Crosslinked Poly(vinyl alcohol) and Starch Composite Films. II. Physicomechanical, Thermal Properties and Swelling Studies

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ABSTRACT: Poly(vinyl alcohol) (PVA) was blended with 10, 20, 30, 40, and 50 wt % of starch with and without crosslinking by solution casting process. The solution-casted films were dried and tested for physicomechanical properties like tensile strength, tensile elongation, tensile modulus, tear and burst strengths, density, and thermal analysis by differential scanning calorimetry (DSC). These PVA/starch films were further characterized for moisture content; solubility resistance in water, 5% acetic acid, 50% ethanol, and sunflower oil; and swelling characteristics in 50% ethanol and sunflower oil. The crosslinked PVA/starch composite films show significant improvement in tensile strength, tensile modulus, tear and burst strengths, and solubility resistance over the uncrosslinked films. Between the crosslinked and uncrosslinked films, the uncrosslinked films have higher tensile elongation, moisture content, moisture absorption, and swelling over the crosslinked films. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 909–916, 2007

Key words: poly(vinyl alcohol); glutaraldehyde; starch; mechanical properties; swelling studies

INTRODUCTION

Long life and attractive properties have made plastics a material of choice for many applications. Because of tremendous growth in applications, Plastics are one of the fastest growing segments of the waste stream. This is because, the vast majority of plastic products are made from petroleum-based synthetic polymers that do not degrade in a land fill site or in a composite-like environment. Especially, polyolefins such as polyethylene (PE) and polypropylene (PP) are very resistant to hydrolysis and are totally nonbiodegradable. As a consequence, the disposal of these products poses a serious environmental threat. An environmentally-conscious alternative is to design and synthesize polymers that are biodegradable. Biodegradable plastics provide opportunities for reducing municipal solid waste through biological recycling to the ecosystem and can replace the conventional nonbiodegradable synthetic plastic products. In addition, it is desirable that these biodegradable polymers come primarily from agriculture or other renewable resources for a sustainable environment.

Starch is one of the most abundant naturally occurring polymers in nature second to cellulose. The most important sources of starch are wheat, potato, rice, tapioca, and corn. Starch is the major polysaccharide reserve of plants. Starch occurs in nature as water-insoluble granules and is a polymer of D-glucose. The average granule size of starch varies from source to source; rice starch granules are roughly 3 μm in diameter, corn starch has an average granular size of 10 μm, and potato starch granules are about 35 μm in diameter. The starch granules consist of highly branched amylopectin and linear amylose molecules, with some minor components such as lipids and proteins. Amylose is a crystalline linear molecule with molecular weight ranging from 10^5 to 10^6 g/mol, which constitutes nearly 20% of starch and is soluble in hot water; whereas amylopectin is a highly branched molecule with molecular weight ranging from 10^6 to 10^8 g/mol and is insoluble in hot water. Starch has been considered as a low-cost alternative to synthetic plastics in production of disposable plastics.[1,2] Starch is totally biodegradable in a wide variety of environmental conditions and permits the development of totally biodegradable products. Starch by itself was plasticized and shaped into consumer items.[3–6] But plasticized starch alone swells and deforms on exposure to moisture. To compensate for the inconvenience of plastics made by pure starch, starch was blended with petroleum polymers.[7–9]

Polymeric blends containing starch have been developed for different applications and are the subject of several patents.[10–12] The first important commercial application of starch plastics has been the blending of PE with starch as a filler. It was assumed that starch would accelerate the degradation of PE, but PE is virtually nonbiodegradable.[13,14] Currently,

plastic films used in agriculture mulch are made with low-density PE containing transition metal compounds soluble in the thermoplastic matrix and about 6–15% starch. However, the degradation duration is still high and can reach a few years for some of these products that do not respond to certain norms of biodegradability. Then blending of starch with biodegradable synthetic polymers like poly(caprolactone) (PCL),[15–19] poly(hydroxybutyrate) (PHB), poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV),[20–25] poly(lactic acid) (PLA),[26–30] and poly(vinyl alcohol) (PVA)[31–37] have become the objective.

