

Crosslinked Poly(vinyl alcohol) and Starch Composite Films: Study of Their Physicomechanical, Thermal, and Swelling Properties

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Received 14 June 2005; accepted 19 April 2006

DOI 10.1002/app.24612

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Crosslinked poly(vinyl alcohol) was blended with 10, 20, 40, and 50 wt % starch by a solution-casting process. The solution-cast films were dried, and then their physicomechanical properties including tensile strength, tensile elongation, tensile modulus, tear strength and density, and burst strength and density were tested. Thermal analysis was performed by differential scanning calorimetry. A moisture analysis of the PVA/starch films was performed and their moisture content determined. Also investigated were the films' resistance to solubility in

water, 5% acetic acid, 50% ethanol, and sunflower oil and their swelling characteristics in 50% ethanol and sunflower oil. The prepared PVA/starch blends showed significant improvement in tensile modulus and in resistance to solubility in water, 5% acetic acid, and 50% ethanol. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1127–1132, 2007

Key words: composites; mechanical properties; differential scanning calorimetry (DSC); films; poly(vinyl alcohol)

INTRODUCTION

With the growing concern about environmental pollution from nondegradable synthetic plastics like polyethylene and polypropylene, the accumulation of plastic waste needs immediate resolution. Biodegradable plastics have been intensively studied in recent years^{1–6} and have been used commercially in various products such as garbage bags, composting yard bags, and grocery bags and for agricultural needs. Generally synthetic thermoplastics are blended with starch^{1–7} or natural fibers^{8–12} to make them environmentally friendly and degradable. Poly(vinyl alcohol) is one of the few degradable synthetic polymers¹³ available today. PVA is a water-processable polymer. The excellent chemical resistance and physical properties of PVA have resulted in its broad industrial use. But a limiting factor is the cost of PVA, which has to compete with low-cost thermoplastic materials like polyethylene, polypropylene, and poly(vinyl chloride) in packaging applications. Hence, it is necessary to incorporate a low-cost, naturally occurring filler or polymer like starch. Starch is a polysaccharide produced by many plants as a storage polymer. It is composed of glucose monomers joined by 2-(1-4) linkages. The average granule

size varies from source to source; rice starch granules are roughly 3 μm in diameter, cornstarch has an average granule size of 10 μm , whereas potato starch granules are about 35 μm in diameter. The use of granular starch as a filler in plastics would be advantageous because (1) starch is an abundant, low-cost, and easily available renewable resource and (2) starch is biodegradable and is useful in applications in which recovery or recycling would be difficult.^{14–22}

Within the context of the ongoing research efforts aimed at the preparation and evaluation of hydrophilic/biodegradable polymers,^{23–28} this article reports a study that has modified PVA films by crosslinking with glutaraldehyde and blending with starch. Various physicomechanical and thermal properties of the modified films were characterized. The aim of crosslinking PVA was to improve the mechanical properties and water resistance of PVA films.

EXPERIMENTAL

Materials

The raw materials used in this study, poly(vinyl alcohol) (weight-average molecular weight of 125,000, degree of hydrolysis of 80%–90%, 0.75% ash) and starch (potato starch, 0.55% ash, extrapure) were supplied by M/S S. D. Fine Chem. Ltd. (Mumbai, India). These polymers were kept in a dry environment to prevent absorption of moisture prior to use. Glutaraldehyde (25%) was supplied by M/S Rolex Chemicals (Mumbai, India).

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TABLE I
Composition of Poly(vinyl alcohol) and Starch Composite Films

| Sample code | Poly(vinyl alcohol) (g) | Starch (g) | Glutaraldehyde (mL) |
|-------------|-------------------------|------------|---------------------|
| A | 20 | — | — |
| Ax | 20 | — | 4 |
| Bx | 18 | 2 | 4 |
| Cx | 16 | 4 | 4 |
| Dx | 12 | 8 | 4 |
| Ex | 10 | 10 | 4 |

Procedure for solution casting

A series of PVA/starch blends were processed into films by solution casting through varying the starch content from 10% to 50%. The PVA powder was dissolved in hot water at 80°C–90°C. Then 4 mL of 25% glutaraldehyde solution was added as a cross-linking agent for PVA, and the starch powder made into paste was mixed according to the composition given in Table I and stirred well for about 30 min with constant stirring. Later the solution was filtered through cotton and cast into a glass plate mold (20 × 12 cm in size) lined with a polyethylene sheet. The cast solution was evaporated at room temperature (25°C ± 3°C) for 48 h. After evaporation, the films were removed from the glass plate and used for further study.

