Thermal and Surface Characterization of Plasticized Starch Polyvinyl Alcohol Blends Crosslinked with Epichlorohydrin

B. Sreedhar,[1] D. K. Chattopadhyay,[2] M. Sri Hari Karunakar,[2] A. R. K. Sastry[2]

[1]*Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India*
[2]*Organic Coatings and Polymers Division, Indian Institute of Chemical Technology, Hyderabad 500007, India*

ABSTRACT: Starch-polyvinyl alcohol (PVA) blends in 2:8 wt % were prepared with various plasticizers such as polyethylene glycol (PEG-200, PEG-400) and glycerol. The crosslinking of starch-PVA blends by epichlorohydrin was carried out in the presence of a plasticizer in situ. The obtained films were analyzed by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), dynamic mechanical and thermal analysis (DMTA), and X-ray photoelectron spectroscopy (XPS), and remarkable changes in thermal stability and glass-transition temperature have been observed on plasticizing and crosslinking in different concentrations. Different kinetic models such as Coats–Redfern, Broido, Friedman, and Chang were used to calculate the kinetic parameters of thermal decomposition. The results suggest that the thermal stability and activation energy of thermal decomposition passes through maxima at a critical concentration of plasticizer and increases with increasing crosslinker concentration. High-resolution C 1s XPS analysis was used to provide a method of differentiating the presence of various carbons associated with different environment in the films. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 25–34, 2006

Key words: starch-PVA blend; crosslinking; thermal; XPS

INTRODUCTION

The high molecular weight and hydrophobic properties of petroleum polymers have resulted in a high degree of chemical stability. Thus, conventional plastics manufactured from these polymers are generally recalcitrant and degrade very slowly in the environment. Environmental as well as health issues associated with the recycling and disposal of single-use consumer products made from such recalcitrant plastics are enormous,[1–3] and the scientific community is in search for an alternative biodegradable plastic that can degrade easily in the natural environment.[4] The approach toward formulating biodegradable plastics is to modify the synthetic polymers by introducing easily degradable linkages or to blend with natural degradable polymer. Since synthesis of new biodegradable polymer is a time consuming process and may not always meet the customer criteria at low cost,[5] the easiest way to formulate a polymeric material with improved properties is to blend polymers so that the resulting material has properties superior to those of the individual components.[6] Therefore, the properties of the blend materials can be tailored to meet the customer requirements and specification for new application with satisfactory balance of wide range of material properties.[5] Quite often, starch-based polymers are blended with high-performance polymers [e.g., aliphatic polyesters and polyvinyl alcohols (PVA)] to achieve the necessary performance properties for various applications. Starch-PVA blend films are one of the most popular biodegradable plastics, and are widely used in packaging and agricultural sector.

The use of abundantly available starch is increasing in many applications as it increases the biodegradability of plastic at low cost.[7] The sources of starch include crops such as corn (maize), wheat, or potatoes. Starch is a linear polymer (polysaccharide) made up of repeating glucose units linked by glucosidic linkages in the 1–4 carbon positions. There are two major molecules in starch: amylose and amylopectin. The α linkage of amylose starch allows it to be flexible and digestible. Starch-based biodegradable plastics may have starch contents ranging from 10% to greater than 90%. As the starch content increases, the polymer blends become more biodegradable.

PVA is well suited for making biodegradable blends with natural polymers due to its good film-forming capability[2] and water solubility. The polarity of PVA helps the blend in accelerating the hydrolytic attack by atmospheric moisture that results in breakdown in the sugar molecules of natural polymers. In addition, the

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Correspondence to: B. Sreedhar (sreedharb@iict.res.in).

incorporation of PVA into starch improves the thermal as well as mechanical properties of the material and thus modifies the polymer structure at both molecular and morphological levels.[8] For a further improvement in mechanical properties of starch-PVA blends, researchers from time to time have added different amounts of plasticizers such as polyethylene glycol (PEG) and glycerol.[8–11] A plasticizer is a low-volatile organic compound that causes a decrease in polymer glass-transition temperature (T_g) and an increase in flexibility and workability of the films.[9]

Crosslinking agent enhances not only the thermal properties but also the mechanical properties of starch-PVA blends by reinforcing the intermolecular binding with the introduction of covalent bonds to supplement natural intermolecular hydrogen bonds.[10] Epichlorohydrin has been used as a crosslinking agent of starch by forming the glycidylether linkage through the reactions with hydroxyl groups of polysaccharide.[12–14] Additionally, PVA can also react with epichlorohydrin because it contains a number of hydroxyl groups in its structure. Therefore, while preparing the PVA-starch plasticized blend films, the poor mechanical properties of the blends can be overcome by simultaneous crosslinking reactions of epichlorohydrin with the hydroxyl groups of starch, PVA, and plasticizer.[15]

The objective of this work was to study the thermal decomposition profiles of various plasticized and epichlorohydrin crosslinked starch-PVA blends. The blends with different concentrations of PEG 200, PEG 400, and glycerol plasticizers were prepared and crosslinked with epichlorohydrin. The plasticized and crosslinked films were subjected to structural characterization with Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), dynamic mechanical and thermal analysis (DMTA), and a surface tool X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Materials

Native water-soluble starch (amylose content ~21%), epichlorohydrin, and sodium hydroxide from S. D. Fine Chemicals (Mumbai, India) and PVA (NH-17R) from Nippon Ghosai (Japan) were used in making the blends. Deionized water was used in all the cases. Glycerol, PEG of molecular weights 200 (PEG-200) and 400 (PEG-400) from Aldrich (Milwaukee, WI) were used as-received.

