Ecofriendly Poly(vinyl alcohol) and Coconut Shell Powder Composite Films: Physico-Mechanical, Thermal Properties, and Swelling Studies

B. Ramaraj, P. Poomalai

Central Institute of Plastics Engineering and Technology, Mysore 570 016, India

ABSTRACT: Poly(vinyl alcohol) (PVA) composites with 10, 20, 33, and 50 wt % of coconut shell (CCS) powder were prepared by aqueous mixing. The solution was casted as films and tested for physicomechanical properties such as tensile, tear, burst strengths, density, moisture content, moisture vapor transmission rate, moisture analysis; solubility resistance in water, 5% acetic acid, 50% ethanol, sunflower oil; swelling characteristics in 50% ethanol, sunflower oil; and thermal characteristics by differential scanning calorimetry. The PVA/CCS powder composite films show enhancement in elastic modulus, degradability, solubility resistance in water, 5% acetic acid, 50% ethanol, and moisture resistance. However, the introduction of CCS powder varies the tensile strength and affects percentage of elongation, tear and burst strengths, moisture content, density, and swelling capacity. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3862–3867, 2006

Key words: poly(vinyl alcohol); films; coconut shell powder; mechanical properties; swelling studies

INTRODUCTION

Thermoplastic composites based on synthetic polymers with various amounts of organic fillers from renewable resources are considered as low environmental impact materials.[1] The need for economically feasible degradable products, which do not adversely affect the environment upon disposal, has intensified the attention as an alternative source of raw materials. The biodegradable polymeric materials availability and its production costs are limiting factors for many application requirements. More over such materials have to compete with the low cost commodity plastics like polyethylene (PE) and poly(vinyl chloride) (PVC). So, the research interest has moved toward the use of inexpensive polymeric materials such as starch and cellulosic materials along with the synthetic polymers. The resulting materials are not only cost effective, but also environment friendly in nature.

Successful blending of synthetic materials with starch or ligno-cellosic materials depends on matching the structural properties and interaction characteristics of the polymeric components. Breaking the inter- and intrachain hydrogen bonds of natural polymers to establish a new interaction between the natural polymers and the added synthetic polymer is one possible approach. Indeed the hydrophilic character of the fillers makes difficult their blending with hydrophobic polymers such as PE and polypropylene (PP) unless compatibility agents are added.[2,3] However, this approach is, often, too expensive and manufacturing process become rather complicated. In this respect, poly(vinyl alcohol) (PVA) can be selected as the synthetic polymer because hydroxyl and carboxyl groups are suitable for hydrogen bonding, thus resulting in a good compatibility with natural hetero-functional fillers. In addition, PVA is water soluble, thus allowing for the film production by solution casting. In the past, PVA and starch films were prepared by casting and melt extrusion,[4–7] and the resulting products were suitable for agriculture mulch films and water soluble laundry bags.[8] Further, PVA and cellulosic materials presented good miscibility in casting films probably because of their mutual compatibility to form strong hydrogen bonds.[9] Intermolecular interactions were also observed in PVA and chitin composites[10] as well as in chitosan or pectin composites.[11]

As a part of our continuing research aimed at the preparation and evaluation of hydrophilic/biodegradable polymers,[12–16] this study reports the effect of coconut shell (CCS) powder on PVA film properties such as tensile, burst, tear strength, moisture content, MVTR, moisture analysis; solubility resistance in water, 5% acetic acid, 50% ethanol, sunflower oil; and swelling characteristics in 50% ethanol, sunflower oil. These studies were carried out to assess PVA/CCS composite films suitability as packaging films. The design of a biodegradable composite with predeter-

