

Thermal, Mechanical, and Surface Characterization of Starch–Poly(vinyl alcohol) Blends and Borax-Crosslinked Films

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ABSTRACT: Starch–poly(vinyl alcohol) (PVA) blends with different compositions were prepared and crosslinked with borax by *in situ* and posttreatment methods. Various amounts of glycerol and poly(ethylene glycol) with a molecular weight of 400 were added to the formulations as plasticizers. The pure starch–PVA blends and the crosslinked blends were subjected to differential scanning calorimetry, thermogravimetry, and X-ray photoelectron spectroscopic studies. Broido and Coats–Redfern equations were used to calculate the thermal decomposition kinetic parameters. The tensile strengths and elongation percentages of the films were also evaluated. The results suggested that the glass-transition temperature (T_g) and the melting

temperature strongly depended on the plasticizer concentration. The enthalpy relaxation phenomenon was dependent on the starch content in the pure blend. The crosslinked films showed higher stability and lower T_g 's than pure PVA and starch–PVA blends, respectively. High-resolution X-ray photoelectron spectroscopy provided a method of differentiating the presence of various carbons associated with different environments in the films. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1313–1322, 2005

Key words: blends; crosslinking; mechanical properties; thermal properties.

INTRODUCTION

The accumulation of solid waste is a menace to modern society. Any environmentalist will look back with a great sense of dismay over the gross misuse of reserves. In these circumstances, it is necessary to formulate proper ways and means of reducing the menace. Land filling is a method of disposal, but it has created aesthetic problems. Therefore, there is a need for polymers that are completely degradable. The use of starch is increasing in many applications, such as additives and fillers for thermoplastic materials, to increase the biodegradability.^{1,2} Starch-based blends have enormous potential for biomedical and environmental fields because they are biodegradable and inexpensive and are an almost unfailling source of raw material.^{3,4}

The incorporation of poly(vinyl alcohol) (PVA), a biodegradable and water-soluble crystalline polymer, into starch changes the thermomechanical properties of the material and thus modifies the polymer structure at both the molecular and morphological levels; it is widely used because of its flexibility and good film-

forming capability.^{5–7} The relatively poor mechanical properties of starch-based materials have been tentatively overcome by the addition of large amounts of plasticizers, such as glycerol and ethylene glycol, or by the modification of the chemical properties of starch itself. Since the first studies, improvements in the mechanical properties have been made through blending with PVA. The coprocessing of starch and PVA significantly improves the strength and flexibility of gelatinized starch. The mechanical properties and biodegradability of starch–PVA blended films have been reported by several researchers.^{8–11}

The addition of borax as a crosslinking agent also enhances the mechanical properties of starch–PVA blends. Crosslinking of starch reinforces the intermolecular binding by introducing covalent bonds to supplement natural intermolecular hydrogen bonds.¹²

In this investigation, starch–PVA blends and starch–PVA blends with glycerol and poly(ethylene glycol) (PEG) plasticizers were cast. Borax-crosslinked blends were also prepared, and their thermal, mechanical, and surface properties were evaluated.

EXPERIMENTAL

Materials

Soluble starch from S.D. Fine Chemicals (Mumbai, India; amylose content = 21%) and PVA (NH-17R)

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from Nippon Ghosai (Japan) were used in making the blends, and deionized water was used in all cases. Glycerol, poly(ethylene glycol) with a molecular weight of 400 (PEG-400) from Aldrich (United States), and borax from Ranbaxy Chemicals (Mumbai, India) were used.

Preparation of the starch–PVA blends

Calculated amounts of starch and PVA were mixed homogeneously with stirring in 75 mL of deionized water for 3 h and at 80°C in a water bath. At the end, the mixture was cooled to room temperature, and films were cast onto clean glass plates. Starch–PVA films prepared with this process were brittle and opaque. Two distinct phases of starch and PVA were observed. To make flexible and transparent films with good mechanical properties, we added the plasticizer (glycerol and PEG-400) to the starch–PVA blend during the preparation. Films were prepared with various compositions of starch, PVA, and glycerol or PEG.

Crosslinking of the starch–PVA films

The crosslinking of PVA and PVA–starch was achieved by *in situ* crosslinking and posttreatment methods with borax as the crosslinking agent.

In situ crosslinking

PVA and PVA–starch were crosslinked by the addition of borax to the prepared starch–PVA blend solutions. Starch–PVA films crosslinked with 2, 2.5, or 3% borax were prepared.

