[11,25,30,35]. Similarly the endotherms around 60 and 125°C in the DTA of WPI (Fig. 5 (a)) may be attributed to the loss (10-15%) of free and bound moisture and protein denaturation respectively . The endotherms around 100, 200 and 300°C for PVA were attributed to loss of moisture, loss of water via elimination reaction with loss of plastisizer and backbone degradation involving cyclisation etc reactions.

The initial endotherms in the DTA of polymer blend films were attributed to moisture and plasticizer loss( glycerol) and protein SPI and WPI denaturation . The multiple pyrolytic endotherms beyond 185°C for the polymer blend films were attributed to the break down of the backbone covalent bonds of the constituent polymers, crosslinks etc, elimination reactions etc

## D. FT-IR Spectra

The FT-IR spectra of PVA, SPI, WPI and their blends PS, PW, PSG, PWG, PSU, and PWU are shown in Figure 6. The ATR-FTIR spectra of SPI and WPI showed absorption bands at 1650 (C=O stretching amide I), 1520 (NH bending -amide II) and at 1446 CH (deformation) cm<sup>-1</sup>. The absorption bands at 1150-1100, 1470 and 1230 cm<sup>-1</sup> were attributed to C-O and C-N bond stretchings and N-H bending vibrations



**Fig. 6. FT-IR Spectra of PVA, WPI, SPI, PW, PS, PSG, PWG, PSU and PWU films**

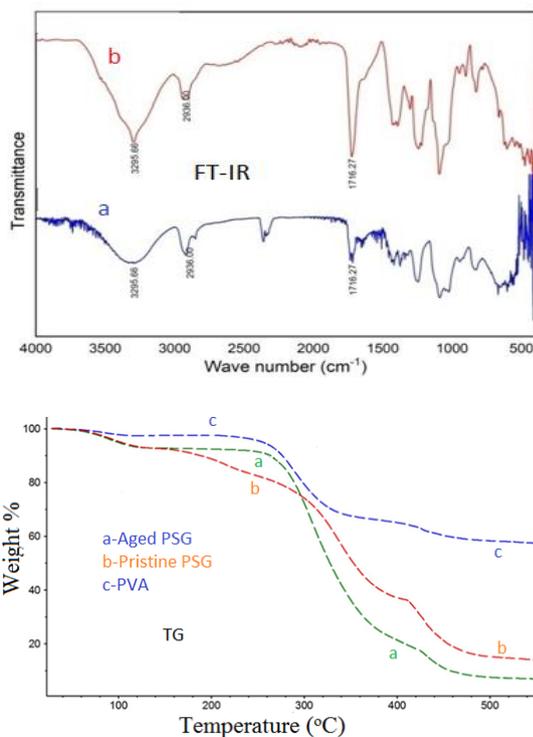
respectively. The broadabsorption band around 3271cm<sup>-1</sup> was attributedto the O-H and N-H stretchings of -OH and -NH<sub>2</sub> groups. Thecharacteristic CH stretching of the >CH<sub>2</sub> and -CH<sub>3</sub> groupsof saturated structures was observed around 2926 cm<sup>-1</sup>[14,25,36].

All these absorption peaks were also observed in the blends of SPI and WPI with PVA. The band around 1710-1730  $\text{cm}^{-1}$  in PVA and its blend with WPI and SPI were due to the unhydrolysed acetate group present in PVA.

**E. Biodegradability Study**

The biodegradability of the polymer films were analyzed using the IR spectra (Fig. 7) and TG traces ( Fig 7) of a typical polymer blend film namely PSG before and after three weeks biodegradation under soil .

Comparison of peak height ratios ( $h_{3295.66 \text{ cm}^{-1}} / h_{2936 \text{ cm}^{-1}}$  ( $=2.714 : 1.537$ ) of the absorption bands at 3295.66 and 2936  $\text{cm}^{-1}$  and that ( $h_{2936 \text{ cm}^{-1}}/h_{1716.27 \text{ cm}^{-1}}$ ) ( $=0.304: 0.731$ ) of the absorption peaks at 2936 and 1716.27 $\text{cm}^{-1}$  Before and after biodegradation (Figure 7) revealed that these ratio are quite different indicating that the blend film was biodegradable. The absorption peak at 3296 $\text{cm}^{-1}$  was broad in the blend sample subjected to