With the ongoing research efforts aimed at preparation and evaluation of hydrophilic/biodegradable polymers,[38–43] this study reports the preparation of PVA/starch composite films with glutaraldehyde (GLA) as crosslinking agent for PVA. The modified films were characterized for different physicomechanical and thermal properties. The crosslinking of PVA was aimed at improving mechanical properties and water resistance of PVA films.

PVA is the largest synthetic water-soluble polymer produced in the world. The prominent properties of PVA may include its biodegradability[44] in the environment. The generally accepted biodegradation mechanism occurs via a two-step reaction by oxidation of hydroxyl group followed by hydrolysis. It was concluded that the initial biodegradation step involves the enzymatic oxidation of secondary alcohol group in PVA to ketone groups, and hydrolysis of the ketone groups results in cleavage. The biodegradation of PVA is influenced by the stereo-chemical configuration of the hydroxyl groups of PVA. The isotactic material of PVA preferentially degraded.[45,46] PVA has been studied extensively because of its good biodegradability and mechanical properties. These properties have made PVA as attractive material for disposable and biodegradable plastic substitutes.

EXPERIMENTAL

Materials

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

Procedure for solution casting

A series of PVA/starch blends with and without crosslinking were processed into films by solution casting process by varying the starch content from 10% to 50%. The PVA powder was dissolved in hot water at 80–90°C, then 4 mL of 25% GLA solution was added as crosslinking agent for PVA and then the starch powder made into paste was mixed as per the composition and stirred well for about 30 min with constant stirring. Later the solution was filtered through cotton and casted into a glass plate mold ($20 \times 12 \text{ cm}^2$ size) lined with PE sheet. The casted solution was evaporated at room temperature ($25°C \pm 3°C$) 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 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 $63 \times 76 \text{ mm}^2$. Burst strength measurements were made as per ASTM D774-67 in CIPET Burst strength tester (BST: A1 01) using films of size ($6 \times 6 \text{ cm}^2$). Differential scanning calorimetry (DSC) measurements were made using TA instruments (2010 DSC) from 40°C to 250°C in nitrogen atmosphere at a heating rate of 10°C/min. Moisture absorption was measured for equilibrated samples in laboratory conditions. Three replicas were tested for each sample.

The density of the films was measured using Mettler PM200 electronic weighing balance as per ASTM D 792 displacement method. The solubility tests
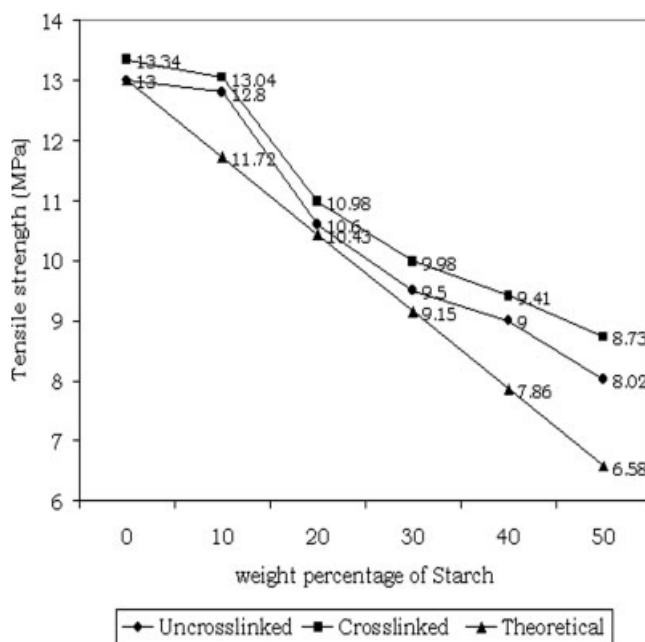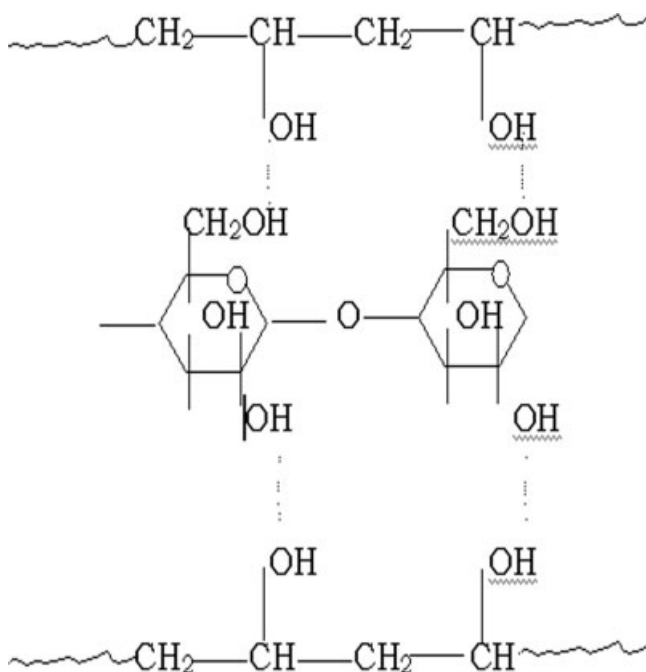