Posttreatment of the starch–PVA films

The starch–PVA films were subjected to posttreatment with borax to form intermolecular and intramolecular crosslinks. An aqueous solution of Na₂B₄O₇ was prepared and poured into a Teflon tray. Dry starch–PVA films prepared with and without a plasticizer were immersed in the borax solution. The films swelled and absorbed all the Na₂B₄O₇ solution. The gelatinous films thus obtained were dried at 50°C for more than 12 h. For a given starch–PVA composition, three different concentrations of Na₂B₄O₇ were used: 4, 8, and 12% with respect to the total weight of the starch–PVA sample taken. The crosslinked films were named with the first letters of the raw materials, a number based on the starch/PVA ratio (i.e., 1 for 50:50, 2 for 40:60, 3 for 30:70, and 4 for 20:80), and A, B, or C for 4, 8, or 12% borax crosslinking (e.g., SPB-1A was a starch–PVA crosslinked film prepared from a 50:50 weight ratio of starch and PVA and subjected to posttreatment with 4% borax). A starch–PVA blends (50:50) treated with 15 wt % glycerol and various amounts of

borax (2, 2.5, or 3 wt %) prepared by an *in situ* method were dubbed SPGB-2, SPGB-2.5, and SPGB-3, whereas those prepared by a posttreatment method with 8 or 12 wt % borax were named SPGB-8 and SPGB-12, respectively.

Characterization

Differential scanning calorimetry (DSC)

DSC thermograms were recorded on a Mettler–Toledo DSC 821^e. The samples were placed in sealed aluminum pans and initially heated at a heating rate of 10°C/min from 0 to 170°C in a nitrogen atmosphere; they were quenched immediately from 170 to 0°C at a cooling rate of 50°C/min to remove the previous thermal history. The samples were subsequently rescanned at a heating rate of 10°C/min from 0 to 300°C. The instrument was calibrated with indium standards before the measurements. The average sample size was 10 mg, and the nitrogen flow rate was 20 cm³ min⁻¹. From these thermograms, the glass-transition temperature (T_g) and melting temperature (T_m) were determined.

Thermogravimetric analysis (TGA)

TGA was carried out on a Mettler–Toledo TGA/SDTA 851^e from 25 to 600°C at a heating rate of 10°C/min and under a nitrogen atmosphere (flow rate = 20 cm³ min⁻¹). The sample size was 10 ± 1 mg.

Kinetic methods

The derivation of kinetic data in the study of the polymer decomposition with TGA has received increasing attention in the last decade, along with much criticism regarding its use in the determination of rate constants, activation energies (E), reaction orders, and pre-exponential factors (Z). Values obtained with TGA can be studied with a variety of techniques. The values depend on several factors (the flow rate of the gas and its nature, the heating rate, and the sample mass and shape) and on the mathematical treatment used to evaluate the data.

A reaction rate can be defined as the derivative of the conversion with respect to time. In TGA, the conversion at time t [$\alpha(t)$] is defined as the ratio of the final mass loss to the total mass loss corresponding to a particular stage of decomposition:

$$\alpha(t) = [w_0 - w(t)] / (w_0 - w_\infty) \quad (1)$$

where w_0 , $w(t)$, and w_∞ are the initial mass of the sample, the sample mass at time t , and the sample mass at infinite time (i.e., 0), respectively.

The rate of conversion in a dynamic TGA experiment at a constant heating rate (Q) can be expressed as follows:

$$d\alpha/dt = Q(d\alpha/dT) = k(T)f(\alpha) \quad (2)$$

where $k(T)$ is the rate constant and $f(\alpha)$ is the conversion functional relationship.

An Arrhenius expression, which describes the temperature dependence of the rate constant, may be expressed as follows:

$$k(T) = Z \exp(-E/RT) \quad (3)$$

where R is the universal gas constant and T is the temperature (K).

The integral form of the rate equation in a dynamic heating expression experiment may be expressed as follows:

$$g(\alpha) = (ZE/QR)p(x) \quad (4)$$

where $p(x)$ is equal to $\int_{\infty}^x [\exp(-x)/x^2] dx$ and x is equal to E/RT . $g(\alpha)$ is the integral form of the conversion dependence function.¹³⁻¹⁶

To solve the function $p(x)$, several methods have been developed. Broido,¹⁷ Coats and Redfern,¹⁸ and other researchers have solved this function. The equations used in this work are given in the following sections.

Broido equation

E for the thermal degradation processes was evaluated with the Broido equation:¹⁷

$$\ln [\ln(1/Y)] = E/R(1/T) + \text{Constant} \quad (5)$$

where $Y = (w_0 - w_t)/(w_0 - w_{\infty})$ is the fraction of the number of initial molecules not yet decomposed, w_t being the weight at time t . The slope of the plot of $\ln(1/Y)$ versus $1/T$ is related to E .

Coats-Redfern equation

Coats and Redfern¹⁸ provided an approximation to the integral of eq. (4) and thus obtained the following expression:

$$\log_{10}[g(\alpha)/T^2] = \log_{10}(ZR/QE)(1 - 2RT/E) - E/2.3RT \quad (6)$$

Therefore, a plot of $\log_{10}[g(\alpha)/T^2]$ versus $1/T$ should result in a straight line with a slope equal to $-E/2.3R$ for the correct chosen value of n , the order of degradation.