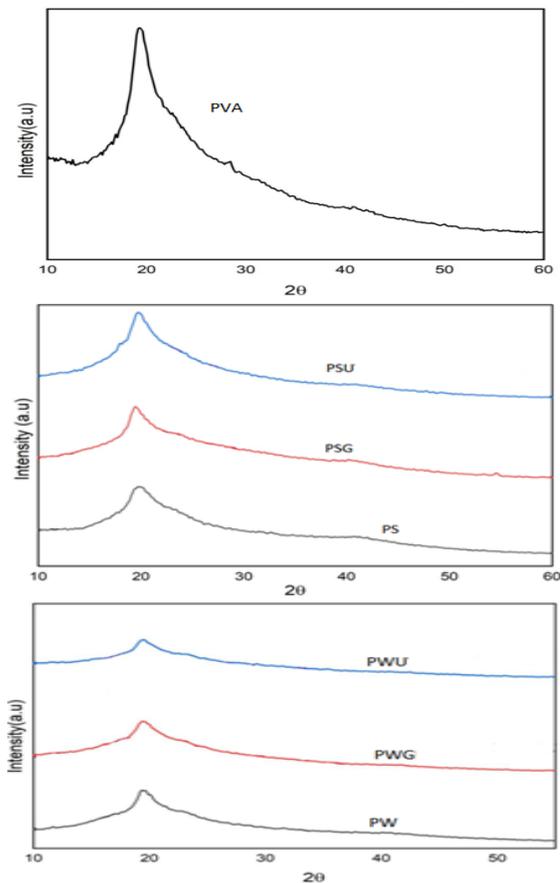
**Fig. 7 FT-IR Spectra and TG traces of PSG after (a) and before (b) biodegradation**

biodegradation and this may be due to the formation of carboxyl, amino groups etc. New absorption peaks were also observed around 1500-1000  $\text{cm}^{-1}$  [37].

Comparison of the TG traces for aged and pristine PSG ( having 66 wt % PVA) indicated enhanced thermal degradation of the former with 7.2 % residue at 500°C where the pristine (unaged) PSG and pure PVA sample showed 16 and 60 % residues respectively. The TG traces were significantly different and implied that PVA also biodegraded along with SPI. If PVA component is not biodegrading TG trace of aged PSG should have registered a % residue  $\gg 7.2\%$  at 500°C. The lower weight loss at 200-300°C in aged PSG is due to the loss of plasticizer during aging.

**F. X - Ray Diffraction**

The XRD patterns of pure PVA, PW ( PVA- WPI), PS(PVA- SPI) blend, glutaraldehyde and UV crosslinked PW (PWG& PWU) and PS (PSG & PSU) blends are displayed in the Figure 8. All of them showed single broad diffraction peaks around 19.80° to 19.99° in their pure form, blends, cross linked blends. This indicated that the morphology was not affected significantly by blending and cross linking[11,27,38 ]. Comparison of these diffraction peaks indicated that PVA is comparatively less amorphous and hence more crystalline than the blend samples.



**Fig. 8. X- Ray Diffractograms of PVA, PW, PWG, PWU, PS, PSG and PSU**

**G. WVP and Moisture Pick-up by Polymer Films**

The measured water vapour permeability of the polymer films are furnished in Table 1. Analysis of the permeability data indicated that the films permits the moisture to limited extent and these values are within the acceptable limit [7] for food packaging applications.

**Moisture Pickup**

The moisture pick-up by PS, PSU, PSG, PVA, PW, PWB and PWG films for the temperatures 35, 55 and 65oC are shown in Figure 9. In all the films water pickup

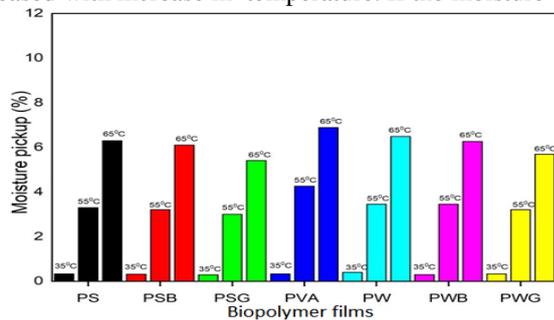
**Table 1 Water vapor permeability of polymer films at different temperatures**

Polymer film	Water vapor permeability ( $\text{g}/\text{cm}^2\text{h}$ ) $\times 10^5$		
	33°C (RH-75.1)	36°C (RH-4.8)	39°C (RH-74.7)
PVA	6.77	7.29	7.81
PW	5.208	6.25	5.72