TABLE I
Composition and Tensile Properties of PVA/CCS Powder Composite Films

S. no	Sample code	PVA (g)	CCS powder (g)	Tensile strength (N/mm^2)	Percentage of elongation	Elastic modulus (N/mm$^{2)}$
1	A	30	–	13.62	397.80	003.68
2	B	27	3	15.07	229.90	018.07
3	C	24	6	11.99	123.70	028.27
4	D	20	10	14.93	058.22	068.43
5	E	15	15	12.12	005.66	431.10

mined life time is essential for many applications. Soil burial test is a traditional way to test samples for biodegradation because of its similarity to actual conditions of waste disposal. Generally, the samples are buried in soil at the end of the testing periods and changes in properties like weight, mechanical strength, shape etc, were studied. PE is a widely used material for packaging, when it is tested by soil burial test, it is believed to be bioresistant for many years.[17] Whereas PE-starch composites show extensive removal of starch within 40 days.[17] Further, the biodegradation rate of starch was 4–5 days, starch-g-polyhexylene adipate was 9.4% in 30 days,[18] poly(hexylene adiapate) was 5.4% in 30 days,[18] polybutylene-*co*-hexylene (2:1) succinate (PBH (2:1)S) was 6.46%, 58 days,[19] poly(butylene succinate) (PBS) 1.76% in 89 days,[19] polyester (poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), polylactic acid, PBS, and cellulosic composites show weight loss of 30% for 90 days in soil burial test.[20] The starch (10%) filled cellulose acetate blends show a weight loss of 8.91% in 90 days.[21] Fifty percent wood flour-filled polycaprolactone (PCL), PBS, and polybutylene succinate-butylenecarbonate (PBSC) composites show 40% weight loss in 50 days.[22]

CCS powder is made from the most versatile part of the CCS, which is organic in nature. The shell is similar to hard wood in chemical composition though lignin content is higher and cellulose content is lower. This filler is successfully used in various products such as mastic abrasives, cast resins, and bitumins, where it acts as absorbent as well as enhances the surface finish. The presence of ligno-cellulosic fillers in the composites bound to degrade directly in the field to provide added value effect of releasing the ligno-cellulosic in the soil, which will convert to humic substances with positive agronomic effects.

EXPERIMENTAL

Materials

The polymer used in this study was polyvinyl alcohol (weight average molecular weight of 125,000, degree of hydrolysis 80–90%, ash 0.75%) supplied by S.D. Fine Chem. Ltd, India. The polymer was kept in a sealed container to prevent moisture absorption prior to use.

Coconut shell powder

The coconut shell (CCS) of fully matured nuts were first cleaned by removing the adhering pithy matter and broken down into small pieces. These small pieces were dried in sunlight for 8 h. to remove the surface moisture and then subjected to repeated grinding in grinding mill to make fine powder. The resulting powder was sieved and the fraction passing through a 70 mesh (0.212 mm) was collected. This powder with bulk density of 0.50 g/cc and 6% moisture content was used in the preparation of composites.

Alkalisation of CCS powder

The CCS powder was chemically treated to remove the waxy substances and impurities covering the external surface of the powder. This gives roughness to the external surface. Sodium hydroxide (NaOH) is the most commonly used chemical for bleaching or cleaning the surface of natural fillers. In this work, the CCS powder was put into 5 wt % aqueous solution of sodium hydroxide for 24 h with intermittent stirring, rinsed, and washed with water until water becomes neutral. After filtration, the powder was dried for further use. The alkali treatment may change the native cellulose by a process known as alkalization.

$$MVTR = (W \times 24)/t \times a \quad (1)$$

Procedure for solution casting

The solid content of PVA and CCS powder composite was optimized at 7.5% solution in water and the system was made into a homogeneous solution by constant stirring at a temperature of around 80–90°C for 30 min. Later, the solution was poured into a glass plate mold lined with PE sheet. After drying the solution at room temperature, the films were removed from the mold and tested. The PVA/CCS powder

composite films were prepared as per the composition given in Table I.