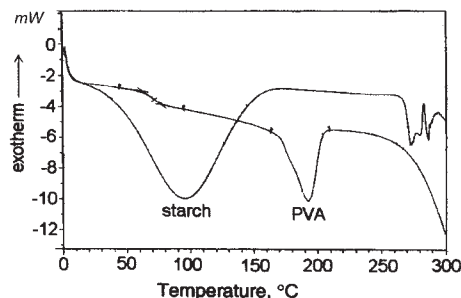


Figure 1 DSC thermograms of pure PVA and starch.

Tensile properties

The tensile properties of the polymer films were measured with an AGS-10k NG universal testing machine (Shimadzu, Japan). The test specimens were in the form of dumbbells according to ASTM D 638. The gauge length was 50 mm, and the crosshead speed was 20 mm/min. The reported data are the averages of five measurements.

X-ray photoelectron spectroscopy (XPS) analyses

The surface of the samples was analyzed with a Kratos Axis 165 X-ray photoelectron spectrometer. The X-ray gun was operated at a 15-kV voltage and 20 mA. Survey and high-resolution spectra were collected with 80- and 40-eV pass energies, respectively. The pressure in the analyzer chamber was approximately 10^{-8} Torr. A thin film 0.1 mm thick was used for XPS analysis. Peak fitting and presentation output were produced by an integrated Vision 2 control and information system. All spectra were charge-balanced and energy-referenced to C1s at 284.6 eV. The total acquisition time per sample was 15 min.

RESULTS AND DISCUSSION

DSC analyses

Figure 1 shows DSC thermograms of pure PVA and starch. Pure PVA has a T_g of 70.9°C and a T_m of 194.6°C. The T_g , T_m , and enthalpy values of the starch-PVA blends and the borax-crosslinked blends are listed in Table I. The DSC endotherms of the starch-PVA blends (Fig. 2) show that T_g or T_m did not shift much, to either lower or higher temperatures, with increasing or decreasing amounts of starch, but the melting enthalpy (ΔH) of PVA changed in the blends.¹⁹ Starch is amorphous and hygroscopic in nature and does not have a definite T_g or T_m . The T_g value for pure starch could not be observed in this work.

The DSC trace (first scan) of the starch shows a broad endothermic peak from 23°C up to a tempera-

TABLE I
Thermal Characteristics of Starch–PVA Blends, Blends Treated with Plasticizer, and Borax-Crosslinked Blends

System		T_g	T_m	ΔH (J/g)
Starch:PVA	20:80	71.1	190.8	29.3
	30:70	72.2	191.8	27.0
	40:60	71.3	190.3	25.1
	50:50	72.4	190.0	24.7
Starch–PVA blend (20:80) glycerol (%)	5	69.0	188.8	15.5
	10	67.1	176.8	11.3
	15	62.1	176.3	9.6
	20	57.6	162.3	8.1
Starch–PVA blend (20:80) PEG (%)	5	67.7	192.3	11.2
	10	61.9	189.8	10.7
	15	58.0	188.5	10.2
	20	51.9	178.3	6.2
50:50:4	SPB-1A	44.5	186.0	16.7
40:60:4	SPB-2A	38.6	187.5	18.5
30:70:4	SPB-3A	38.4	129.3	20.8
20:80:4	SPB-4A	53.0	186.1	22.2
50:50:8	SPB-1B	37.1	147.0	14.4
40:60:8	SPB-2B	35.0	185.8	17.9
30:70:8	SPB-3B	30.2	178.3	20.4
20:80:8	SPB-4B	31.8	147.1	20.5
40:60:12	SPB-2C	21.7	142.0	7.0
20:80:12	SPB-4C	38.5	135.0	10.1
Starch:PVA:Gly (42.5:42.5:15; <i>in situ</i>)	SPGB-2.0	35.6	156.0	8.9
	SPGB-2.5	45.3	147.8	4.6
	SPGB-3.0	54.8	147.8	1.9
Posttreated (42.5:42.5:15):8	SPGB-8	34.0	133.3	9.1

ΔH values were normalized with respect to the PVA content.

ture greater than 160°C. The enthalpy of the process was 239.5 J/g. The peak was assigned to the gelatinization of the material, which could be due to the disruption of the hydrogen bond. The enthalpy of transition strongly depended on the moisture content. The endothermic peak observed in the pure starch was always observed in the blends, but with a smaller area.²⁰ The absence of a clear T_g for starch may be due to the following factors: amorphous chains surrounded by crystalline domains, the presence of moisture, physical crosslinks inhibiting the movements of the amorphous chain segments, and the presence of intercrystalline phases not showing normal thermal behavior.^{21–25}