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PS	5.208	5.72	5.72
PGW	5.208	5.72	5.72
PGS	5.208	5.208	5.72
PBW	5.72	6.25	6.77
PBS	5.72	6.25	6.25

increased with increase in temperature. If the moisture

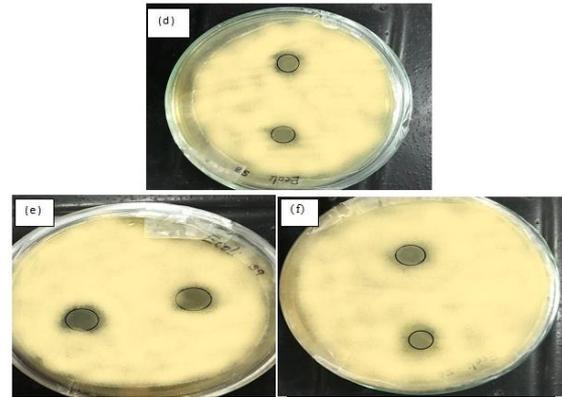
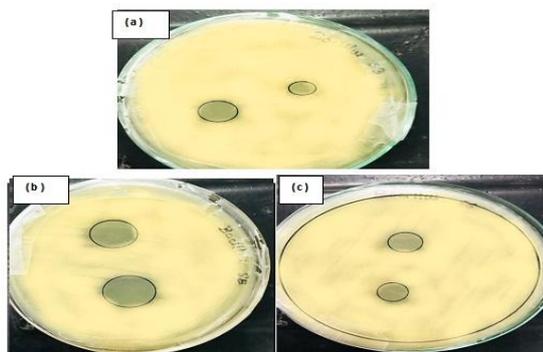


**Fig. 9. Temperature dependent moisture pickup of the polymer films**

pickup occurs purely by adsorption one may anticipate a decrease in moisture uptake with temperature. But contrary to this expectation an increase in moisture pickup (0.2-6%) for the temperature range (35–65°C) was observed with increase in temperature for the humidity range (74-75%). This may be attributed to increase in solubility of water in the film with increased temperature perhaps due to improved water - polymer interaction.

## H. Antimicrobial Test by Disc Diffusion

It was reported [39] that biopolymers could promote antibacterial properties. WPI had been found to contain immunoglobulins and glycomacropptides, constituents that bind toxins and help prevent bacterial infection[40]. Since free glutaraldehyde is toxic, only the films of PWG and PSG were tested for their antibacterial activity by disc diffusion method for gram positive (*Bacillus subtilis*) and gram negative bacteria (*E.coli*) [41,42]. Comparison of the zones of inhibition in Figure 10 indicated that the antimicrobial property of PSG was comparatively higher than that of PS and the antimicrobial properties of PWG and PW were nearly the same.



**Fig.10. Antimicrobial activity of gram positive (*E.coli*-a,b,c) and gram negative (*Bacillus subtilis*-d,e,f) bacteria on PS (a, d), PSG (b,e) and PWG (c,f) films**

## IV. CONCLUSION

Composite polymer films from PVA, WPI/ or SPI using plasticizers like glycerol, etc with and without cross linking were fabricated successfully and evaluated. Crosslinking was done using glutaraldehyde, and UV light with benzoyl peroxide as photo initiator. The tensile strength and % elongation of the films measured as breaking force on non standard dimension of the films were in the range 1.6 -4.7 kgf and 75 - 400 % respectively. SEM images indicated that glutaraldehyde cross linked film appears to be more porous than the uncross linked ones. The films displayed increased moisture pick-up with increased temperature due to the increased solubility of moisture with temperature. The structures and biodegradation of the polymer films analyzed by FT-IR and TGA studies implied that the films are biodegradable. TGA indicated that the polymer films were stable up to 180°C in nitrogen atmosphere. XRD studies indicated that the polymer film seems to have roughly the same morphological features with predominant amorphous features. Glutaraldehyde cross linked polymer films seems to have improved antimicrobial properties compared to uncross linked polymer. However the antimicrobial property can be improved by adding plant derived antimicrobial materials. Water vapour permeability of the fabricated films are within the reported range of value 5.208 -7.81 x 10<sup>-5</sup> g/cm<sup>2</sup>h . The above discussed result indicated that the films can be exploited as promising packaging material for food and other materials.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

## ACKNOWLEDGMENT

The authors are thankful to the management of Bannari Amman Institute of technology, Sathyamangalam, Tamil Nadu for supporting this research work and to DST-FIST, DST, GoI for providing TGA-DTA test facility.

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# Preparation and Characterization of Biodegradable Composite Films from Poly (vinyl alcohol) and Natural Proteins for Food and other Packaging Applications

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