Testing methods

The tensile tests were carried out on cast films as per ASTM D 882 in universal testing machine (Lloyds UK, Model LR 100K) with a cross head speed of 50 mm/min. Tear strength measurements were made as per ASTM D 1992 in ATSFAAR Elmendorf Tear Tester (ATS 100, Italy) using films of size 63×76 mm^2. Burst strength measurements were made as per ASTM D774–67 in CIPET burst strength tester (BST: A1 01) using films of size (6×6 cm^2). Differential scanning calorimetry (DSC) measurements were made using TA instruments (2010 DSC) from 40 to 250°C in nitrogen atmosphere at the heating rate of 10°C/min. The DSC instrument was calibrated using indium metal. Moisture content was measured for equilibrated samples in laboratory conditions. Density of the modified films was measured using Mettler PM200 electronic weighing balance as per ASTM D 792. The moisture analysis tests were carried out in the humidity chamber made up of acrylic box ($60 \times 30 \times 20$ cm^3) containing saturated solution of sodium chloride. The solubility tests and swelling analysis were carried out on dried film samples. The moisture vapor transmission rate (MVTR) measurements were made as per the procedure outlined below.

The film was covered on a petridish containing known quantity of highly hygroscopic anhydrous calcium chloride and sealed with wax. The whole assembly was placed in humidity chamber maintained at 90% RH at 32°C and the MVTR was measured after 24 h using the formula

$$\text{Cell-OH} + \text{NaOH} \rightarrow \text{Cell-O}^-\text{Na}^+$$
$$+ \text{H}_2\text{O} + \text{Surface impurities} \quad (2)$$
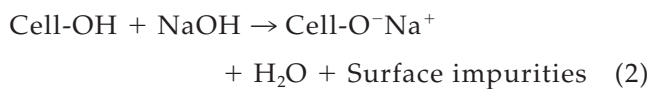
where W is weight gain, t is thickness, and a is area.
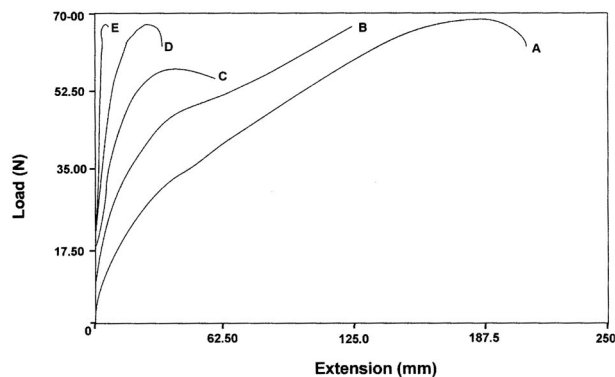

Figure 1 Stress–strain curves of PVA/CCS powder films.
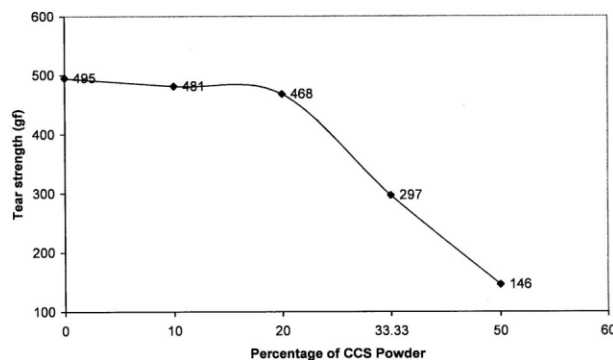

Figure 2 Tear strength of PVA/CCS powder composite films.

Biodegradability of different PVA/CCS composite films was evaluated by exposing the samples to compost soil containing manure and measuring the weight loss. Soil was kept moistened at a 30% content with deionized water.[17,23] The soil burial test period was 90 days, after the soil test the samples were washed with water and dried to their constant weight in oven at 40°C.

RESULTS AND DISCUSSION

Mechanical and thermal properties

Mechanical properties were measured for the PVA blends containing 10, 20, 33, and 50 wt % of CCS powder. Tensile strength, elongation, and elastic modulus results of the composites are given in Table I. From the table, it is clear that the modulus of elasticity increases significantly from 3.67 N/mm^2 (sample A) to 431.10 N/mm^2 with increase in CCS powder content. The percentage of elongation of composites decreased gradually. However, the tensile strength remains almost in the same range. This may be due to the strong interaction of PVA with alkali treated CCS powder. The stress–strain curves of the composites at different CCS powder levels are shown in Figure 1, which shows that there is an increase in modulus and decrease in elongation with filler loading. From Figure 2, it is observed that the internal tear resistance of 495 gf in plain PVA decreased to 146 gf in PVA with 50% CCS content. The decrease in tear resistance for the films with more CCS content may be due to particulate nature of CCS powder. The effect of CCS content on the burst strength of PVA/CCS films are shown in Figure 3, where burst strength of the films decreased from 71 psi (sample A) to 19 psi (sample E) with filler loading, even though there is a little increase initially.