Figure 1 Effect of crosslinking on tensile strength of PVA/starch composite films.

Scheme 1 Hydrogen bond formation between PVA and starch in PVA/starch composite films.

were carried out by immersing the dried sample at 25°C in distilled water, in 50% ethanol, 5% acetic acid, and sunflower oil. The swelling tests were carried out by immersing the dried sample at 25°C in 50% ethanol and sunflower oil for specified time intervals, removed from water, and weighed after removing the surface liquid. Three replicas were tested for each sample. The percentage swelling was calculated on a dry weight basis.

RESULTS AND DISCUSSION

Mechanical and thermal properties

The tensile strength, tensile elongation, and tensile modulus of PVA/starch composite films with and without crosslinking are shown in Figures 1–3, respectively. From these figures it is clear that the tensile strength and tensile elongation decreases, whereas tensile modulus increases with increase in starch content from 10% to 50%, which indicates that the addition of granular starch to PVA matrix follows the general trend of filler effects on polymer properties. The reduction in tensile strength and tensile elongation of PVA matrix with the addition of starch is well supported by the literature reports,[32] whereas the tensile modulus increased due to the stiffening effect of starch granules. These results can be interpreted using composite models.

Several theories of the dependence of composite properties on filler-volume fraction "Φ" and geometry have been investigated in a simple model. Nicolais

and Narkis[47] developed a geometric model for the tensile strength "σ" of a composite with uniformly distributed spherical filler particles of equal radius

$$\sigma_c = \sigma_0(1 - 1.21\Phi^{2/3}) \qquad (1)$$

The subscripts "c" and "0" represent the composite and the matrix polymer, respectively. The tensile strength calculated using Eq. (1) and the experimental results are plotted in Figure 1. The data are slightly linear with respect to $\Phi^{2/3}$, but have slopes that are less negative than the value of -1.21 predicted by the Eq. (1). This model is based on the assumption that there is no adhesion between the matrix and the filler particles. But the slope seen in the Figure 1 suggests some degree of adhesion between the PVA matrix and starch filler (Scheme 1), although it is not sufficient to prevent the area reduction mechanism from reducing the tensile strength. Between the crosslinked and uncrosslinked films, the crosslinked films have higher tensile strength over the crosslinked films.