Testing methods

The tensile tests were carried out on cast films according to ASTM D 882 in a Universal testing machine (Lloyds UK, model LR 100K) with a cross-head speed of 50 mm/min. Tear strength was measured according to ASTM D 1992 in a ATSFAR Elmendorf Tear Tester (ATS 100, Italy) using films 63 × 76 mm in size. Burst strength was measured according to ASTM D 774-67 in a CIPET burst strength tester (BST; A1 01) using films 6 × 6 cm in size. Differential scanning calorimetry (DSC) measurements were made using TA instruments (2010 DSC) from 40°C to 250°C in a nitrogen atmosphere at a heating rate of 10°C/min. Moisture content was measured for equilibrated samples in laboratory conditions. The density of the modified films was measured using a Mettler PM200 electronic weighing balance according to the ASTM D 792 displacement method. Moisture analysis was carried out with dried samples in a humidity chamber made up of an acrylic box (60 × 30 × 20 cm) containing a saturated solution of sodium chloride. Solubility testing and swelling analysis were carried out on dried film samples.

TABLE II
Tensile Properties of PVA/Starch Composite Films

| Sample code | Tensile strength (Kg/cm ²) | Elongation (%) | Elastic modulus (Kg/cm ²) |
|-------------|--|----------------|---------------------------------------|
| Ax | 136 | 500 | 42 |
| Bx | 133 | 207 | 46 |
| Cx | 112 | 182 | 52 |
| Dx | 96 | 51 | 2040 |
| Ex | 89 | 13 | 3150 |

RESULTS AND DISCUSSION

Mechanical and thermal properties

From Table II, which shows the tensile properties of the films made of starch filler and poly(vinyl alcohol) (PVA) matrix at different filler loadings, it is clear that the tensile strength of the films decreased from 136 (sample Ax) to 89 (sample Ex) kg/cm² and that the percentage of tensile elongation decreased from 500% (sample Ax) to just 13% (sample Ex), whereas the tensile modulus increased from 42 (sample Ax) to 3150 (sample Ex) kg/cm² when starch loading was increased from 10% to 50%. The addition of granular starch to PVA followed the general trend of the effects of filler on polymer properties. Tensile strength and elongation decreased as the amount of starch added increased, and tensile modulus increased because of the stiffening effect of the granules. The starch fillers increased the modulus, modified the shape, and induced a yield point in the stress–strain diagram (Fig. 1) of ductile polymers like PVA. The yielding phenomenon was really a

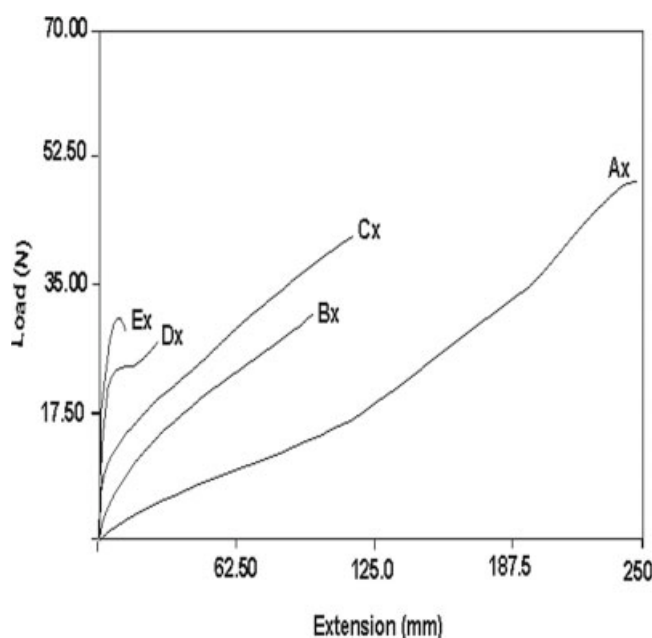


Figure 1 Stress–strain curves of PVA/starch composite films.

result of a crazing or a dewetting effect, in which the adhesion of the filler with the matrix phase was destroyed. The development of yield point at a high concentration of filler is shown clearly in Figure 1 (sample Dx).