Preparation of starch-PVA blend films

A calculated amount of starch and PVA in 2 : 8 weight ratios were mixed homogenously with stirring in 75 mL of deionized water in a beaker and heated in a

water bath for 3 h at 80°C. At the end, the mixture was cooled to room temperature, and films were casted onto clean glass dishes. Starch-PVA films prepared by this process were brittle and opaque. Two distinct phases of starch and PVA were observed.[11] To make flexible and transparent films with good mechanical properties, plasticizers PEG-200, PEG-400, and glycerol were added to the starch-PVA blends during the preparation. Films were prepared with various concentrations of plasticizers. The blended solutions were casted and kept at 25°C for film formation and complete drying for 2–3 days. Fungal growth was observed during the storage of films and that was avoided by addition of a small amount of formaldehyde. The plasticized films were named with the first letters of the raw material (P for PVA and S for starch) and X, Y, Z for plasticizers PEG-200, PEG-400, and glycerol respectively. The subscripts on the plasticizer, 1–5, indicate 5, 10, 15, 20, and 25 wt % of the plasticizer respectively. For example, PSX_2 represents PVA-starch (8 : 2) plasticized film prepared with 10 wt % PEG-200 plasticizer.

In situ crosslinking of starch-PVA films

Calculated amount of starch and PVA powders were mixed homogenously with stirring in 75 mL of deionized water in a beaker. Then epichlorohydrin (5–20 wt %) was added to the mixture and pH was adjusted to 10 using NaOH solution. The addition of NaOH was carried out dropwise, and pH was continuously checked with a pH paper. The crosslinking reaction was carried out at 40°C for 2 h. After the completion of the reaction, plasticizers (PEG-200, PEG-400, and glycerol) of 10 wt % were added and the mixture was cooled to room temperature. The mixtures were casted on glass petridish and allowed for the film formation. The crosslinked films were named with the first letters of the raw material, E is for crosslinker epichlorohydrin, A–D for the amount of crosslinker 5–20 wt %, and X, Y, and Z for plasticizers PEG-200, PEG-400, and glycerol respectively. The subscript on the plasticizer indicates the concentration of the plasticizer added. For example, $PSECX_2$ represents PVA-starch crosslinked film prepared from an 8 : 2 weight ratio of PVA and starch, subjected to 15 wt % crosslinking and 10 wt % plasticizer treatments with PEG-200 respectively.

FTIR analysis

FTIR spectra of the crosslinked films on dried KBr pellet were obtained using a Thermo Nicolet Nexus 670 spectrometer. Each sample was scanned 64 times with a resolution setting of 4 cm^{-1} and averaged to produce each spectrum.

Dynamic thermogravimetric measurements

Thermogravimetric measurements were carried out on a Mettler-Toledo TGA/SDTA 851^e thermal system (Zurich, Switzerland) from 25 to 600°C in N_2 environment (flow rate, 20 mL/min) at a heating rate of 20°C/min. The sample size was between 10 and 12 mg.

Kinetic model

TGA is a technique used to measure changes in the weight (mass) of a sample as a function of temperature and/or time. In TGA, typical weight loss profiles are analyzed for the amount or percent of weight loss at any given temperature, the amount or percent of non-combusted residue at some final temperature, and the temperature of various degradation steps. The derivation of kinetic parameters in the study of the polymer decomposition by exploiting thermogravimetric (TG) data is useful in the determination of rate constants, activation energies (E; kJ mol^{-1}), reaction orders (n), and pre-exponential factors (Z; min^{-1}).[11] The values of kinetic triplet (E, n, and Z) depend on several factors such as the flow rate and the nature of gas flowing, heating rate, sample mass, as well as the mathematical methods used to evaluate the data.[11]

A reaction rate in TGA can be defined as the derivation of the conversion with respect to time. 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[11]:

$$\alpha(t) = [W_0 - W_t]/(W_0 - W_\infty) \qquad (1)$$

where w_t is the mass at any degradation time, w_0 is the initial mass, and w_∞ is the final mass at the end of the degradation process.

All the kinetic studies assume that rate of conversion, $d\alpha/dt$, is a linear function of temperature-dependent rate constant, k, and a temperature-independent function of conversion, α, that is:

$$d\alpha/dt = k(T)f(\alpha) \qquad (2)$$

where $f(\alpha)$ depends on the particular decomposition mechanism.

The temperature dependence of the kinetic constant can be expressed according to the following Arrhenius equation:

$$k(T) = Z\ e^{-E/RT} \qquad (3)$$

where the pre-exponential factor (Z; min^{-1}), is assumed to be independent of temperature, T is the absolute temperature, and R is the universal gas constant.

Combination of eqs. (2) and (3) gives:

$$d\alpha/dt = Zf(\alpha)e^{-E/RT} \qquad (4)$$

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

$$d\alpha/dt = Q(d\alpha/dT) = k(T)f(\alpha) \qquad (5)$$

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

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

$$g(\alpha) = (ZE/QR)p(x) \qquad (6)$$

where $p(x) = \int_\infty^x [exp(-x)/x^2]dx$ and $x = E/RT$.

$g(\alpha)$ is the integral form of the conversion dependence function.

To solve the function $p(x)$, several differential as well as integral methods have been developed. In the present study, the equations used are given in the following section:

Coats–Redfern equation[16]

Coats and Redfern provided an approximation to the integral of eq. (6) and thus obtained the following expressions:

$$\ln[-\ln(1-\alpha)/T^2] = \ln[ZR/QE(1-2RT/E)]$$
$$- E/RT \text{ for } n = 1 \quad (7)$$

where Q is the linear constant heating rate and is equal to dT/dt. The plot of $\ln[-\ln(1 - \alpha)/T^2]$ *versus* $1/T$ gives the value of activation energy in the regression analysis. The slope of this plot gives the value of E/RT, from which we get the value of the activation energy.