Nielsen[48,49] derived the following relationship between elongation and volume fraction of the filler F

$$\varepsilon_c = \varepsilon_0(1 - \Phi^{1/3}) \qquad (2)$$

where "ε_c" is the elongation to break or yield of the composite and "ε_0" is the corresponding elongation of the unfilled polymer. The tensile elongation calculated using Eq. (2) and the experimental results are plotted in Figure 2. It can be seen from the graph that the experimental results are more negative than the predicted
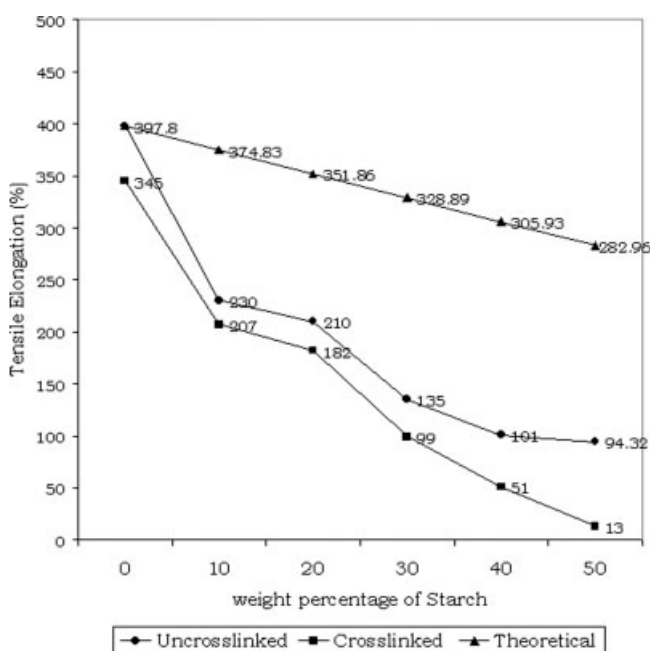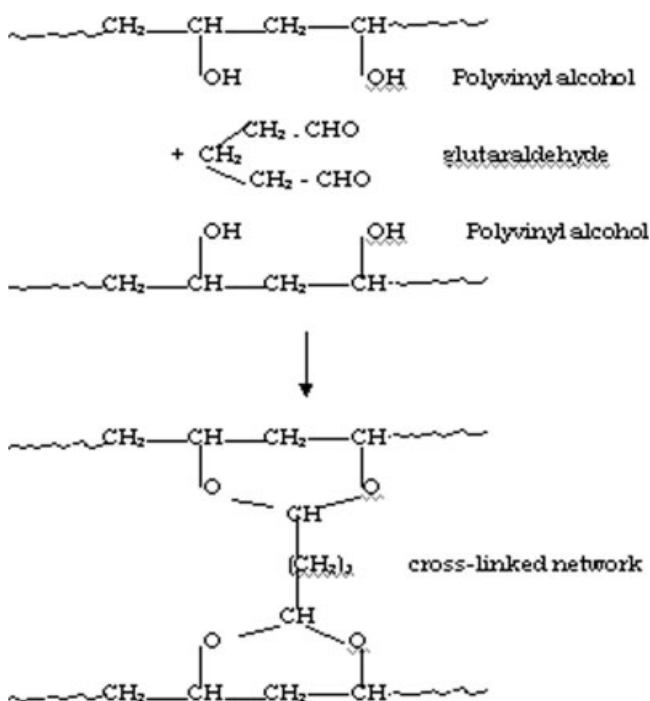

Figure 2 Effect of crosslinking on tensile elongation of PVA/starch composite films.

Scheme 2 Crosslink formation between PVA and glutaraldehyde in PVA/starch composite films.

Figure 4 Effect of crosslinking on tear strength of PVA/starch composite films.