Several theories have been investigated about why the composite properties depend on the filler-volume fraction, Φ , and on geometry. Nicolais and Narkis²⁹ developed a simple geometric model for the tensile strength, σ , of a composite with uniformly distributed spherical filler particles of equal radius

$$\sigma_c = \sigma_o(1 - 1.21 \Phi^{2/3}) \tag{1}$$

where the subscripts c and o are the composite and the matrix polymer, respectively. The experimental and theoretical tensile values were calculated based on eq. (1), and the tensile strength results are plotted and shown in Figure 2. The data were slightly linear with respect to $\Phi^{2/3}$ but had slopes that were less negative than the value of -1.21 predicted by eq. (1). This model was based on the assumption that there was no adhesion between the matrix and the filler particles. But the slope seen in Figure 2 suggests some degree of adhesion between the PVA matrix and starch filler, although not sufficient to prevent the area reduction mechanism from reducing the tensile strength.

Nielsen^{30,31} derived the following relationship between elongation and volume fraction of the filler, Φ

$$\epsilon_c = \epsilon_o(1 - \Phi^{1/3}) \tag{2}$$

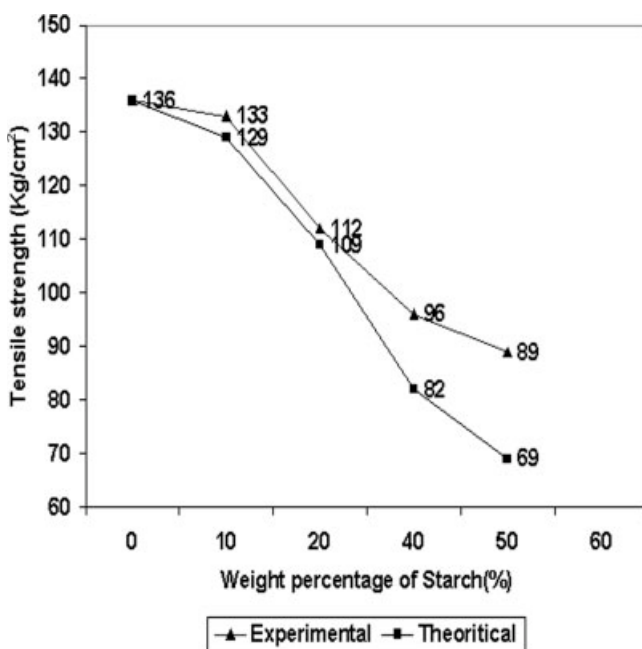


Figure 2 Relative tensile strength of PVA/starch composite films.