When n is not equal to 1, the equation takes the form:

$$\ln[1 - (1-\alpha)^{1-n}/(1-n)T^2]$$
$$= \ln[ZR/QE\ (1-2RT/E)] - E/RT \quad (8)$$

Thus a plot of $\ln[1 - (1 - \alpha)^{1-n}/(1 - n)T^2]$ versus $1/T$ gives the value of E for the correct chosen value of n.

Broido[17] has developed a model and the equation has the form:

$$\ln[\ln(1/Y)] = E/R(1/T) + \text{Constant} \qquad (9)$$

where $Y = (w_0 - w_t)/(w_0 - w_\infty)$ is the fraction of the number of initial molecules not yet decomposed, w_0, w_t, and w_∞ are the weight of the sample at the beginning of TGA evaluation, at time t, and at infinite time $(= 0)$ respectively. Thus a plot of $\ln[\ln(1/Y)]$ *versus* $1/T$ is related to E.

Friedman[18] developed the following equation

$$\ln(d\alpha/dt) = \ln Z + n\ln(1 - \alpha) - E/RT \qquad (10)$$

Therefore, a plot of $\ln(d\alpha/dt)$ versus $1/T$ gives the values of E in the regression analysis from eq. (10).

Chang method[19] is a modified form of Friedman method and uses the equation:

$$\ln[d\alpha/dt/(1 - \alpha)^n] = \ln Z - E/RT \qquad (11)$$

A plot of $\ln[d\alpha/dt/(1 - \alpha)^n]$ *versus* $1/T$ will produce activation energy and order of degradation from the best fit plot in the linear regression analysis.

From time to time the above equations are being extensively used for calculating the activation energies and other parameters to supplement the qualitative thermostability data and this has resulted in considerable controversy in the literature. The controversy arises due to different assumptions and approaches used for solving the function $p(x)$ by different researchers. Budrugeac[20] has suggested that the evaluation of the kinetic parameters of thermal and thermooxidative degradation of a polymeric material using a single TG curve recorded at a certain heating rate does not lead to reliable results. Vyazovkin and Wight[21] have critically analyzed different methods for the evaluation of kinetic triplet (E, Z, and n). These authors noted that different kinetic models ignore the fact that the correlation coefficient and the other statistical measures are subject to random fluctuations. However, some authors[22–26] claim a physical meaning to these parameters, and have shown that a TG curve may be correctly described by several various kinetic models.

Dynamic mechanical analysis

The response of the network to small strain mechanical deformation was measured as a function of temperature using dynamic mechanical thermal analyzer DMTA IV instrument (Rheometric Scientific, USA) in tensile mode. The testing of the plasticized and the crosslinked starch-PVA blends were carried out at a frequency of 1 Hz and with a heating rate of 3°C/min. The approximate dimension of the film samples used was 15 mm × 10 mm × 0.15 mm, and the temperature range of the study was from 30°C to 200°C. Flexural storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) were recorded as a function of temperature.

XPS measurements

The surface of the samples was analyzed using a KRATOS AXIS 165 X-ray photoelectron spectrometer (UK). The X-ray gun was operated at 15 kV voltage and 20 mA. Survey and high-resolution spectra were collected using 80 and 40 eV pass energy, respectively. The analyzer chamber was degasified and pressure in the analyzer chamber was kept as low as $\sim 10^{-8}$ torr. A thin film of thickness 0.3 mm was used for XPS evaluation. Gaussian/Lorentzian in $7:3$ ratio peak deconvolution and presentation output is produced by integrated VISION control and information system software attached with the unit. All spectra are presented charge balanced and energy referenced to C 1s at 284.6 eV.

RESULTS AND DISCUSSION

FTIR spectral studies

Starch and PVA molecules are in general associated with inter- and intramolecular hydrogen bonding in the blends. An increase in the plasticizer concentration resulted in decreasing the cohesive force of attraction between the starch and PVA and increases the hydrogen bonding strength between PVA and plasticizer or starch and plasticizer. The crosslinking of these blends results in a decrease in the intermolecular hydrogen bonds. At first, the lone pair of electrons in the hydroxy functions of starch, PVA, and plasticizer attacks the epoxide ring of epichlorohydrin and makes ether linkages. In the subsequent crosslinking steps, the removal of chloride ions takes place from the bonded epichlorohydrin by S_N^2 mechanism. Therefore, the crosslinking reaction results in a decrease in hydroxyl functionality available for hydrogen bonding and makes random covalent linking between starch, PVA, and plasticizer. In the FTIR spectra of different plasticized and crosslinked starch-PVA blends (figure not shown), we have observed a peak at 2361 cm^{-1}, which is attributed to the atmospheric carbon dioxide. Peaks due to water in the films occur at 1631 and around 3240 cm^{-1}. The latter peak overlaps with the peak due to the O—H stretching of hydroxyl groups. The broad high absorption peak at 3237 cm^{-1} is assumed to arise from the O—H stretching frequencies of PVA, starch, and the absorbed moisture. The band at 1735 cm^{-1} is attributed to the carbonyl functional groups arising from the residual acetate groups that remain after the manufacture of PVA by hydrolysis of polyvinyl acetate or oxidation during manufacturing and processing.[7,27] The peak occurring at 1412 cm^{-1} was due to the deformation vibration of —CH$_2$ in —CH$_2$—OH. Asymmetric flexible vibrational peaks of C—O—C occurred at 1096 and 1027 cm^{-1}. The —CH$_2$ stretching vibration occurred at 2923 cm^{-1}. We also observed a

decrease in intensity of —OH band upon crosslinking with epichlorohydrin.