Plasticizers are low-molecular-weight, nonvolatile liquid substances. They were added to the polymers to improve their flexibility, processibility, and compatibility. With an increasing amount of glycerol, T_g of the blends decreased. The T_g value of a blend (20:80 starch/PVA) with 5% glycerol was 69.0°C, whereas a blend formulated with 20% glycerol had a T_g of 57.6°C. T_m of a 20% glycerol-plasticized blend was 28°C lower than that of the pure blend (Table I). The ΔH values of starch–PVA blends plasticized with 5 and 20% glycerol were 15.5 and 8.1 J/g, respectively. Similarly, a decrease in T_g , T_m , and ΔH with increasing PEG concentration was observed for the blends. The reduction in T_g , T_m , and ΔH was attributed to the

reduction in the cohesive forces of attraction between the polymer chains. The plasticizer molecules penetrated the polymer matrix because they were smaller than the polymer molecule. As a result, polar attractive forces were established between the plasticizer and chain segments, which were responsible for the reduction of the cohesive forces and, therefore, a reduction of T_g .

Thermal characteristics of the crosslinked starch–PVA blends (without the plasticizer)

DSC thermograms of starch–PVA crosslinked blends are shown in Figure 3. Borax forms a di-diol complexation with PVA, in which four —OH groups of PVA form bonds with boron.²⁶ Because the molecules of both starch and PVA are capable of forming hydrogen bonds, we expected that some specific interactions could be formed between the molecules of different species. Several factors, such as the main-chain rigidity, moisture content, crosslinking density, and chemical structure of the crosslinker could influence the T_g values of the crosslinked films. The PVA hydroxyl groups contributed, by hydrogen bonding, to the stiffness of the linear polymer. By introducing borax (4%) as a crosslinking agent to pure PVA, we found that T_g decreased from 70.9 to 54°C. This could be explained by the regularity of the —OH groups already existing

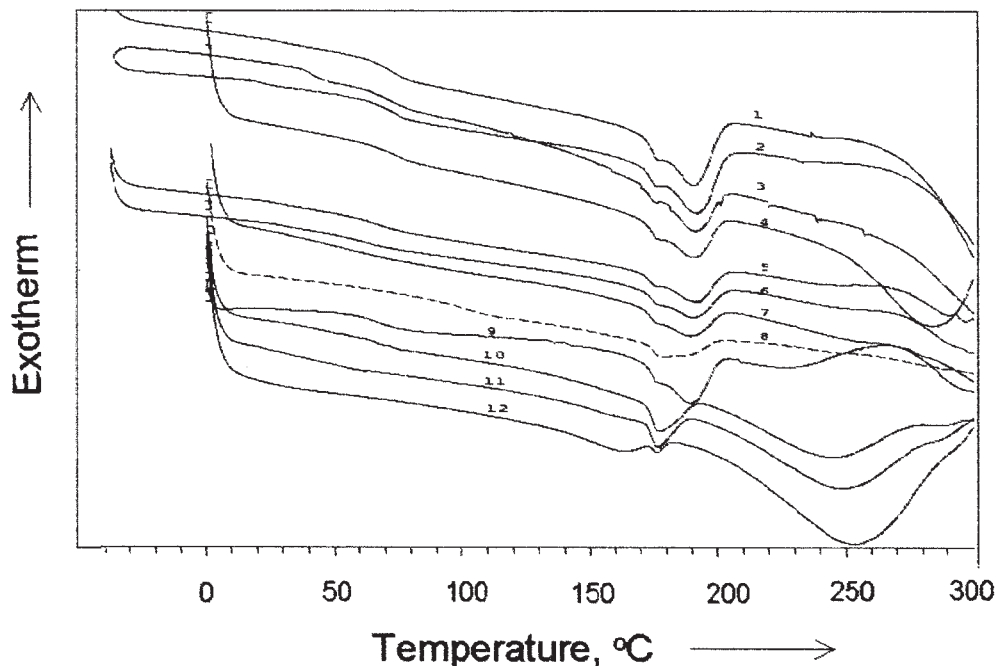


Figure 2 DSC thermograms of (1–4) starch–PVA blends with increasing starch content, (5–8), starch–PVA blends (treated with PEG) with increasing PEG content, and (9–12) starch–PVA blends (treated with glycerol) with increasing glycerol content.

in PVA, which were lost because of crosslinking. We also found that with an increasing concentration of borax, the enthalpy and crystallinity decreased. When pure starch was crosslinked with borax, the films appeared transparent and highly brittle. Thermograms showed an absence of a clear T_g , but there was a shift in T_m . The T_g values of SPB-1A and SPB-1B were 44.5 and 37.1°C, respectively. Simi-

larly, for other crosslinked blends, T_g was less than the T_g values observed for pure PVA and starch–PVA blends. For all the crosslinked systems, T_m and ΔH decreased with an increasing concentration of the crosslinker.