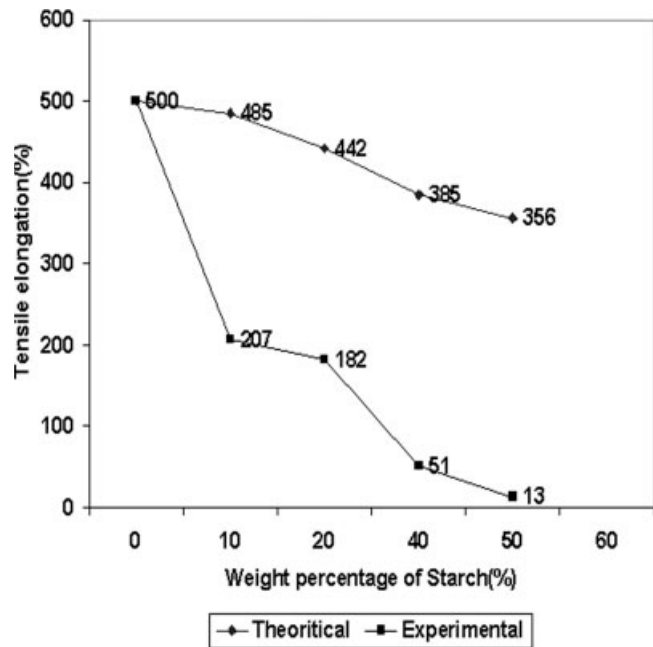


Figure 3 Relative tensile elongation of PVA/starch composite films.

where ϵ_c is the elongation at break or yield of the composite and ϵ_o is the corresponding elongation of the unfilled polymer. Tensile elongation was calculated using eq. (2), and the experimental results are plotted in Figure 3. It can be seen from the graph that the experimental results were more negative than the predicted value of -1 . The greater slope seen in Figure 3 may reflect more adhesion of the filler to the matrix than that assumed in eq. (2). Given the hydrophilic nature of PVA and starch, a high degree of adhesion would be expected.

Internal tear resistance is an important property for films used in packaging. Tear strength of the crosslinked PVA films and its blends containing various amounts of starch in terms of gram force is shown in Figure 4, from which it can be observed that the tear resistance of crosslinked PVA (sample Ax), 510 gf, decreased to 158 gf (sample Ex) with an increase in starch content.

Another important mechanical property of the film was burst strength, which is a measure of the overall strength of a film. The effect of starch content on the burst strength of PVA/starch films is shown in Figure 5, which indicates the burst strength of the films decreased from 5.976 kg/cm² (sample Ax) to 4.991 kg/cm² (sample Ex) with an increase in starch content. The decreases in tear strength and burst strength of the films with an increase in starch content may be attributed to the particular nature of starch, which does not support the tear strength and burst strength of crosslinked PVA films.

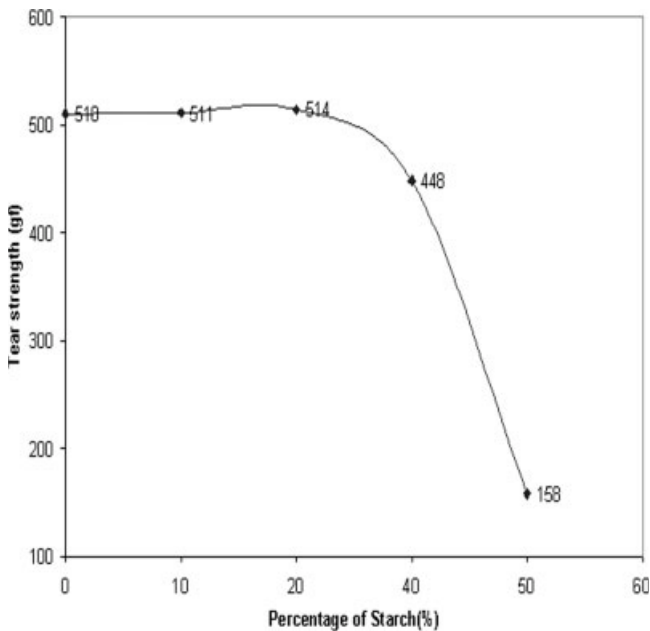


Figure 4 Tear strength of PVA/starch composite films.

From the DSC thermograms of PVA and PVA/starch blends shown in Figure 6, it is clear that PVA (sample A) showed a broad T_g at 101.58°C and a T_m at 189.78°C. When PVA was crosslinked with glutaraldehyde (sample Ax), the T_g and T_m peak maximums increased to 106.17°C and 191.26°C, respectively. As a general rule, any structural features that reduce segmental mobility or free volume will increase the T_g . The crosslinking of the PVA matrix introduced restrictions on segmental mobility and