Thermal studies

Thermal degradation of polymeric materials is a consequence of the fact that the organic macromolecules inside the polymer matrix as well as low-molecular-weight organic molecules are stable only up to a certain temperature range. Their stability depends on the inherent characteristics of the samples as well as the specific interactions associated between the different macromolecules or molecules present in the polymer. These interactions are due to the dipole–dipole interaction, van der Waals, London, and hydrogen bonding forces. Since molecules/macromolecules consist of atoms or groups linked together by covalent bonds, and the strength of these bonds are limited, a high thermal stability of the blend can be explained at the molecular level because of the less scission of chemical bonds under the influence of heat. Chain scission or bond dissociation takes place when the supplied thermal energy exceeds the bond dissociation energy of the respective bond or group. Thermal degradation of PVA has been extensively reported in literature. Below 300°C, the major degradation product reported is water, produced by elimination of the hydroxyl side group.[28] In the case of native starch, different degradation rates of amylose and amylopectin were reported.[29–31] In our earlier study,[11] we have reported the thermal properties of different starch-PVA blends and the borax crosslinked blend. In this study, different plasticized PVA-starch blends and epichlorohydrin crosslinked blends were subjected to thermal studies and the thermal decomposition profiles are shown in Figure 1(a–f). Figure 1(a–c) shows a comparison of the thermograms of PVA-starch blends plasticized with 5–25 wt % of PEG-200, 5–20 wt % of PEG-400, and 5–25 wt % of glycerol blends, respectively. Figure 1(e, f) shows a comparison of the TGA thermograms of 5–20 wt % epichlorohydrin crosslinked and 10 wt % plasticized PEG-200, PEG-400, and glycerol films. The corresponding DTG curves show a single step decomposition profile except for a few samples, where a sort tail of one more step was also observed. The following characteristic thermal data were taken from the TGA computer software and are tabulated in Table I: the onset decomposition temperature (T_{on}), the temperature at which the decomposition rate was maximum (T_{max}), endset decomposition temperature (T_{en}), and percent weight remains at 270 and 500°C respectively. As can be seen from Figure 1(a), the thermal stability of PEG-200 plasticized starch-PVA blends increases with increasing plasticizer concentration and passes through a maximum stability at 15 wt % loading of plasticizer and then started to decrease. The T_{on}, T_{max}, and T_{en} values of these films show an increasing trend upto 15 wt % loading of plasticizer PEG-200 and then started to decrease. Similarly, the percent weight remaining at 270°C were 92.5, 93.0, 96.2, 89.6, and 86.4% for 5, 10, 15, 20, and 25 wt % loading of PEG-200 to starch-PVA blend, respectively (Table I). The polar nature of the plasticizer PEG could have enhanced the hydrogen bonding phenomenon between the lower stable amylose unit and PEG-200 molecule, causing a higher thermal stability up to 15 wt % loading, and beyond that limit the excess plasticizer may remain unassociated with either PVA or starch molecule, which results in lower thermal stability at higher loading content of plasticizer. In Figure 1(b), the stability of starch-PVA blends increases upto 15 wt % loading of plasticizer PEG-400, and showed the lowest stability for the blend at 25 wt % loading of plasticizer. This phenomenon holds good upto the temperature 400°C, and at higher temperatures, 25 wt % PEG-400 loaded sample showed superior stability. The high temperature decomposition of starch-PVA blend consists of the decomposition of the polyene structure of PVA and the residual amylopectin portion of the starch. Therefore, a high weight fraction remaining at 500°C or higher stability above 400°C [Fig. 1(b)] for 25 wt % loaded PEG-400 could be due to the formation of some stable structural intermediate by chain scission and crosslinking between the residual fraction of PEG-400, the polyene structure of PVA, and the residual amylopectin portion of the starch. In the case of glycerol plasticized blends, a 10 wt % loading of plasticizer showed higher thermal stability, and further increase in the plasticizer concentration has resulted in a decrease in the thermal stability [Fig. 1(c)]. In Table I, the T_{on} and percent weight remaining at 270°C for 10 and 25 wt % loaded films were 287.0°C, 91.9% and 237.3°C, 81.3% respectively. The comparison of thermal stability for epichlorohydrin crosslinked films with 10 wt % PEG-200 [Fig. 1(d)] shows a lower stability for 20 wt % crosslinked film at low temperature (near the onset of decomposition), and a high thermal stability at high temperature than the other blends investigated. For instance, the T_{on} values of 10 and 20 wt % crosslinked blends were 290.0 and 278.1°C respectively, whereas the T_{en} values increase with increasing crosslinker concentration from 478.3°C at 5 wt % to 489.1°C for 20 wt %. Similarly T_{max} values also increased from 352.0 for PSX_2EA to 385.0°C for PSX_2ED. This phenomenon could be due to the fact that the steric crowding of different groups at a high crosslinker concentration may act as steric assistance for the thermal decomposition at lower temperature, whereas at higher temperature, the decomposition of side bulky groups by scission or free radical means produce a stable intermediate with higher thermal stability. Figure 1(e) is a comparison of thermal stability of 10 wt % PEG-400 plasticized and epichlorohydrin crosslinked starch-PVA blends with different
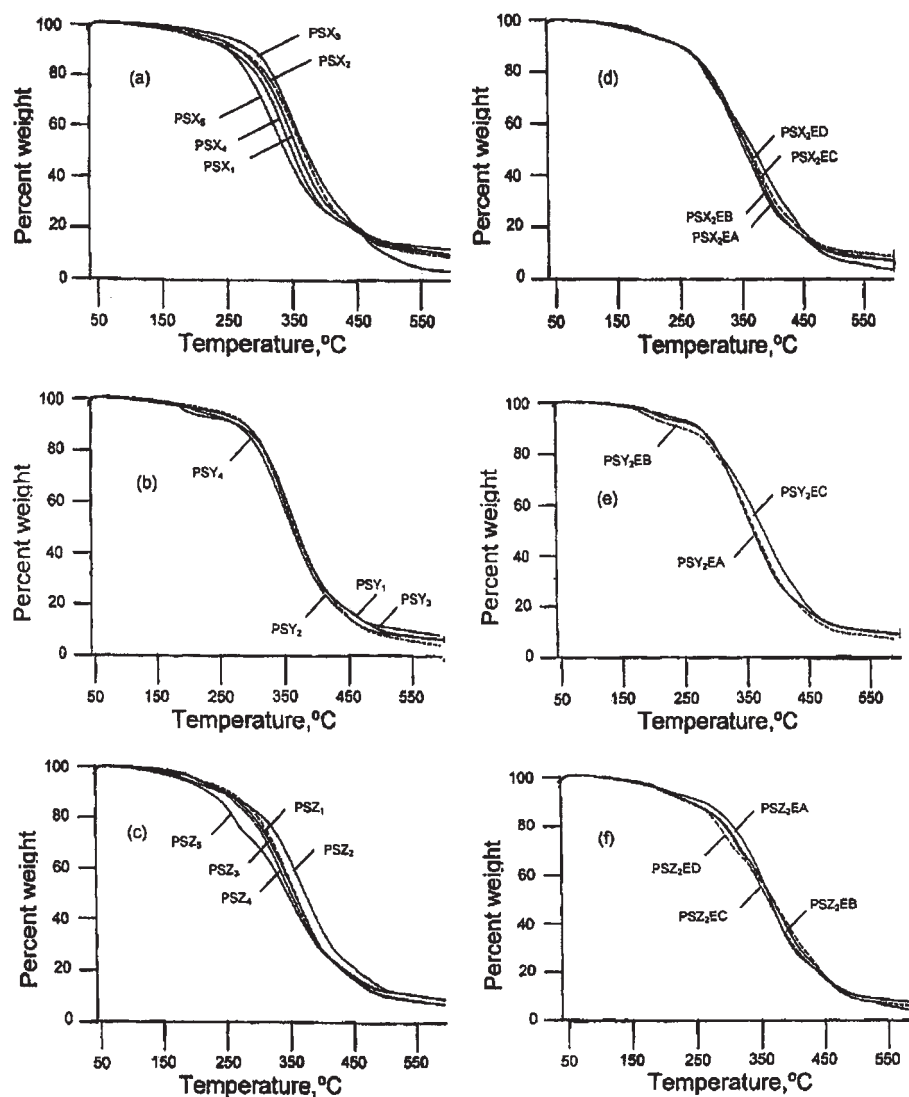
Figure 1 The TGA thermograms of PVA-starch blends plasticized with different wt % of PEG-200 (a), PEG-400 (b), glycerol (c) and the corresponding different wt % epichlorohydrin crosslinked blends with 10 wt % plasticizer PEG-200 (d), PEG-400 (e), and glycerol (f) respectively.

