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Thermal Stability of Biodegradable Films Based on Soy Protein and Corn Starch

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Summary: In this paper, films were prepared from soy protein and corn starch in different proportions and thermal stability and kinetic parameters were determined through degradation reactions in an inert atmosphere. Solid residues and decomposition products were identified by infrared spectroscopy. Films from corn starch were less thermally stable than soy protein films. The films containing both components had lower thermal stabilities when compared to those of the pure biopolymers. The mechanism of starch thermal degradation seems to occur in a single step, which can be confirmed by the constant *E*-values during the thermal degradation reaction. For the pure protein and its mixtures an increase in the activation energy was observed during the reaction. Solid residues for protein at different temperatures showed mainly bands related to C=O stretching, angular deformation of N–H and C–H groups. For starch, absorptions related to free and bound O–H, C=O stretching of CO_2, CO and carbonyl compounds were observed. For the 50/50 mixture bands related to soy protein and corn starch were observed. The gaseous products for soy protein showed absorptions related to CO_2, CO, C=O, NH_3 and C–H stretching. For pure starch absorptions related to O–H stretching from alcohol, C=O from CO_2, CO and carbonyl compounds. The 50/50 mixture had the same characteristics as pure soy protein and corn starch.

Keywords: biodegradable; biopolymers; protein; starch; thermogravimetric analysis (TGA)

Introduction

Environmental concerns associated with the handling of plastic waste have emphasised the importance of developing biodegradable materials to alleviate the plastic waste disposal problems. In other words, the continuously increasing extent of pollution of the environment has recently given rise to demands for novel biodegradable polymers, mainly for applications related to food packaging and agriculture. The term ''biodegradable'' materials is used to describe those materials that are degraded by the enzymatic action of living organisms and the end products of this degradations process being CO_2, H_2O and biomass under aerobic conditions and hydrocarbons, methane and biomass under anaerobic conditions.[1,2]

Edible films and coatings offer the possibility to maintain or even improve food quality, stability and storage life by retarding moisture exchange with the surrounding environment or between food components. Research has focused on barriers consisting of proteins, polysaccharides and lipids or waxes. Proteins and polysaccharides are good film-forming materials that are used for their mechanical and structural properties; on the other hand, the knowledge about their thermal degradation properties is poorly known what justifies the necessity of the present work. Thermal decomposition analysis of starch/soy protein films is important because comprehensive studies on their

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stability will allow their applicability in some different fields, being mainly food, pharmaceutical and agricultural soil research.[3,4]

According to the literature soy protein films has been described as a two-step process involving the heat denaturation of the proteins followed by surface dehydration. In this process, the unfolded proteins link through intermolecular interactions, leading to the formation of a network. Protein films tend to be brittle and the addition of starch as raw material to the polymeric matrix before drying can improve film properties in order to overcome the brittleness. Starch is a high molecular-weight polymer of anhydro-glucose units linked by alpha-D glycoside bonds. The major polymers in starch are amylose and amylopectin, amylose being a linear molecule with a molecular weight (MW) of 1–1.5 million while amylopectin is a branched molecule with MW of 50–500 million.[3–6]

Considering previously important aspects such as solubility and compatibility between protein and polyssacaride, the goals of this work were to investigate the thermal stability (TGA) in relation to degradation reaction of films based on soy protein and starch in different proportions and identify the solids and main gaseous decomposition products by infrared spectroscopy (FTIR) in inert atmosphere.

Material and Methods

Film Preparation

All Films were prepared by mixing different solutions using water as the solvent. For soy protein the pH of solutions was adjusted to 10 by the addition of ammonium hydroxide. The solutions were then mixed under stirring and heated to 70 °C. These solutions were maintained under stirring during the cooling. After 2 h, the mixture was casted onto a Petri dish (15 cm in diameter). After evaporation at room temperature, all films were dried under vacuum for two days before being submitted to analysis.

Thermal Analysis

Film samples (approx. 15 mg) were submitted to thermogravimetric analysis in Shimadzu TGA-50 equipment under nitrogen atmosphere (50 $mL \cdot min^{-1}$). Non-isothermal experiments were performed in the temperature range 25–500 °C at heating rates of 10, 20 and 40 $°C \cdot min^{-1}$ for each sample. The thermogravimetric data were analyzed using the Osawa method and the kinetic parameters determined using the associated TGA-50 software. The activation energy was derived from the slope of the dependence of the heating-rate upon the reciprocal absolute temperature, at defined mass loss.