DSC thermograms of PVA and PVA/CCS powder composites are shown in Figure 4. From the figure, it is clear that PVA (sample-A) shows a broad Tg at 101.58°C and Tm at 189.78°C. PVA/CCS composite
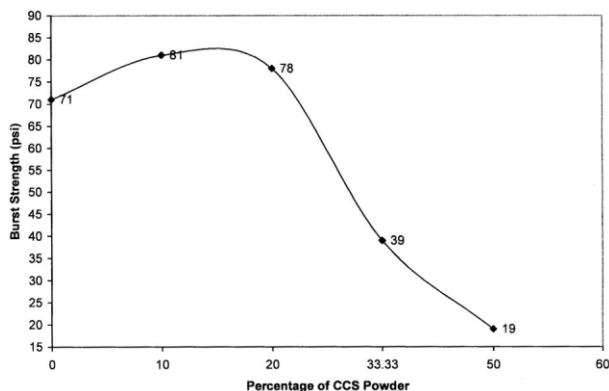
Figure 3 Burst strength of PVA/CCS powder composite films.

TABLE II
Effect of CCS Powder on Moisture, MVTR, and Density of PVA/CCS Powder Composite Films

S. no.	Sample code	Moisture content (%)	MVTR (g/m^2) at 90% RH	Density (g/cc)
1	A	12.07	190.14	1.263
2	B	11.44	145.94	1.266
3	C	11.23	157.54	1.283
4	D	10.35	286.97	1.296
5	E	9.38	679.90	1.145

because CCS being a powder, not dissolved in aqueous medium, can have only surface level interaction with PVA.

with 10% CCS content (Sample-B) shows Tg and Tm at 124.49 and 188.72°C, respectively. PVA is a linear aliphatic hydroxyl polymer containing secondary hydroxyl groups in every alternate carbon, and the concentration of hydroxyl groups has significant impact on Tg and Tm. The incorporation of CCS (10%) powder (Sample B) increases the Tg peak maximum from 101.58 to 124.49°C and Tm changed from 189.78 to 188.92°C. As a general rule, any structural features that reduce segmental mobility or free volume will increase Tg. Here, the incorporation of CCS powder into PVA matrix reduces segmental mobility of hydroxyl groups further because of strong interaction between treated CCS powders, which increases the Tg peak maximum. Because both PVA and CCS powder are polar materials, they have strong interaction. However, when the CCS concentration is increased to 50% in the PVA matrix, the Tg of the PVA/CCS (Sample E) film reduced to 98.67°C. As the concentration of CCS material increased, the interaction of PVA and CCS does not increase proportionately, which may be
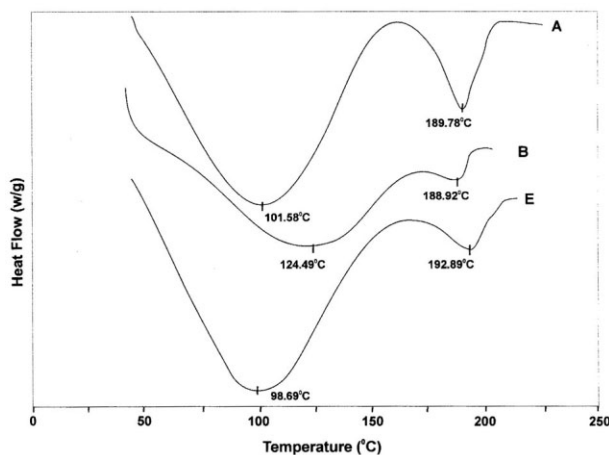
Moisture content and MVTR

The moisture content of PVA and PVA/CCS powder composites are given in Table II, from the table, it is clear that there is decrease in the moisture content for plain PVA (12.07%) to PVA with 50 wt % CCS powder(9.38%), because PVA is more hydrophilic than that of CCS powder.