crosslinker content. The corresponding thermal decomposition data show an increasing trend in stability as shown in Table I. For the 10 wt % glycerol plasticized and epichlorohydrin crosslinked starch-PVA blends [Fig. 1(f)], the stability order follows a trend similar to that shown in Figure 2(d). Since the thermal stability is associated with both the initial decomposition temperature and the rate of degradation of the blend, it is useful to determine the kinetic parameters by kinetic analysis for the degradation process. The importance of reliable kinetic analysis cannot be overestimated as it may provide information on the energy barriers of the process as well as offer mechanistic clues. Finding a reliable approach to kinetic analysis presents a certain challenge, as the thermal analysis literature describes a great number of kinetic methods that make use of either single or multiple heating rate

data. The activation energy (E) and the order of decomposition (n) values of all the samples calculated by Coats–Redfern, Broido, Friedman, and Chang methods are tabulated in Table II.

The activation energy values for different amount of PEG-200 plasticized starch-PVA blends show an increasing trend and passes through a maximum at 15 wt % loading. For instance, the E values of 15 and 25 wt % PEG-200 plasticized blends as calculated by Coats–Redfern, Broido, Friedman, and Chang methods were 123.1 and 86.4, 76.4 and 52.3, 82.3 and 41.2, and 90.6 and 39.3, respectively. The order of decomposition n, calculated from Coats–Redfern and Chang methods were between 1.9 and 2.5. The correlation coefficient values in all the calculations show a good data fit with greater than 0.987. Similarly, for PEG-400 and glycerol plasticized blends, an increase in E values

TABLE I
Characteristic Thermal Decomposition Data of Different Plasticized and Epichlorohydrin-Crosslinked Starch-PVA Blends