IR Spectroscopy

To evaluate the formation of gaseous products formed in the thermal degradation processes, film samples were heated under nitrogen atmosphere (50 $mL \cdot min^{-1}$), in a tubular oven coupled with an infrared spectrophotometer (Bomen, FTLA 2000). FTIR analysis was performed with a resolution of 4 cm^{-1} in the range of 4 000–400 cm^{-1}.

Results and Discussion

The films all displayed a similar behavior in the first stage of weight loss, as can be observed in Figure 1. This stage was observed primarily between 50 and 150 °C and it is related to the loss of free and absorbed water which was not considered in the obtention of kinetic parameters. The second and third stages (when present) are associated with the thermal degradation and were analyzed in more detail in order to determine the kinetic parameters for pure starch and protein as well as their blends.

Starch thermal degradation starts at 302.39 °C and its maximal degradation is at around 340.10 °C. Protein thermal degradation seems to occur in two steps, the second peak being at 349.80 °C. Table 1

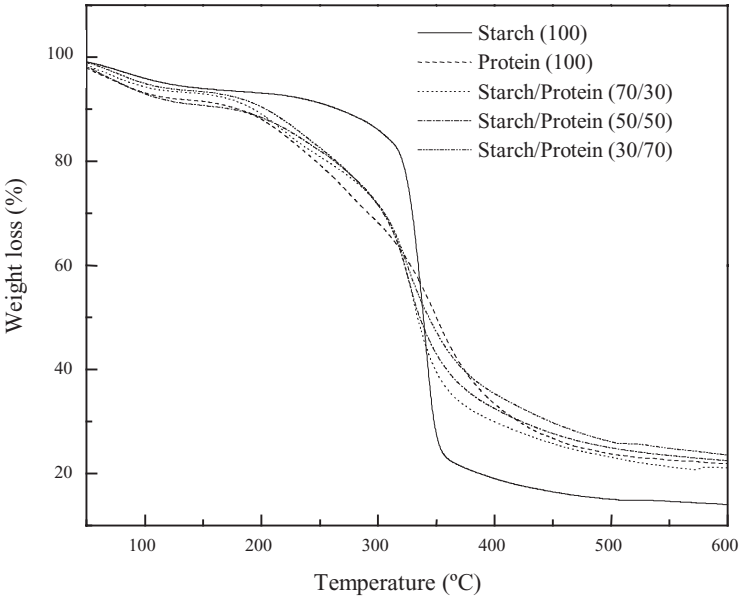

Figure 1.
Thermogravimetric curves for protein and starch films and their blends (70/30 protein/starch, 50/50 protein/starch, 30/70 protein/starch), with heating rate of 10 °C · min^{-1}.

shows that starch addition to the films decreases the initial and maximal degradation temperature. This fact may be an indication that starch has some influence on the thermal stability when added to protein films. Analogously, a reduction in thermal stability can also be promoted by changes in the protein structure, provoked by the rupture of low energy intermolecular bonds which maintain the protein conformation.[7]

During the heating, the initial ordered structure of the films obtained from the pure components and their blends was gradually destroyed. This is possible because of inter- and intramolecular hydrogen bonds which are responsible for the polymeric matrix in the proteic films.[8]

Table 1.
Thermogravimetric parameters for protein and starch films and their blends.

Film	$T_{initial}$	T_{max}	T_{final}	E	Residue
	°C	°C	°C	kJ · mol^{-1}	%
Protein	320.89	349.80	351.91	120.43	32.16
70/30	311.32	324.12	378.37	133.69	27.54
50/50	284.72	325.42	352.34	116.34	30.32
30/70	297.35	328.78	368.44	137.00	26.28
Starch	302.39	340.10	357.45	116.64	16.65

In relation to residual mass (%) after heating at 600 °C, the values are between 16 and 32% for all studied systems. All films presented similar residual masses, which can be attributed to a similar protein structure in all films. These residual masses represent inorganic compounds derived from thermal degradation. The activation energy (E) for thermal degradation was determined using the Osawa method. The E-values versus weight loss are represented in Figure 2. As can be observed, except for starch, a significant increase in activation energy occurs for all films at a weight loss (α) higher than 0.5. This increase in energy may be related to cross-linkages, as described in the literature for concentrated proteins and gelatins. Reactive groups of aminoacids (hydroxyl groups, carbonyl, sulfhydryl and amine groups) are responsible for cross-linking during heating.[8]

For mixtures of protein and starch (70/30), a synergistic effect was observed when compared to pure polymers. This synergistic behavior may be related to changes in the reaction mechanism during the thermal degradation reaction.[9,10]