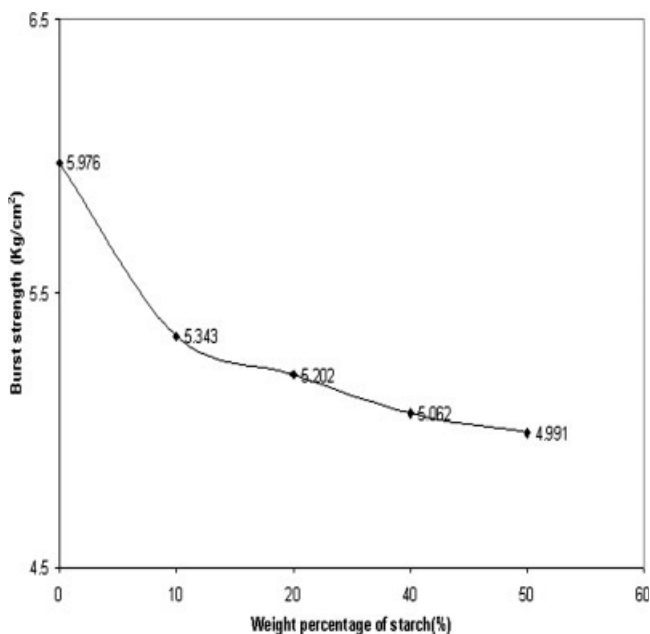


Figure 5 Burst strength of PVA/starch composite films.

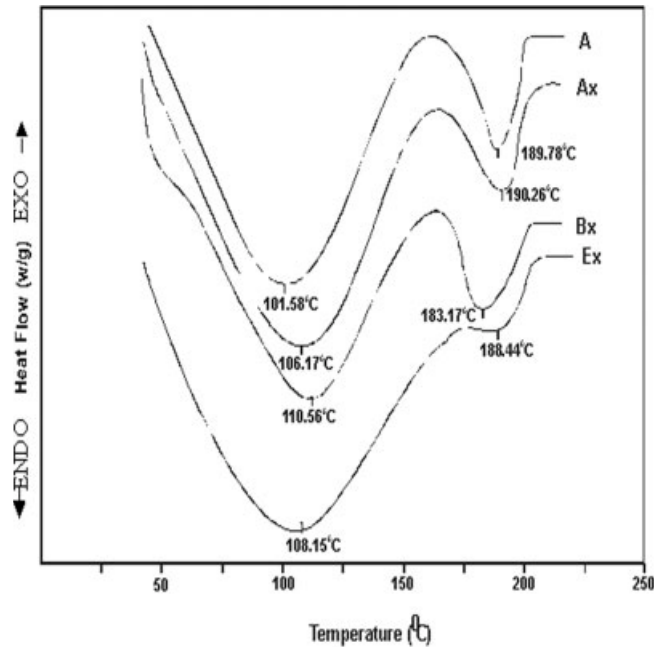


Figure 6 DSC thermograms of PVA/starch composite films.

enhanced T_g . The DSC thermogram of PVA/starch blend with 10% starch content (sample Bx) showed T_g and T_m at 110.56°C and 183.17°C, respectively.

Poly(vinyl alcohol) is a linear aliphatic hydroxyl polymer containing secondary hydroxyl groups in every alternate carbon, and the concentration of hydroxyl groups has a significant impact on T_g and T_m . The incorporation of starch (10%) powder (sample Bx) increased the T_g peak maximum from 106.17°C to 110.56°C. In this case the incorporation of starch into the PVA matrix introduced more hydroxyl groups and enhanced hydrogen bonding, which increased the T_g peak maximum because both PVA and starch are polar polymers with hydroxyl groups. However, at 50% starch loading, because too many starch particles were confined between PVA polymer chains, the T_g decreased to 108.15°C and the T_m increased to 188.44°C compared with those in the Bx film.

Moisture content and density

The moisture content of the PVA/starch films is reported in Table III, from which it can be observed that the moisture content of PVA (12.07) decreased slightly (11.05) because of crosslinking with glutaraldehyde. The addition of starch to the crosslinked PVA did not produce much variation in moisture content. This may be because both PVA and starch are polar polymers containing hydroxyl groups.