value of −1. The more slope seen in Figure 2 may reflect more adhesion of filler and matrix than that assumed in Eq. (2). Given the hydrophilic nature of PVA and starch, one can expect a high degree of adhesion. Starch acted as filler in PVA matrix, as the blends were subjected to an external tensile load, and the PVA matrix was the main load-bearing phase. As the starch content increased, the effective cross-sectional area of
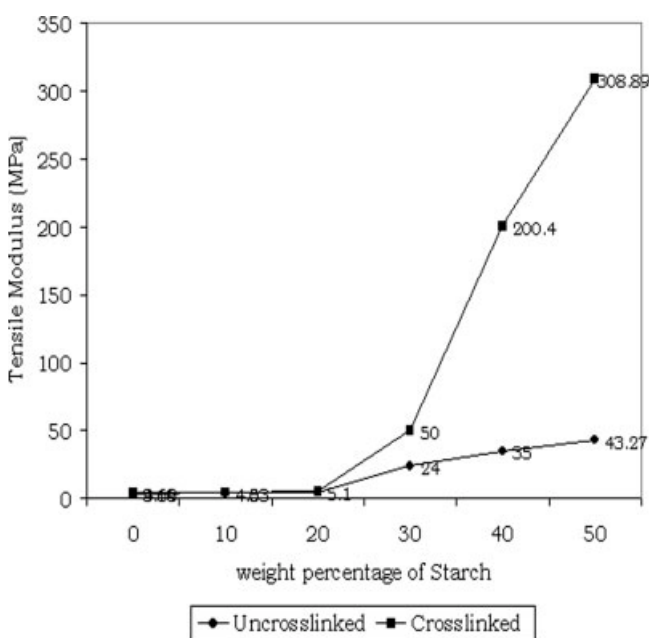
the PVA continuous phase was reduced, resulting in decreased strength and elongation. As expected, the starch granules in the PVA matrix without crosslinking acted as stress concentrators, often inducing cracks which results in low strength and elongation. However, strong adhesion existed between PVA matrix and starch in the presence of GLA. So, the mechanical properties of the blend are improved greatly in the presence

Figure 3 Effect of crosslinking on tensile modulus of PVA/starch composite films.

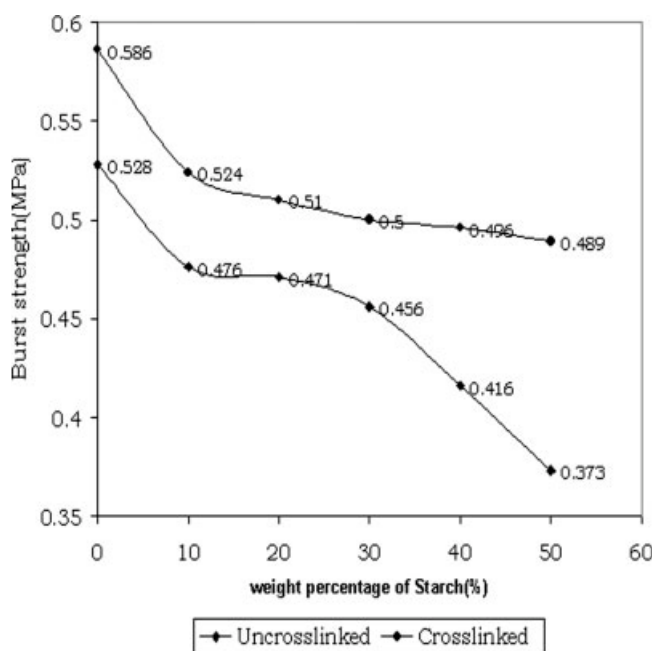Figure 5 Effect of crosslinking on burst strength of PVA/starch composite films.

Composition (%)		Glass-transition temperature, T_g (°C)		Melting temperature, T_m (°C)	
PVA	Starch	Uncrosslinked	Crosslinked	Uncrosslinked	Crosslinked
100	–	101.58	106.17	189.78	190.26
90	10	124.62	110.56	191.65	183.17
50	50	110.55	106.15	186.95	188.44

of GLA. With GLA, a covalent bond likely to be formed at the PVA/starch interface, so that the interfacial adhesion was enhanced and consequently had improved the tensile strength. Crosslinking or bridging changes the structure into a network (Scheme 2), while increasing its resistance to mechanical shear. Meanwhile such adhesion might not cause severe restriction of elongation by forming a proper entanglement, which is capable of being stretched along the matrix.