Crosslinked films prepared by the *in situ* method and containing glycerol as a plasticizer showed lower ΔH values. This fact may be attributed to the reduction

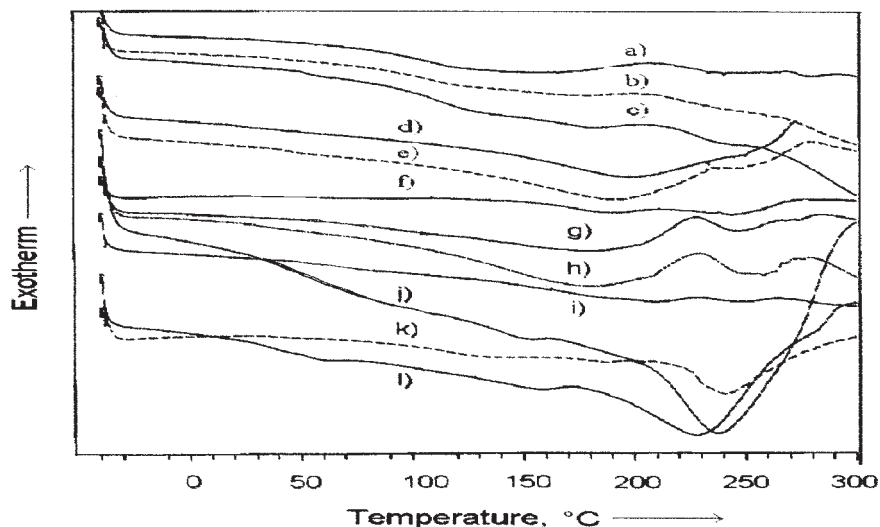


Figure 3 DSC thermograms of starch–PVA crosslinked blends: (a–c) 4% borax-crosslinked blends with increasing PVA content, (d–f) 12% borax-crosslinked blends with increasing PVA content, (g–i) 8% borax-crosslinked blends with increasing PVA content, and (j–l) glycerol-plasticized borax-crosslinked blends with increasing borax content (*in situ*).

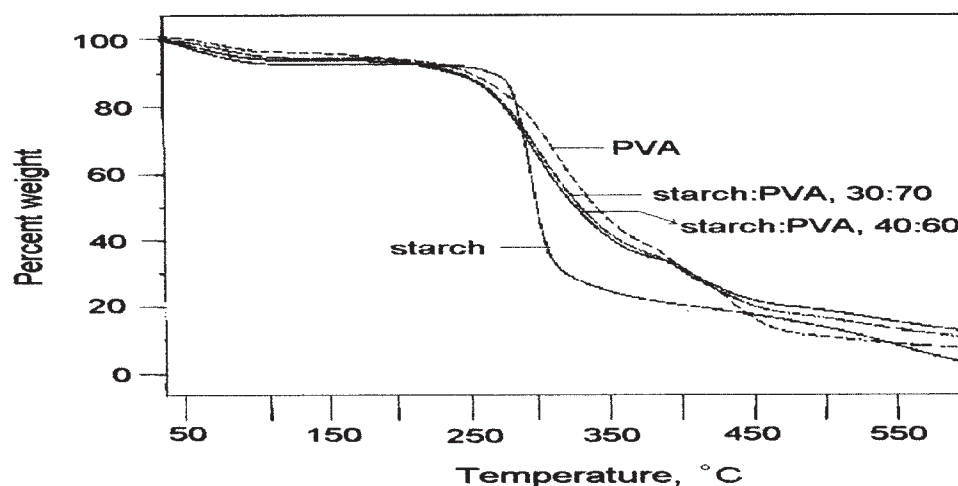


Figure 4 TG curves of native starch and PVA and starch-PVA blends.

in the intermolecular forces due to the presence of borax-crosslinked glycerol networks.

TGA

The pure starch-PVA blends and the blends crosslinked by two methods (*in situ* and posttreatment) were subjected to thermal degradation studies. The thermogravimetry (TG) curve of the native starch showed a one-step decomposition pattern with the onset temperature (T_{ON}) at 279°C and the endset temperature (T_{EN}) at 310°C. Pure PVA showed two-step decomposition: the first step (T_{1ON}) began around 200°C, and the second step (T_{2ON}) began around 382°C (Fig. 4). The first step of weight loss could be attributed to the loss of loosely bound water, accompanied by the formation of volatile disintegrated products. The residue was predominantly macromolecules of a

polyene structure. Further heating yielded carbon and hydrocarbons. T_{EN} was around 460°C. The decomposition of the pure starch-PVA blends was a two-step process. The shoulder in the starch degradation peak that was observed for all the blends may have been due to the different degradation rates of amylose and amylopectin, the former probably being degraded first because of its linear structure.²⁷ T_{1ON} slightly increased with increasing PVA content in the blend.

The TG curves of the starch-PVA films treated with borax (posttreated and without the plasticizer) showed two-step decomposition. T_{1ON} for the borax-crosslinked blends were lower than that of the corresponding pure blend, as shown in Table II, whereas the weight residue at 450°C increased after crosslinking. The TG data suggested that the thermal stability of the borax-crosslinked films for the second stage of decomposition was higher than that of the pure blend.