From Table III, which also shows the density of the different PVA/starch films, it can be observed

TABLE III
Effect of Starch on Moisture Content and Density of PVA/Starch Composite Films

| Sample code | Moisture content (%) | Density (g/cm ³) |
|-------------|----------------------|------------------------------|
| A | 12.07 | 1.26 |
| Ax | 11.05 | 1.24 |
| Bx | 11.85 | 1.26 |
| Cx | 11.84 | 1.29 |
| Dx | 11.80 | 1.34 |
| Ex | 11.78 | 1.37 |

that the density of PVA (1.26) decreased slightly (1.24) because of crosslinking with glutaraldehyde. This may be because crosslinking reduced the number of hydroxyl groups per unit mass of the sample and hence decreased hydrogen bonding interaction, which led to a decrease in density. The addition of starch to the crosslinked PVA network increased the density from 1.24 g/cm³ (sample Ax) to 1.37 g/cm³ (sample Ex). This may have been because both PVA and starch are polar polymers containing hydroxyl groups that make strong hydrogen bonds between them.

Solubility resistance and swelling analysis

The solubility resistance of PVA and PVA/starch composites in water, 5% acetic acid, 50% ethanol, and sunflower oil as model food stimulants is shown in Table IV. In water and in 5% acetic acid, solubility resistance, measured in terms of dissolution time, increased with an increase in starch content. Even though the difference was only marginal, the resistance to water and aqueous solutions would be beneficial in a variety of applications of the polymer as a degradable plastic material.

The sensitivity of both PVA and starch, being hydrophilic polymers, to moisture was analyzed in a humidity chamber at 90% RH (Fig. 7). As can be seen in Figure 7, the starch films had a faster and higher moisture transmission rate than that of the unfilled PVA matrix.

TABLE IV
Effect of Starch on Solubility of PVA/Starch Composite Films

| Sample code | Dissolution time (min) | | | |
|-------------|------------------------|----------------|-------------|---------------|
| | Water | 5% Acetic acid | 50% Ethanol | Sunflower oil |
| A | 10 | 30 | Not soluble | Not soluble |
| Ax | 30 | 60 | Not soluble | Not soluble |
| Bx | 15 | 45 | Not soluble | Not soluble |
| Cx | 25 | 50 | Not soluble | Not soluble |
| Dx | 45 | 165 | Not soluble | Not soluble |
| Ex | 75 | 190 | Not soluble | Not soluble |

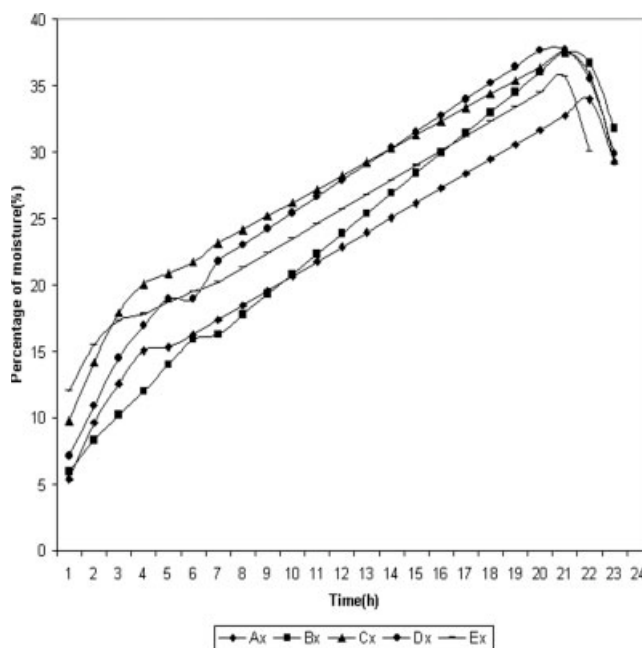


Figure 7 Moisture analysis of PVA/starch composite films.