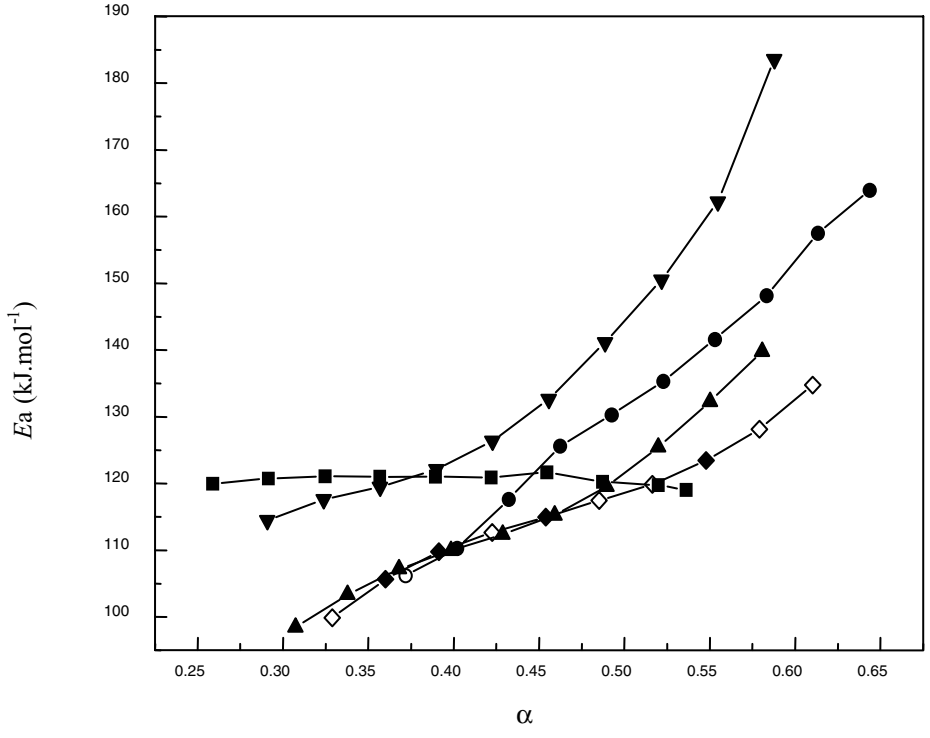

Figure 2.
Plots of activation energy (E) versus weight-loss fraction (α) for: (■) starch, (◆) protein, (▲) protein/starch (50/50), (▼) protein/starch (70/30), (◇) protein/starch (30/70).

For 50/50 and 30/70 (protein/starch) mixtures an additive effect of the compounds was observed proportional to their amount in the mixture. In general, changes in the reaction mechanism are associated with multiple competing steps during the thermal degradation reaction.[11]

The activation energy values for all studied systems were between 100 and 190 kJ · mol^{-1} until a weight loss fraction of $\alpha \cong 0.65$. Considering that weak link scissions are associated with activation energy (E) lower than 100 kJ · mol^{-1}, the results obtained suggest that the presence of protein in the films results in a change in the thermal degradation reaction, it occurring via random scission of strong bonds in the proteic chain.[12]

Figure 3 shows the FTIR spectra for the solid residues of the starch, protein and blend (50/50—protein/starch) at different degradation temperatures. These temperatures for FTIR analysis were defined using TGA curves and also the maximum degradation temperature for all films which can be seen in Table 1.

For soy protein [Figure 3(A)], at room temperature, bands related to C=O stretching at 1 630 cm^{-1} (amide I), angular deformation of N–H at 1 530 cm^{-1} (amide II) and C–H deformation at 1 450 cm^{-1} are shown. The absorption band at 1 230 cm^{-1} is attributed to C–N stretching and the vibrational band of N–H (amide III). The band at 1 100 cm^{-1} is formed by different groups which have angular deformation (out of the plane).

A broad band observed between 3 600 and 3 000 cm^{-1} is attributed to free and bound O–H and N–H groups. The presence of O–H and N–H groups in soy protein and O–H from the absorbed water, leads to inter and intra hydrogen bonds with C=O groups from the aminoacid structure