The tensile modulus results of PVA/starch composite films with and without crosslinking are shown in Figure 3, where the tensile modulus increased with addition of starch. The increase in tensile modulus is due to the stiffening effect of starch granules. Both GLA and starch had a positive effect on Young's modulus. In blend, the molecular mobility of PVA is restricted by rigid starch granules, which have high modulus, and covalent GLA bonding at the interface. The resistance of PVA molecules to stretch resulted in a higher Young's modulus.

The internal tear resistance is an important property for the films used in packaging. The tear strength of the films in terms of gram force for the crosslinked and uncrosslinked PVA films containing various amounts of starch are shown in Figure 4. From the figure, it can be observed that the tear resistance of crosslinked films decreased from 540 to 158 gf with increase in starch content from 10% to 50%, whereas the tear resistance of uncrosslinked films decreased from 490 to 90 gf. The decrease in tear resistance with increase in starch content may be because the starch powder, being granular in nature, does not support the tear resistance. However, the crosslinked films are having higher tear resistance compared with uncrosslinked films in all the compositions because of crosslink network formation in the PVA matrix.

Another important mechanical property of the film is the burst strength, which is a measure of overall strength of the film. The effect of starch content on the burst strength of PVA/starch films is shown Figure 5. From the figure, it can be observed that the burst strength of crosslinked films decreased from 0.586 to 0.489 MPa with increase in starch content from 10% to 50%, whereas the burst strength of uncrosslinked films decreased from 0.528 to 0.373 MPa. The reduction in burst strength of PVA matrix with the addition of starch is well supported by the literature reports.[32] However, the crosslinked films are having higher burst strength compared with uncrosslinked films in all the compositions because of network formation in the PVA matrix.

The thermal analysis results of PVA/starch composites films are given in Table I, which shows that T_g and T_m of PVA matrix increased after crosslinking by GLA. As a general rule, any structural feature that reduces segmental mobility or free volume will increase T_g and T_m. Here, the crosslinking of PVA matrix introduces restrictions on segmental mobility and enhances T_g and T_m. However, when the starch granules are introduced, T_g and T_m of the matrix are reduced to a certain extent, and this may due to the increase in free volume and discontinuity of PVA matrix, because at higher starch loading too many starch granules are confined in between the PVA chains.

Moisture content and density

Moisture content results of different PVA/starch films are reported in Table II. From the table, it can be observed that the moisture content decreased from 12.07% to 11.05% because of crosslinking with GLA. Even though this decrease is small, it is signifi-

Composition (%)		Moisture content (%)		Density (g/cm^3)	
PVA	Starch	Uncrosslinked	Crosslinked	Uncrosslinked	Crosslinked
100	–	12.07	11.05	1.26	1.24
90	10	12.02	11.85	1.27	1.26
80	20	11.58	11.84	1.29	1.29
70	30	11.50	11.82	1.31	1.33
60	40	11.45	11.80	1.33	1.34
50	50	11.13	11.78	1.38	1.37

TABLE III
Effect of Crosslinking on Solubility of PVA/Starch Composite Films

| Composition (%) | | Solubility time (min) | | | | | | | |
| | | In water | | In 50% ethanol | | In 5% acetic acid | | In sunflower oil | |
PVA	Starch	Uncross linked	Cross linked	Uncross linked	Cross linked	Uncross linked	Cross linked	Uncross linked	Cross linked
100	–	10	30	30	60	Not soluble	Not soluble	Not soluble	Not soluble
90	10	10	15	30	45	Not soluble	Not soluble	Not soluble	Not soluble
80	20	20	25	45	50	Not soluble	Not soluble	Not soluble	Not soluble
70	30	30	35	70	75	Not soluble	Not soluble	Not soluble	Not soluble
60	40	40	45	120	165	Not soluble	Not soluble	Not soluble	Not soluble
50	50	60	75	180	190	Not soluble	Not soluble	Not soluble	Not soluble

cant. Crosslinking or bridging changes the structure into a network, while reducing water retention. The addition of starch in the crosslinked PVA does not show much variation in moisture content. This may be because both PVA and starch are polar polymers containing hydroxyl groups.