Sample	T_{on} (°C)	T_{en} (°C)	T_{max} (°C)	Percent weight at 270°C	Percent weight at 500°C
PSX$_1$	293.8	455.2	348.4	92.5	13.6
PSX$_2$	304.7	459.5	358.0	93.0	14.3
PSX$_3$	305.2	465.3	360.2	96.2	17.0
PSX$_4$	285.9	451.5	342.9	89.6	12.4
PSX$_5$	265.1	442.1	325.2	86.4	7.8
PSY$_1$	288.3	481.6	346.7	92.6	12.8
PSY$_2$	292.4	487.7	354.9	95.1	13.6
PSY$_3$	291.7	471.7	350.5	97.1	11.0
PSY$_5$	295.8	474.4	346.7	94.7	10.1
PSZ$_1$	275.5	499.6	350.6	89.1	13.2
PSZ$_2$	287.0	502.3	363.4	91.9	16.2
PSZ$_3$	273.8	484.4	356.6	87.5	15.6
PSZ$_4$	263.5	482.7	338.7	89.0	11.7
PSZ$_5$	237.3	480.5	346.1	81.3	9.7
PSX$_2$EA	284.7	478.3	352.0	89.4	12.6
PSX$_2$EB	290.0	479.2	352.0	90.7	11.1
PSX$_2$EC	286.7	481.7	367.0	89.0	12.8
PSX$_2$ED	278.1	489.1	385.0	89.8	12.1
PSY$_2$EA	286.5	471.0	351.4	93.0	13.4
PSY$_2$EC	284.4	478.7	355.9	90.6	11.2
PSY$_2$ED	273.0	480.0	382.8	93.8	12.9
PSZ$_2$EA	291.4	480.0	360.4	90.8	12.8
PSZ$_2$EA	281.8	483.9	355.8	87.3	13.8
PSZ$_2$EA	287.6	477.6	373.8	90.1	12.6
PSZ$_2$EA	266.9	477.5	384.3	86.5	11.3

with increasing plasticizer concentration was observed upto a critical concentration of the plasticizer, which were 15 and 10 wt % for PEG-400 and glycerol respectively, as shown in Table II. The E values found in all the plasticized starch-PVA blends showed lowest for 25 wt % loading. For the PEG-200, PEG-400, and glycerol 10 wt % plasticized and epichlorohydrin crosslinked starch-PVA blends, an increasing trend in the E values were observed upto 20, 15, and 10 wt % crosslinker concentration, respectively. For instance the E values of 10 wt % PEG-200 plasticized and crosslinked blends as calculated by Broido method were 46.7, 49.8, 52.8, and 64.7 kJ mol^{-1} at 5, 10, 15, and 20 wt % crosslinker, respectively. Other mathematic models used also showed the same trend with good data fit and correlation coefficient values greater than 0.972. The order of decomposition are in between 1.7 and 2.5 for 10 wt % plasticized and crosslinked blends as calculated by Coats–Redfern and Chang methods. For a particular wt % loading of plasticizer, it is very difficult to conclude from Table II the variation in activation energy with different plasticizer used in the studied 2:8 wt % starch-PVA blends. An interesting observation made by comparing the activation energy values of 10 wt % plasticized blends and the corresponding crosslinked blends on the addition of

crosslinker was an initial reduction in E values. Further increase in crosslinker concentration resulted in increase in the E values. For instance, the E values of 10 wt % glycerol plasticized starch-PVA blends with 0, 5, 10, 15, and 20 wt % epichlorohydrin were 49.8, 32.6, 36.4, 39.2, and 51.2 kJ mol^{-1} as calculated by Broido method. Additionally, different kinetic approaches have resulted in significant difference in the kinetic parameters calculated in this study.

Dynamic mechanical analysis

Polymer chemists recognize that the polymer films are viscoelastic, and to study their behavior, several techniques are available. Of them, DMTA is one that measures the dynamic mechanical properties of the films. DMTA measures the deformation of a material in response to vibrational forces. In principle, DMTA technique detects the viscoelastic behavior of polymeric materials and yield quantitative results for the tensile storage moduli E' and the corresponding loss moduli E''; the loss factor tan δ can then be expressed as the quotient of loss and storage, E''/E'. E' and E'' characterize the elastic and viscous component of a
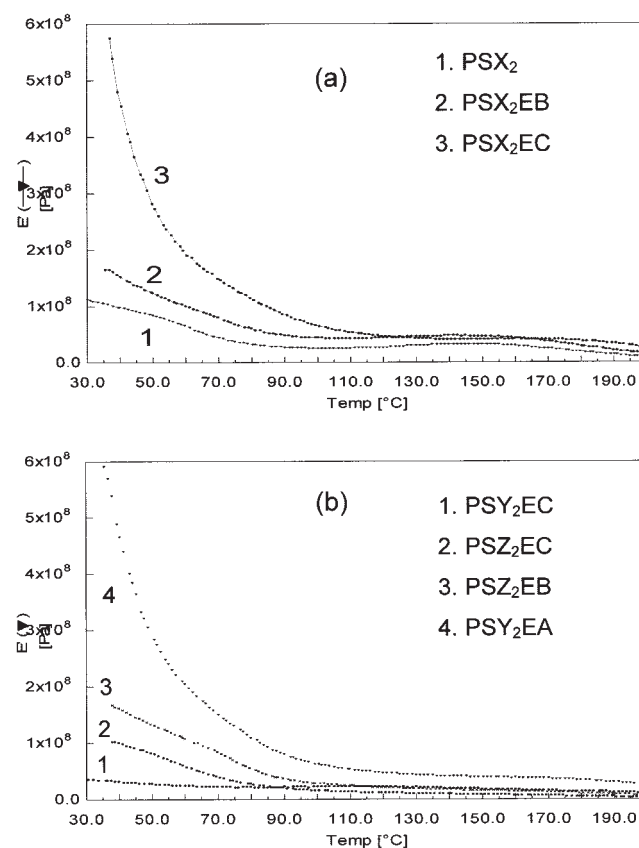

Figure 2 Variation of E' with temperature for (a) 10 wt % PEG-200 plasticized starch-PVA blends with and without crosslinker, (b) 10 wt % PEG-400 and glycerol plasticized crosslinked starch-PVA blends.