The swelling analyses of PVA/starch blends in 50% ethanol and sunflower oil are shown in Figures 8 and 9, respectively. As can be seen from the graph, the swelling rate of PVA matrix was higher than that of the starch-filled composites in 50% ethanol, whereas in sunflower oil, the maximum swelling was found to be in the reverse order one of that

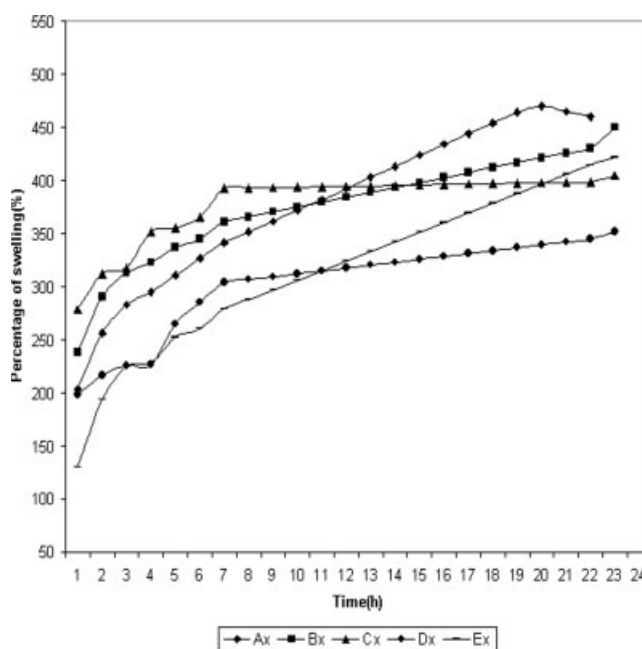


Figure 8 Swelling analysis of PVA/starch composite films in 50% ethanol.

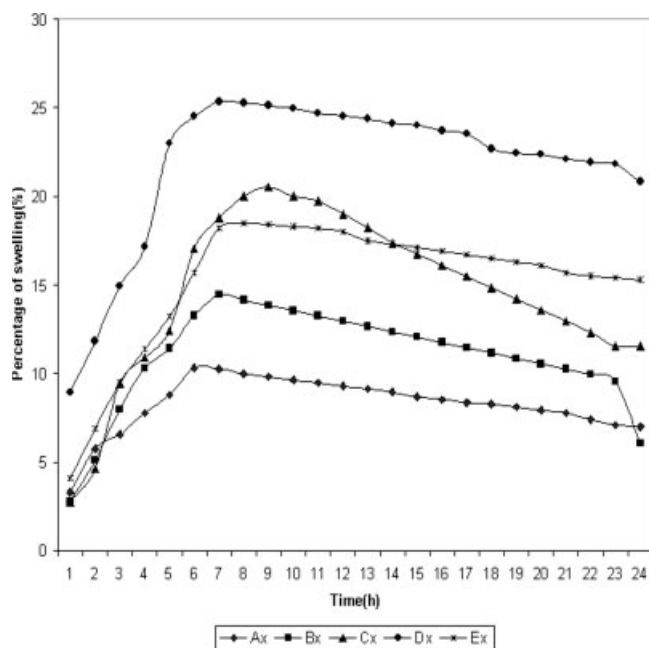


Figure 9 Swelling analysis of PVA/starch composite films in sunflower oil.

observed in 50% ethanol. Sunflower oil finds widespread use as a cooking oil; hence, the resistance of PVA/starch films in sunflower oil was studied in a similar way. Maximum swelling was found in the crosslinked PVA (sample Ax) film, and it decreased with increasing in starch content.

CONCLUSIONS

PVA and starch composites were prepared with the objective of using a naturally occurring biodegradable polymer in the preparation of polymeric films. PVA/starch composites containing different starch concentrations ranging from 10 to 50 wt % were prepared. These blends showed improved tensile modulus and solubility resistance. However, the results showed that tensile strength, tensile elongation, tear strength, and burst strength decreased. The reduction in mechanical strength with the addition of starch was a general phenomenon, however; the main objective of this work was to find a low-cost and environmentally friendly packaging material.

The author is grateful to Dr. Sushil K. Verma, director general, CIPET, for his constant encouragement and necessary support.

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