Density of different PVA/starch films are reported in Table II. From the table, it can be observed that the density decreased from 1.26 to 1.24 g/cm^3 because of crosslinking with GLA. This may be because crosslinking reduces the number of hydroxyl groups per unit mass of the sample and hence decreases hydrogen bonding interaction, which leads to a decrease in density. The addition of starch in the crosslinked PVA network increases the density from 1.24 to 1.37 g/cm^3. This may be due to the fact that both PVA and starch are polar polymers containing hydroxyl groups, which results in strong hydrogen bonding between them.
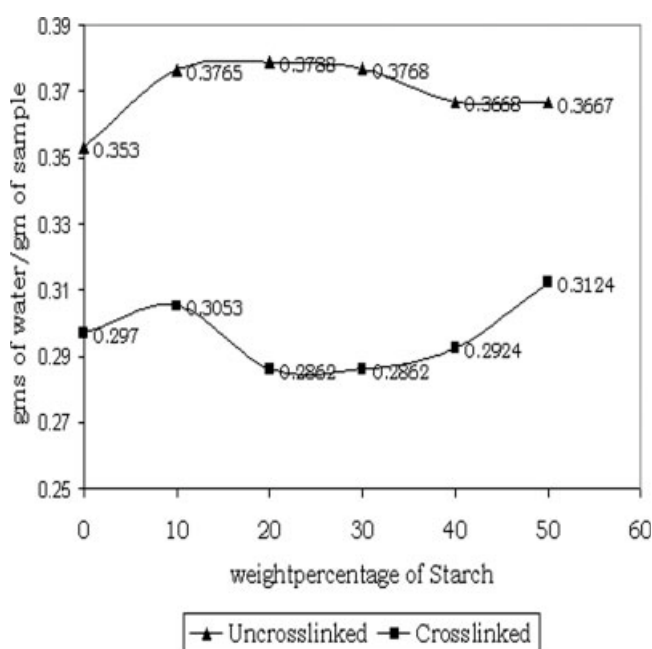
Solubility resistance and swelling analysis

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 III. In water and 5% acetic acid, the solubility resistance in terms of dissolution time increased with increase in starch content. Even though the difference is only marginal, the resistance to water and aqueous solution is beneficial in a variety of applications of the polymer as a degradable plastic material. The solubility of a polymer in a solvent is determined by the balance of polymer–polymer and polymer–solvent interactions. When a polymer is containing chemical groups with very different chemical affinities, for instance polar–hydrophilic and nonpolar–hydrophobic groups, each group contributes independently to the solubility.
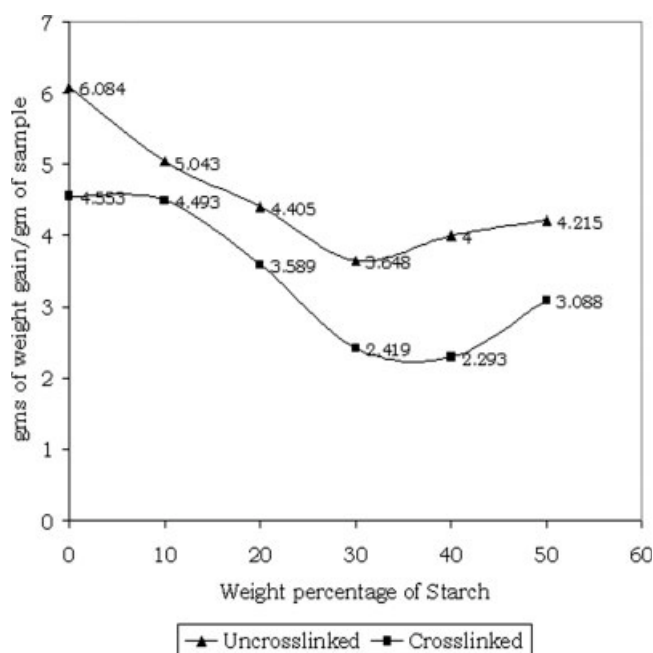

Figure 6 Effect of crosslinking on moisture absorption behavior of PVA/starch composite films.