TABLE II
Kinetic Parameters in the Thermal Decomposition of Plasticized and Epichlorohydrin-Crosslinked Starch-PVA Blends

Sample	Coats–Redfern E (kJ/mol)	n	Broido E (kJ/mol)	Friedman E (kJ/mol)	Chang E (kJ/mol)	n
PSX_1	92.8	2.0	65.0	47.4	55.2	2.0
PSX_2	95.3	2.1	70.4	62.3	78.1	2.0
PSX_3	123.1	2.5	76.4	82.3	90.6	2.2
PSX_4	90.0	2.1	58.2	44.3	44.3	2.1
PSX_5	86.4	1.9	52.3	41.2	39.3	2.0
PSY_1	79.2	1.5	52.6	66	68.0	2.0
PSY_2	84.7	1.9	64.2	78.0	73.0	2.1
PSY_3	98.6	2.2	69.8	80.7	91.4	2.0
PSY_5	72.4	2.0	50.6	62.6	64.2	2.0
PSZ_1	78.3	2.0	48.8	46.8	72.3	2.0
PSZ_2	86.2	2.0	49.8	57	76.4	2.0
PSZ_3	74.8	2.1	44.2	44.6	60.6	2.1
PSZ_4	73.6	1.9	38.6	42.3	56.6	2.1
PSZ_5	70.5	1.7	33.2	41.2	44.0	2.0
PSX_2EA	61.7	2.1	46.7	49.4	61.3	2.0
PSX_2EB	63.3	2.0	49.8	51.5	67.3	2.0
PSX_2EC	65.9	1.9	52.8	67.8	76.2	2.0
PSX_2ED	67.2	1.7	64.7	72.1	96.5	2.0
PSY_2EA	68.1	2.2	46.0	67.2	60.9	2.0
PSY_2EB	79.5	1.9	48.9	72.3	62.0	1.9
PSY_2EC	83.4	2.5	52.8	74.1	63.3	1.9
PSZ_2EA	58.1	1.6	32.6	23.9	44.8	2.0
PSZ_2EB	61.1	1.7	36.4	39.1	53.2	2.2
PSZ_2EC	64.8	1.8	39.2	44.6	57.3	2.0
PSZ_2ED	68.6	1.8	51.2	52.2	69.8	2.0

material under deformation, and E' is a measure of mechanical energy stored under load. The tan δ compares the amounts of dissipated and stored energy. The maxima of the tan δ curve correspond to the glass-transition temperature (T_g) above which significant chain motion takes place. The dynamic mechanical spectrum shown in Figures 2(a) and 2(b) provided some useful insight on the effect of structural parameters on the properties of the blends.

Since the molecules of both starch and PVA are capable of forming hydrogen bonds, it is expected that some specific interactions could be formed between the molecules of different species. Several factors such as main chain rigidity, percentage of moisture content, crosslinking density, and the chemical structure of the crosslinker introduced can influence the T_g values of the crosslinked films. The PVA hydroxyl groups contribute, by hydrogen bonding, to the stiffness of the linear polymer. By introducing epichlorohydrin as a crosslinking agent to PSX_2, it was seen that the T_g was coming down from 86.6°C to 76.0°C at 15 wt % crosslinker content. The T_g value of PSX_2EB was 80.0°C. The vertical height of the tan δ curve at T_g is tan δ_{max}. The tan δ_{max} values of PSX_2, PSX_2EB, and PSX_2EC were 0.22, 0.18, and 0.16, respectively. Similarly the T_g and tan δ_{max} values of PSY_2EA and PSY_2EC were 88.4°C, 0.2 and 78.6°C, 0.12 respectively.

For PSZ_2EB and PSZ_2EC crosslinked blends, the values of T_g and tan δ_{max} were 76.9°C, 0.18 and 72.5°C, 0.17 respectively. These results are consistent with our earlier studies on borax crosslinked starch-PVA blends[11] and are due to the decrease in the regularity of —OH groups after crosslinking. Figure 2(a) also shows that crosslinking increases the rubbery moduli in these blends.