TABLE II
Thermal Decomposition Temperature and Char Yield of Starch-PVA Blends (50:50) Treated with Borax

		Characteristic TG temperatures						Percentage of weight at 240°C	Char yield at 450°C (%)
		T_{1ON} (°C)	T_{1max} (°C)	T_{1EN} (°C)	T_{2ON} (°C)	T_{2max} (°C)	T_{2EN} (°C)		
Starch-PVA	40:60	258.7	294.0	344.4	389.8	403.5	451.2	89.5	20.9
	30:70	262.9	299.3	354.7	375.0	398.9	455.2	90.1	19.2
Starch-PVA	4	237.2	268.6	315.3	389.0	404.2	440.3	81.7	24.6
50:50 blends (borax %)	8	252.5	282.8	327.0	395.2	411.7	451.1	75.4	27.9
SPGB-12	12	222.5	263.1	322.2	382.4	401.2	461.5	—	—
Starch-PVA	4	241.8	276.8	343.1	397.2	413.2	455.3	83.4	21.9
40:60 blends (borax %)	8	244.8	265.6	382.4	387.8	407.2	459.9	82.5	24.7
	12	250.5	267.5	393.8	392.5	411.0	465.5	87.8	33.1
Starch-PVA	4	223.9	279.8	337.9	392.1	405.7	451.8	84.3	19.1
30:70 blends (borax %)	8	240.2	269.3	331.2	382.4	408.7	442.1	85.5	26.3
	12	248.3	273.1	350.2	391.3	412.4	449.9	83.6	26.5
Starch-PVA	4	245.5	308.3	330.7	383.7	395.9	452.5	83.5	17.1
20:80 blends (borax %)	8	223.6	267.1	325.5	389.2	398.2	449.9	87.1	37.2
	12	241.6	267.1	346.9	393.5	408.7	448.5	86.8	27.1

TABLE III
Thermal Decomposition Temperature and Char Yield of Starch-PVA Blends (50:50) Treated with Borax and 15% Glycerol Prepared by an In Situ Method

Borax	T_{1ON} (°C)	T_{1EN} (°C)	T_{2ON} (°C)	T_{2EN} (°C)	T_{3ON} (°C)	T_{3EN} (°C)	Conversion (%) at 340°C
SPGB-2	168.5	231.7	261.8	280.0	400.9	402.0	13.4
SPGB-2.5	175.7	240.0	263.3	345.0	402.8	461.9	14.0
SPGB-3	185.1	246.5	272.6	370.9	417.4	483.5	14.9

The thermal stability of the starch-PVA films increased (within some experimental error) with increasing borax concentration, as observed from a comparison of the char yields at 450°C. TG curves of borax-crosslinked blends are shown in Figures 5 and 6.

The T_{1ON} values of the borax-crosslinked films prepared by the *in situ* method were between 168.5 and 185.1°C, being much lower than the values of those prepared by the posttreatment method and the pure blends, and they showed three-step degradation [Table III and Fig. 5(a-c)]. The probable cause of the additional degradation step was the breakdown of the borax-crosslinked glycerol matrix, which degraded during the first stage of decomposition. The E values of all the samples calculated by the Broido and Coats-Redfern methods are shown in Table IV.

The E_1 (activation energy of the first decomposition step) values, calculated by the Broido method for starch-PVA blends with two different compositions (40:60 and 60:40), were 56.1 and 54.2 kJ/mol, and the E_2 (activation energy of the second decomposition step) values ranged from 22.2 to 23.9 kJ/mol (not shown in the table). The observed E values suggested that for the starch-PVA blends with increasing PVA content, increased E_1 and E_2 values were observed. Similar observations were found for E_1 and E_2 values calculated with the Coats-Redfern equation. Both methods showed a good data fit with

correlation coefficients greater than 0.99. The order of decomposition, as calculated by the Coats-Redfern method for the first stage (n_1) and second stage (n_2), suggested a first-order decomposition of the pure blends (not shown in the table). For pure blends, E_2 was less than E_1 .

The starch and PVA ratio of the crosslinked films had an enormous influence on the thermal stability and E values of the thermal decomposition of the final materials. The probable cause of this behavior was the individual decomposition mechanism coupled with other ionic forces, which produced a complex mode of decomposition and a generation of bond formation between PVA/starch and borax. The resulting three-dimensional network behaved differently than the pure blends. The effect of the starch/PVA ratio on the thermal decomposition of the crosslinked films suggested that with increasing PVA content, E_1 first increased and then decreased, whereas E_2 increased. Let us consider the SPB-A series of E data calculated by the Broido method (Table IV). The E_1 value of SPB-2A was 38.5 kJ/mol, and that of SPB-3A was 42.4 kJ/mol. E_1 of SPB-4A was 38.9 kJ/mol. The same trend was followed in the B and C series with both methods. The E_2 values of SPB-2A, SPB-3A, and SPB-4A were 26.4, 28.4, and 33.4 kJ/mol, respectively. Similar observations were found for both the E_1 and E_2 values of the crosslinked films, as calculated by the Coats-Redfern