Figure 7 Effect of crosslinking on swelling behavior of PVA/starch composite films in 50% ethanol.
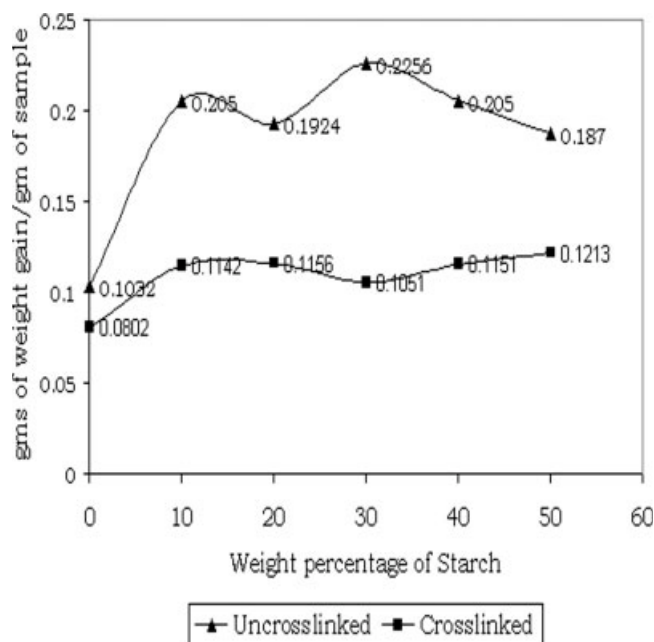
Figure 8 Effect of crosslinking on moisture absorption behavior of PVA/starch composite films in sunflower oil.

The moisture absorption is an important factor when dealing with hydrophilic thermoplastics, because a high water uptake worsens the mechanical properties of the material and changes the dimensions by swelling. One of the objectives of this work was to clarify the influence of crosslinking on the moisture absorption. To study this point, samples with and without crosslinking were exposed to high humidity and the moisture uptake was determined gravimetrically. The results of this experiment are summarized in Figure 6, which show variations in moisture uptake with increase in starch content; but at 50% starch loading, the moisture absorption is higher, and this may due to the increase in free volume and discontinuity of PVA matrix, because at higher starch loading too many starch granules are confined in between the PVA chains, water could saturate the surface of the blends easily, and also penetrate into the blends through voids and absorbed easily by the starch, resulting in higher water absorption. However, the crosslinked films are having lower moisture absorption compared with uncrosslinked films in all the compositions because of network formation in the PVA matrix.

The swelling analysis of PVA/starch blends in 50% ethanol and sunflower oil are shown in Figures 7 and 8, respectively. As can be seen from the graph, the swelling rate of uncrosslinked PVA films are higher than crosslinked films in 50% ethanol, whereas in the case of sunflower oil, the maximum swelling is found in reverse order to the one observed in 50% ethanol. Sunflower oil finds wide spread use as cooking oil; hence the study of resistance of PVA/starch films in sunflower oil is also conducted in the similar way. The maximum swelling was found in crosslinked films and it decreased with increase in starch content.

CONCLUSIONS

The PVA/starch composite films were prepared with 10, 20, 30, 40, and 50 wt % of starch with and without crosslinking, by solution casting process. These films were tested for physicomechanical properties like tensile strength, tensile elongation, tensile modulus, tear and burst strengths, and density. These PVA/starch films were further characterized for moisture content, moisture vapor transmission rate (MVTR), solubility resistance, and swelling characteristics. The crosslinked PVA/starch composite films show significant improvement in tensile strength, tensile modulus, tear and burst strengths, solubility resistance in water, 5% acetic acid, 50% ethanol, and MVTR over the uncrosslinked films. Between the crosslinked and uncrosslinked films, the uncrosslinked films have higher tensile elongation, moisture content, moisture absorption, and swelling over the crosslinked films.

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