XPS analysis

For pure PVA, native starch, and PVA-starch plasticized with 10 wt % PEG-200 blend and 15 wt % epichlorohydrin crosslinked blends with 10 wt % PEG-200, PEG-400, and glycerol plasticizer, the XPS survey scan spectra were recorded over the binding energy range of 0–1200 eV using a pass energy of 80 eV. In all the survey scans, the presence of oxygen (1s) and carbon (1s) at the surface was observed. XPS high-resolution narrow scan were recorded for the elements observed in survey scan with pass energy 40 eV. The observed C 1s spectra were deconvoluted by considering Gaussian/Lorentzian (7 : 3 ratio) curve fitting method into three to four components and the binding energies observed could be attributed to energies distinct for substituted carbon moieties. Figures 3(a) and 3(b) are the high-resolution C 1s XPS spectra of pure PVA and native starch. The peak fitting of the high-resolution C 1s signal for pure PVA exhibits three peaks at 284.6, 285.3, and 288.2 eV, which are attributed to —C—C—/—C—H—; —C—O— and —O—C═O, respectively. The nonhydrolyzed acetate group in PVA contributed 6.9% in the C 1s spectrum. For native starch, deconvoluted peaks for C 1s were observed at 284.6, 286.2, and 287.7 eV, which are contributions from —C—C—/—C—H—; —C—O— and —O—C—O bonds respectively. Figures 3(a)–3(d) show the high resolution C 1s XPS spectra of 10 wt % PEG-200 plasticized blend, 15 wt % epichlorohydrin crosslinked blends with 10 wt % PEG-200, PEG-400, and glycerol plasticizer, respectively. The observed C 1s peaks of the studied blends at 284.50–284.66, 285.27–285.62, 286.31–286.84, and 287.75–288.91 eV can be attributed to —C—C—/—C—H—; carbon singly bonded to one oxygen atom (—C—O—), —O—C—O from the starch and carboxylic groups (—O—C═O) respectively. The nonhydrolyzed acetate group in PVA contributes 6.0% in the C 1s spectrum.[11,32,33] XPS is a surface analysis tool and the spectra were recorded at a takeoff angle of 0°, i.e., at a depth of 7.5 nm from the top surface, calculated from the relation $z = 3\lambda\cos\theta$, where z is the effective sampling depth and λ is the effective mean free path for electrons to escape the surface and was set to the value of 2.5 nm. Figure 3(c,d) shows a decrease in the —C—O— peak contribution from 46.7 to 34.4%. PEG-200 consists of flexible ether linkages and shows a
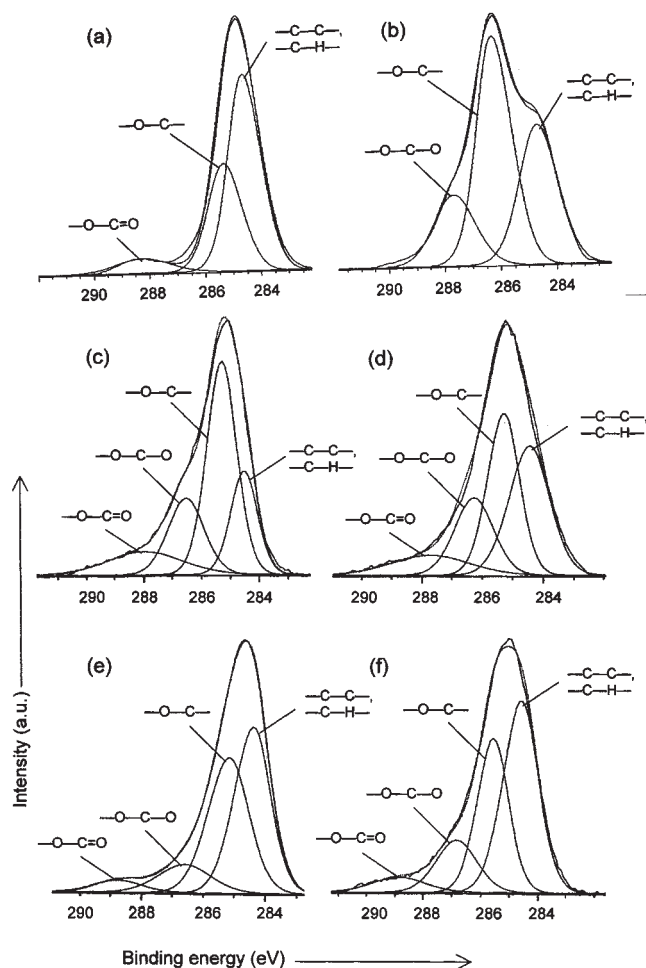
Figure 3 The high-resolution C 1s deconvoluted XPS spectra of (a) pure PVA, (b) native starch, (c) 10 wt % PEG-200 plasticized blend without crosslinker, (d) 15 wt % epichlorohydrin crosslinked blends with 10 wt % PEG-200, (e) 15 wt % epichlorohydrin crosslinked blends with 10 wt % PEG-400, and (f) 15 wt % epichlorohydrin crosslinked blends with 10 wt % glycerol plasticizer, respectively.

preferential movement towards the top surface of the polymer due to the lower air–polymer interfacial energy of the soft segment; therefore, we have observed a higher contribution of —C—O— peak in Figure 3(c). The restriction of such movement due to the crosslinking could led to a decrease in —C—O— peak contribution as is observed in Figure 3(d). On comparison of Figure 3(d,e), the —C—O— peak contribution has changed from 34.4 to 40.4%. This result could be due to the higher molecular weight of PEG-400 in comparison to PEG-200, which makes the preferential movement of ether linkages much easier and hence a high contribution of —C—O— peak results. As glycerol is a low-molecular-weight molecule and does not show any surface segregation behavior, a low —C—O— peak contribution (33.1%) is observed in Figure 3(f).

CONCLUSIONS

Starch-PVA blends with different plasticizers in different concentration were prepared. PEG-200, PEG-400, and glycerol were used as plasticizers. The crosslinking of starch-PVA blends by epichlorohydrin was carried out in the presence of plasticizer *in situ* with different wt % epichlorohydrin. These blends were analyzed by FTIR, TGA, DMTA, and XPS. The results showed a decrease in intensity of the —OH band upon crosslinking of the blends with epichlorohydrin. On the basis of TGA and DTG results obtained with a single heating rate, some important kinetic parameters of thermal degradation, such as the activation energy and the degradation order, have been calculated by using Coats–Redfern, Broido, Friedman, and Chang methods. The thermal stability for plasticized blends passes through a maxima at a critical concentration of plasticizer loading, which again depends on the structure of the plasticizer. For the crosslinked blends, the activation energy increases with increasing crosslinker concentration. Additionally, there are some differences in the kinetic data calculated by using the different methods. The order of decomposition for all the blends studied was close to 2. Crosslinking resulted in a decrease in the glass-transition temperature as well as tan δ_{max} values. High-resolution XPS analysis was used to provide a method of differentiating the presence of different types of carbon bonds in various starch-PVA systems.

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