The results of MVTR performed on PVA/CCS films were reported in Table II. MVTR values increased from 190.14 g/m^2 in plain PVA to 679.90 g/m^2 at 90% RH at 32°C. Even though initially there is decrease in MVTR (sample B) but later it increased to 679.90 g/m^2. The sharp increase in MVTR (Sample E) may be due to increase in free volume of films with filler loading. Such films may find applications in packaging of intermediate moisture products.

Density of different PVA/CCS films are reported in Table II. From the table, it can be observed that the density value of PVA/CCS film shows little increase, but the sharp fall at 50% (sample E) filler loading may be attributed to the increase in free volume in the PVA matrix.

Solubility resistance, moisture, and swelling analysis

The specimens of PVA and PVA/CCS powder were tested for its resistance in water, 5% acetic acid, 50%

Figure 4 DSC thermograms of PVA/CCS powder composite films.

TABLE III
Effect of CCS Powder on Solubility of PVA/CCS Powder Composite Films

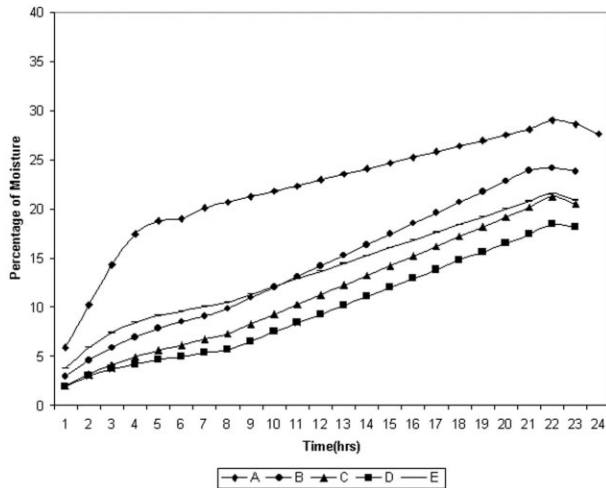| S. no.	Sample code	Dissolution time (min)			
		Water	5% acetic acid	50% ethanol	Sunflower oil
1	A	10	30	Not soluble	Not soluble
2	B	30	60	Not soluble	Not soluble
3	C	75	90	Not soluble	Not soluble
4	D	90	180	Not soluble	Not soluble
5	E	90	195	Not soluble	Not soluble

Figure 5 Moisture analysis of PVA/CCS powder composite films.

ethanol, and sunflower oil as model food stimulants. The films lost their strength in water, 5% acetic acid, but solubility resistance found increased with increase in CCS content and retained its strength in 50% ethanol and sunflower oil (Table III). Both PVA and CCS powder being a hydrophilic in nature, sensitivity of these materials toward moisture was analyzed in the humidity chamber at 90% RH (Fig. 5). From the figure, it is observed that the moisture absorption decreased with the addition of CCS powder. This may be due to higher hydrophilicity of PVA than that of CCS powder. However, the sample E with higher filler loading (50%) absorbs more moisture than the samples with lower filler loading, this may be due to more free volume in the structure.

The swelling analysis of PVA/CCS composites in 50% ethanol and sunflower oil are shown in Figures 6
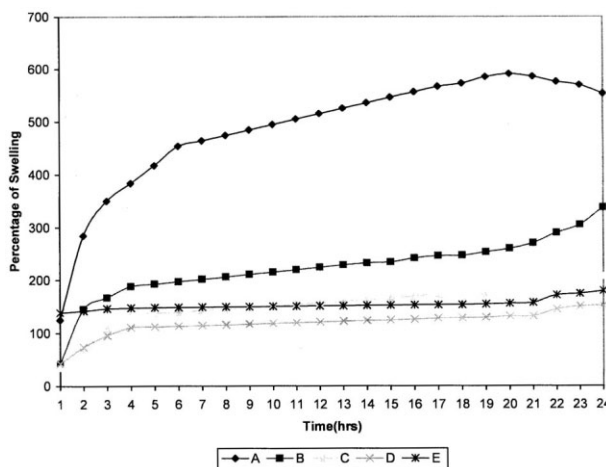