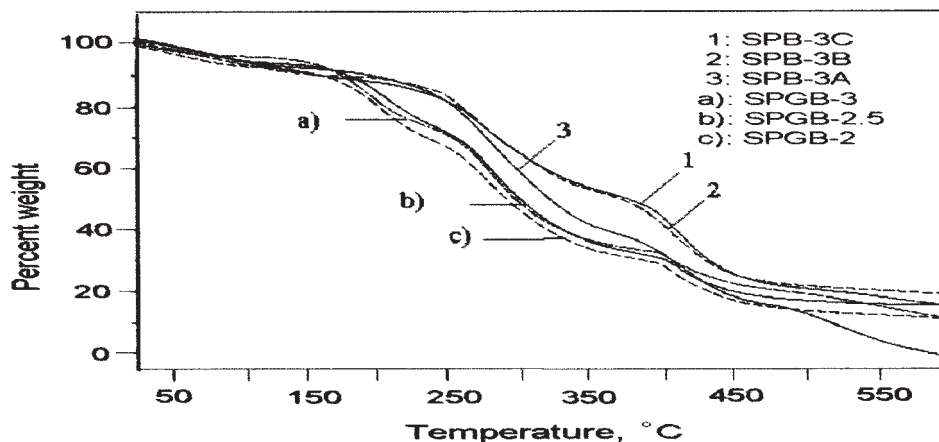


Figure 5 TG curves of (1-3) borax-crosslinked blends and (a-c) glycerol-plasticized borax-crosslinked blends.

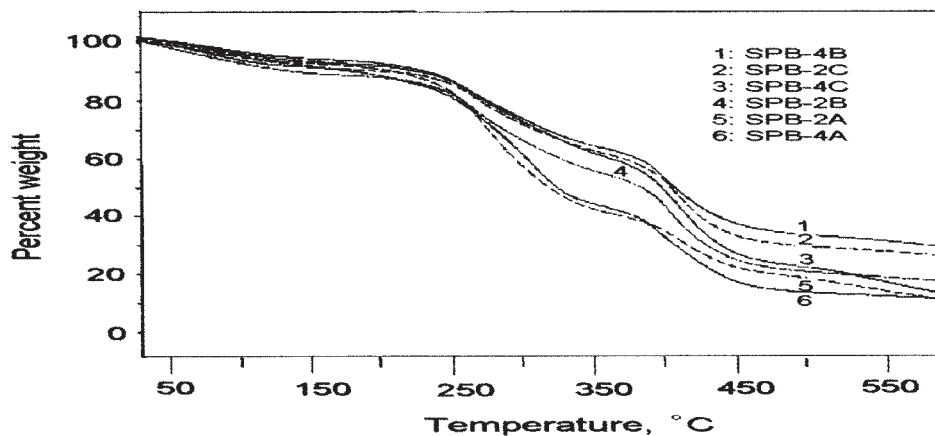


Figure 6 TG curves of borax-crosslinked blends.

equation. Both methods showed a good data fit for the crosslinked blends with correlation coefficients greater than 0.99. The n_1 and n_2 values, as calculated by the Coats–Redfern method, were 2.5–3.0 and 2.5–4.0, respectively. The E_1 values of SPB-2A, SPB-2B, and SPB-2C were 38.5, 29.6, and 27.9 kJ/mol, respectively. The E_2 values were 26.4, 30.7, and 35.3 kJ/mol, respectively. This suggested that E_1 decreased and E_2 increased with increasing crosslinker concentration. The reduction of E_1 with an increasing sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) concentration was probably due to the increasing strain due to the excessive crosslinking. Generally, the strained bonds or weakest bonds with the lowest bond dissociation energies broke during the first stage of decomposition and resulted in a strain-free crosslinked intermediate (after the first stage of decomposition) that decomposed at high temperatures and corresponded to the second stage of degradation. The increasing trend of E_2 with increasing borax content suggested that the strain-free crosslink intermediate contained more effective crosslink points; that is, the crosslink density increased with an increase in the $\text{Na}_2\text{B}_4\text{O}_7$ concentration, and this resulted in more thermal stability in the second decomposition zone.