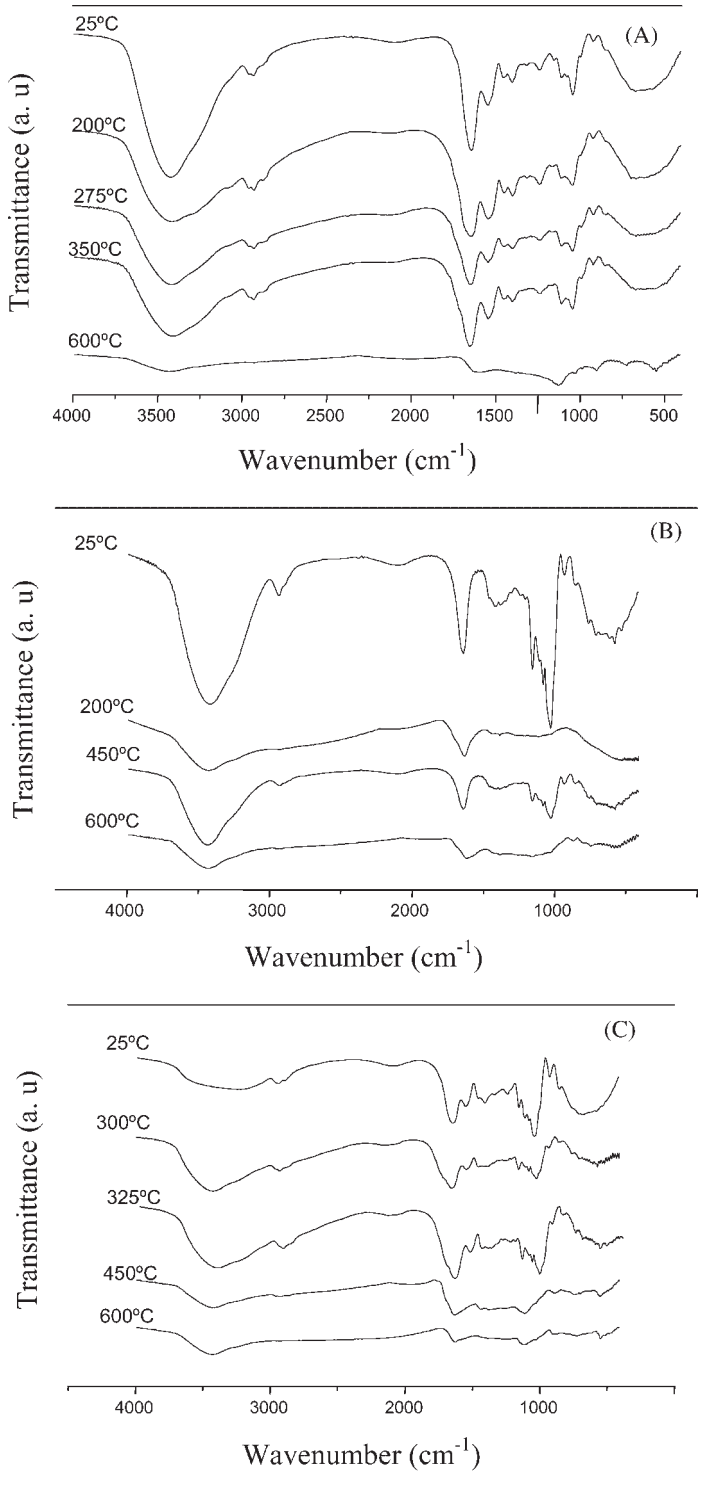

Figure 3.
FTIR spectra of solid residue for films: (A) pure protein, (B) starch and (C) 50/50 blend, at different temperatures.

(peptide and carbonyl groups) of the protein. At room temperature there are also C–H stretching from saturated groups (CH_2 and CH_3) which were observed within a range of 2 980–2 850 cm^{-1}.[13] At 200 °C the same FTIR spectrum was observed. Some modifications occurred at the 3 400 cm^{-1} band, related to a decrease in the O–H and N–H groups. This behavior is related to the temperature increase which provokes a loss of water along with a decrease in the hydrogen bonds in the protein.

At 275 °C, the band at 1 530 cm^{-1} (angular deformation of N–H) changes its intensity when compared to the C=O stretching at 1 630 cm^{-1}. This change related to N–H group is consistent with NH_3 formation at FTIR gaseous products spectrum. The fact that both bands appeared at higher wavenumbers suggests some conformational effect on the proteic molecule, which is to be expected given the inter- and intramolecular hydrogen bond disappearance. This effect was more accentuated at 350 °C when 1 530 cm^{-1} and 1 650 cm^{-1} bands were less accentuated.

Therefore, bands related to C–H stretching between 3 000 and 2 800 cm^{-1}, C–H deformation at 1 450 cm^{-1} and a band at 1 100 cm^{-1} were still on the spectrum, suggesting that the degradation mechanism involved first a scission of weak bonds (C–N, C(O)–NH, C(O)–NH_2 and –NH_2) which are present in some lateral residues of the soy protein molecule. However, at 600 °C smaller amount of solid residue was observed because of the presence of more stable bonds which could not be broken even at this temperature.[13]

In a recent work, Schmidt et al.[14] studied the thermal stability of SDS-containing soy protein isolate cast films by thermogravimetric analysis (TGA) and infrared spectroscopy (FTIR) under nitrogen atmosphere. Although the same raw material had been used, the methodology of film preparations was different which may contributed to the few differences on peaks intensities at FTIR spetra for soy protein only. The researchers had not heated the solutions in this work, heating to 70 °C was done in order to favor protein solubilization.