Figure 6 Swelling analysis of PVA/CCS powder films in 50% ethanol.
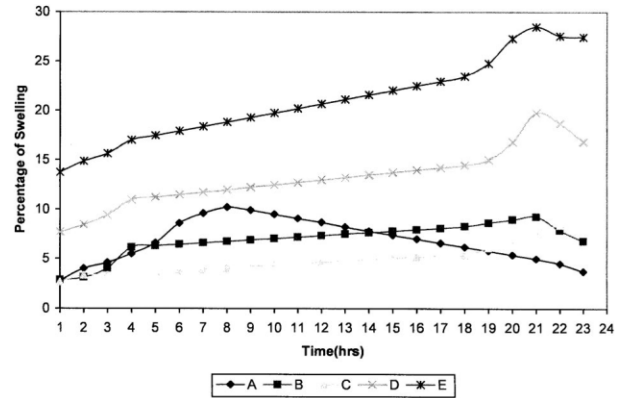

Figure 7 Swelling analysis of PVA/CCS powder films in sunflower oil.

and 7, respectively. As can be seen from the figure, PVA shows more swelling in 50% ethanol, which gradually decreased with filler loading. However, for the sample E with higher filler loading (50%) swells more than the samples with lower filler loading, this may be due to more free volume in the structure. Whereas in sunflower oil, the film with higher filler loading shows higher swelling than that of plain PVA (sample A)

Biodegradability of PVA/CCS powder composites

The soil burial[24] provides qualitative indications of biodegradation. This method will be more effective, compared with enzymatic test, if the samples are buried in suitable climatic conditions and the various populations of microorganisms that are involved. Most of the studies[18–20,25] on the biodegradability have been based on the weight loss. In this investigation, the degradation of plastic was evaluated by measuring its weight loss, which refers to the erosion of molecules from the solid phase. From Figure 8, it is clear that there was about 48% weight loss in 50/50 PVA/CCS composite film in 90 days and which is better than the virgin PVA, PBS 1.76% in 89 days,[19] polyester (polyhydroxy buterate valerate, polylactic acid, PBS, and cellulosic composites 30% in 90 days,[20] and starch(10%) filled cellulose acetate blends 8.91% in 90 days.[21] This may be because higher filler loading means less polymer content, so, it is more easily degradable than virgin PVA. PVA is most readily biodegradable polymer. The initial biodegradation step involves the enzymatic oxidation of secondary alcohol groups in PVA to ketone groups, then hydrolysis of ketone groups results in chain cleavage.

CONCLUSIONS

PVA composite films were prepared with CCS powder at different compositions. These composite films
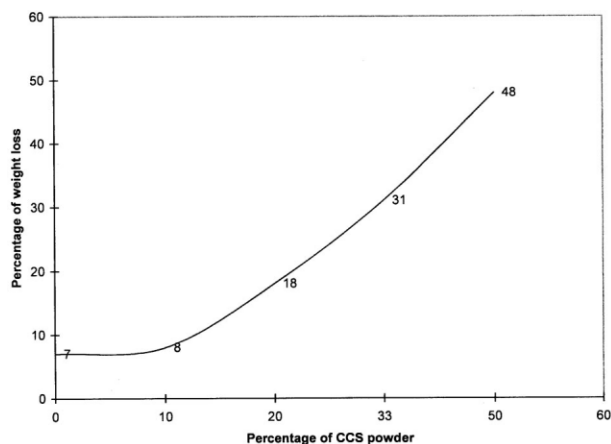
Figure 8 Effect of CCS filler loading on biodegradation weight loss of PVA/CCS composite films.

show enhanced elastic modulus, degradability, solubility resistance, and MVTR with the addition of CCS powder. However, the introduction of CCS powder varies the tensile strength and affects percentage of elongation, tear and burst strengths, moisture content, density, and swelling capacity considerably.

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