XPS analyses

For native PVA, native starch, PVA–starch blends, and PVA–starch borax-crosslinked systems, XPS survey scan spectra were recorded over the binding energy range of 0–1200 eV with a pass energy of 80 eV (figure not shown). In all the survey scans, the presence of oxygen (1s) and carbon (1s) at the surface was observed. In starch–borax, PVA–borax, and starch–PVA–borax films, in addition to O1s and C1s, peaks due to Na (1s) and B (1s) were also seen. High-resolution narrow XPS scans were recorded for the elements observed in the survey scan with a pass energy

of 40 eV. The observed C1s spectra could be deconvoluted into three or four components, and the binding energies could be attributed to energies distinct for substituted carbon moieties. The observed C1s peaks for pure PVA (figure not shown) at 284.7, 285.5, and 288.3 eV could be attributed to $-\text{C}-\text{C}-/\text{C}-\text{H}-$, a carbon singly bonded to one oxygen atom ($-\text{C}-\text{O}-$), and carboxylic groups ($-\text{O}-\text{C}=\text{O}-$), respectively. The nonhydrolyzed acetate group in PVA contributed 6.0% in the C1s spectrum.²⁸ The presence of the $\text{C}-\text{O}-\text{B}$ bond in the borax-crosslinked PVA films was difficult to resolve, and thus the deconvoluted spectrum showed three peaks associated with $\text{C}-\text{H}/\text{C}-\text{C}$, $\text{C}-\text{O}$, and $\text{O}-\text{C}=\text{O}$ [Fig. 7(a)]. With the addition of pure starch to PVA, an additional peak at 286.5 eV was observed that was due to the presence of $-\text{O}-\text{C}-\text{O}-$ bonds in starch [Fig. 7(b)]. The deconvoluted spectrum of borax-crosslinked starch showed three peaks, which were due to $\text{C}-\text{H}/\text{C}-\text{C}$, $\text{C}-\text{O}$, and $\text{O}-\text{C}-\text{O}$ bonds [Fig. 7(c)]. When a crosslinked blend film (starch/PVA/

TABLE IV
E Values of Starch–PVA Blends Posttreated with Borax as Calculated with the Broido and Coats–Redfern Methods

Sample	Starch: PVA: Borax	Broido (kJ/mol)		Coats–Redfern (kJ/mol)	
		E_1	E_2	E_1	E_2
SPB-2A	40:60:4	38.5	26.4	42.6	50.0
SPB-2B	40:60:8	29.6	30.7	34.8	54.2
SPB-2C	40:60:12	27.9	35.3	29.4	66.9
SPB-3A	30:70:4	42.4	28.4	48.7	56.8
SPB-3B	30:70:8	34.8	31.1	35.5	55.0
SPB-3C	30:70:12	30.6	37.3	32.1	58.5
SPB-4A	20:80:4	38.9	33.4	42.8	57.6
SPB-4B	20:80:8	32.9	35.2	34.3	68.6
SPB-4C	20:80:12	27.6	44.2	28.9	69.7

following factors: (1) the intramolecular and intermolecular crosslinking reactions of PVA and borate, (2) the charge repulsion among the complex units, and (3) the electrostatic screen effect on the negative-charge complex unit by free ions. On the basis of the experimental data, a scheme for the proposed structures for the PVA–borax complex in water with various borax concentrations was drawn by Chen and Yu.²⁶ The authors observed the dominating nature of the intermolecular reactions between PVA and borate ions at lower concentrations of borax, and the polymer chain length increased with the borax concentration. Therefore, the mechanical properties of the crosslinked blends depended not only on the extent of crosslinking but also on the electrostatic interactions.

Pure starch–PVA films exhibited poor mechanical properties because of the amorphous nature of starch. Starch–PVA films treated with glycerol were flexible and showed lower tensile strength and higher elongation than the pure starch–PVA blends. Starch–PVA blend films crosslinked with borax without any plasticizer had higher tensile strength and lower elongation at break than pure starch–PVA blends and glycerol-treated samples.

Crosslinked starch–PVA blend films treated with glycerol exhibited lower tensile strength and higher elongation than the pure starch–PVA films. Thus, the mechanical properties of the starch–PVA blends depended on the starch content and the extent of crosslinking by borax.

CONCLUSIONS

Starch–PVA blends in the presence and absence of a plasticizer were prepared and characterized. There was no change in T_g for pure blends prepared in the absence of a plasticizer, whereas a change in the enthalpy was observed as the starch content increased. For starch–PVA blends prepared in the presence of glycerol and PEG, T_g and T_m shifted to lower temperatures as the plasticizer concentration increased.

For starch–PVA blends treated with borax, T_g was lower than T_g of pure PVA, and an endotherm in the region of 150–250°C was found at higher concentrations of borax. For all the crosslinked systems, T_m and ΔH decreased with an increasing concentration of the crosslinker.

The thermal stability of the blends treated with borax was more than that of the pure blends. For the pure blends, E_2 was lower than E_1 . For starch–PVA blends treated with borax, E_2 was higher than E_1 , as

observed by the Coats–Redfern method, whereas the Broido method showed some exception to the trend.

High-resolution XPS analysis provided a method of differentiating the presence of different types of carbon bonds in the various starch–PVA systems.

The mechanical properties of the starch–PVA blends improved after treatment with borax and were higher than those of the pure blends. The tensile strength of the blends increased at the expense of elongation as the concentration of borax in the blends increased.

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