For starch at room temperature, free and bound O–H and N–H (3 750–3 500 cm^{-1}), C=O derived from CO_2 and CO (2 900 and 2 113 cm^{-1}) and carbonyl compounds (1 630 cm^{-1}) were observed.[15] A decrease in intensity was observed at 200 °C and at this temperature the O–H and N–H groups were free. This is consistent with the observation that at this temperature absorbed water was eliminated resulting in a decrease in hydrogen bonds in the starch. At 450 °C the same FTIR spectrum was observed and only the band at 1 630 cm^{-1} for the (CO) appeared with increased intensity.[13]

For the 50/50 blend, the presence of bands related to soy protein and corn starch were observed. However, the spectrum has more similarity with soy protein. This behavior is more evidentiated by the presence of bands at 1 530, 1 450 and 1 230 cm^{-1}. Increasing the temperature causes a decrease on bands intensity as occurred for the pure biopolymers. At 600 °C no solid residue was observed.[13]

The spectra for gaseous products released from degradation from pure polymers and their blends are shown in Figure 4. For soy protein, gaseous products were obtained at temperature of maximum degradation. Its gaseous products showed absorption bands of CO_2 (2 370, 2 340 and 670 cm^{-1}), CO (2 200–2 000 cm^{-1}), C=O (1 730 cm^{-1}), NH_3 (970, 930 and 3 335 cm^{-1}) and also C–H stretchings (2 950–2 850 cm^{-1}) and a vibrational band at around 1 625 cm^{-1} (–NH_3 stretching).[13,14]

For pure starch, absorptions related to alcohol (O–H stretching at 3 500–3 750 cm^{-1}), CO_2, CO and carbonyl compounds 2 360, 2 177 and 1 743 cm^{-1}, were observed. Starch presented a single degradation step, which reflects weaker link scissions, such as that of C–O bonds.[15,16]

Conclusion

This paper allowed to observe that corn starch film showed a less thermal stability

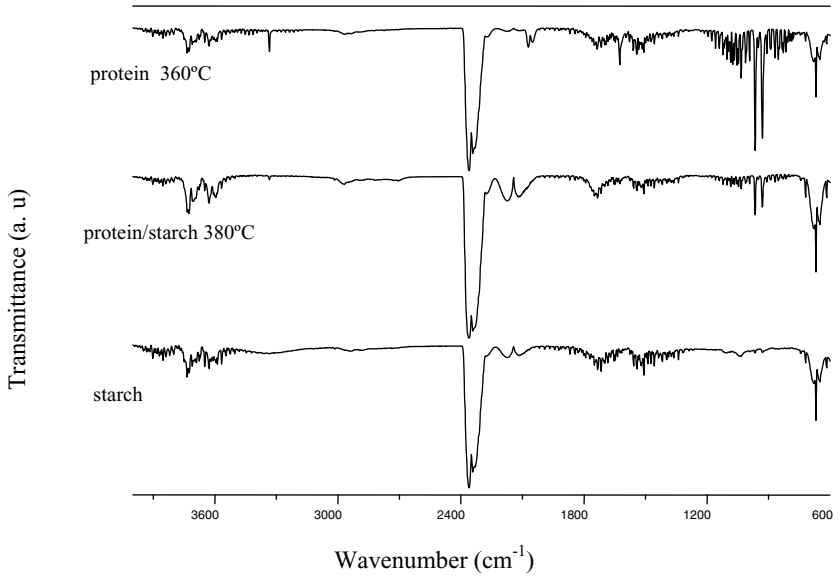

Figure 4.
FTIR spectrum of gaseous products obtained from soy protein, starch and 50/50 blend at maximum degradation temperature.

when compared to soy protein films. The mixture between both biopolymers decreased the thermal stability when compared to pure films. This decrease on thermal stability seems to be related to changes in protein structure provoked to starch addition to the system. The starch thermal degradation mechanism seems to occur at on step, which can be observed by the constant *E*-value. For mixtures of protein and starch (70/30), a synergistic effect was observed when compared to pure polymers. This synergistic behavior may be related to changes in the reaction mechanism during the thermal degradation reaction.

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