# Processing and Characterization of Biodegradable Soy Plastics: Effects of Crosslinking with Glyoxal and Thermal Treatment

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**ABSTRACT:** Processing and modification routes to produce and to improve properties of biodegradable plastics from soy isolate were studied. Soy isolate, acid-treated and crosslinked soy were subsequently compounded, extruded, and injection molded. Acetic acid and glyoxal were examined concerning their suitability for acid treating and crosslinking of soy, and their effect on the final properties of the obtained materials. Heat treatment was also used as a possible methodology to crosslink the protein structure. The molded specimens were tested in terms of their tensile properties and solubility at different pHs, and were also evaluated for the degree of crosslinking and molecular weight distributions. The obtained plastics were rigid and brittle with stiffness ranging from 1436 MPa for soy, to 1229 MPa for glyoxal crosslinked soy, up to 2698 MPa for heat-treated soy. The differences in stiffness were discussed in terms of the crosslinking efficiency and spatial distribution. The solubility profiles were studied as a function of the pH of the immersion solutions and the crosslinking degree of each material. A reduction in protein solubility with decreasing pH was observed, with a minimum between pH 4 and 5 and a resolubilization of the protein at pHs lower than pH 4 and greater than 8. Higher levels of crosslinking resulted in a decrease of the solubility and an aggregation of the protein molecules. The soy plastics proved to be very versatile materials with potential to be used in applications where quite demanding performances are expected, such as in the biomedical field. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 604–610, 2005

**Key words:** extrusion; crosslinking; mechanical properties

## INTRODUCTION

Many studies have shown that various agricultural raw materials could be used as a source of polymers for the production of biodegradable systems.[1–3] Among natural polymers, plant proteins constitute a viable source of biodegradable products because they are renewable, economically competitive, and abundant.[4,5] Proteins are heteropolymers constituted of polar and apolar amino acid residues that are able to form numerous intermolecular bonds and interactions, offering a wide range of potential functional properties.[6,7] Within plant protein sources, soy has several advantages namely: (1) low cost;[8] (2) reduced susceptibility to thermal degradation (allowing for its easy processing by melt based technologies);[9,10] (3) good water resistance; and (4) storage stability.[11,12] The combination of these properties and the similarity to tissue constituents[13] makes soy an ideal template to be used as an alternative biodegradable polymer for biomedical applications. However, the high enzymatic turnover rate of proteins in the human body requires their previous stabilization.

So, crosslinking methods are used to assure the respective material integrity and the desired mechanical properties during an implantation period.[14] In fact, it is often necessary to confer mechanical stiffness and enzymatic resistance through the introduction of exogeneous crosslinks into the protein molecular structure.[14] Soy has many reactive groups (e.g., —$NH_2$, —OH, and —SH), which are susceptible to crosslinking reactions, in addition to the typical disulfide interchain links.[2]

Crosslinks can be created in proteins by a number of ways.15 However, the most used agents are aldehydes, with formaldehyde and glutaraldehyde being the most obvious examples.[14,15] Nevertheless, concerns related with use of these two agents arose from

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**TABLE I**
**Extrusion Processing Conditions**

| Condition | Nomenclature | Screw | Throughput (kg/h) | SME (kJ/kg) | rpm |
|---|---|---|---|---|---|
| 1 | $SI_{tp}$ | St | 4.45 | 246.9 | 200 |
| 2 | $SI_{tp}$ (pH 4) | St | 3.87 | 319.4 | 200 |
| 3 | $0.3XSI_{tp}$ | St | 4.81 | 286.0 | 200 |
| 4 | $0.6XSI_{tp}$ | St | 4.85 | 283.7 | 200 |

an exacerbating effect on the calcification of cardiovascular prosthesis materials,[16] cytotoxicity due to postimplantation depolymerization and monomer release from the crosslinked matrices.[17,18] An interesting alternative to be used for biomedical purposes is glyoxal, a dialdehyde with lower toxicity that has not been much explored so far.[19] Also, heat treatments can result in protein crosslinking by rearrangements in the protein structure.[20]

This article reports on the development of affordable, stiff, and strong bioabsorbable materials based on soy proteins processed by melt-based methods (such as extrusion and injection molding) aimed to be used in biomedical applications. Furthermore, it also examines how crosslinking affects the mechanical properties, the solubility, and the internal structure of the obtained soy protein plastics. Crosslinking with glyoxal and by heat treatment were conducted. The properties of the developed soy materials, with or without crosslinking, were investigated and compared in terms of stiffness and tensile strength, degree of crosslinking, solubility, and molecular weight distributions.

## MATERIALS AND METHODS

### Materials

Soy protein isolate (SI, 83.4% protein, w/w on dry weight base) was supplied by Loders Crocklaan BV (Wormerveer, The Netherlands). Glycerol, glyoxal (40% v/v) and *o*-phthaldialdehyde (OPA) were used as received from the manufacturer, Sigma-Aldrich Chemie BV (Zwijndrecht, The Netherlands). NaCl, NaOH, and HCl were all of analytical grades.

### Soy protein extrusion

Native soy protein was converted into a thermoplastic material ($SI_{tp}$) in a corotating twin-screw extruder (Berstorff, D = 25 mm and L = 40D) in the presence of 35% water and 10% glycerol (w/w relative to the protein amount). The extrusion was carried out at temperatures ranging from 70 to 80°C (temperature necessary for the splitting of the disulphide bridges and loss of the tertiary structure of the protein[21]), using a screw speed of 200 rpm (Table I).

The applied standard screw configuration is represented in Figure 1.

The extrusion was performed at two different pHs: (1) pH 7 using water (Table I, condition 1); and (2) pH 4 using a buffer solution of acetic acid ($CH_3COOH$)/sodium acetate ($CH_3COONa$) 200 mM (Table I, condition 2). These solutions were injected with a piston pump (Pro Minet, Verder BV, The Netherlands) at the second feeding zone. During the pH 7-extrusion procedure, the soy protein was also crosslinked with different amounts of glyoxal, namely 0, 0.3% (Table I, condition 3) and 0.6% (Table I, condition 4) w/w relative to the protein amount ($SI_{tp}$, 0.3X-$SI_{tp}$, and 0.6X-$SI_{tp}$, respectively). The glyoxal was mixed with the water and injected simultaneously.

### Specific mechanical energy input

The processability of the different compounds was quantified by the specific mechanical energy input (SME). This is a characteristic value of each extrusion batch, calculated using eq. (1):[22]

$$\mathrm{SME} = \frac{[\mathrm{rpm} \times \mathrm{torque}\ (\%) \times P_{\max}]}{(\mathrm{rpm}_{\max} \times 100 \times \mathrm{throughput})} \qquad (1)$$

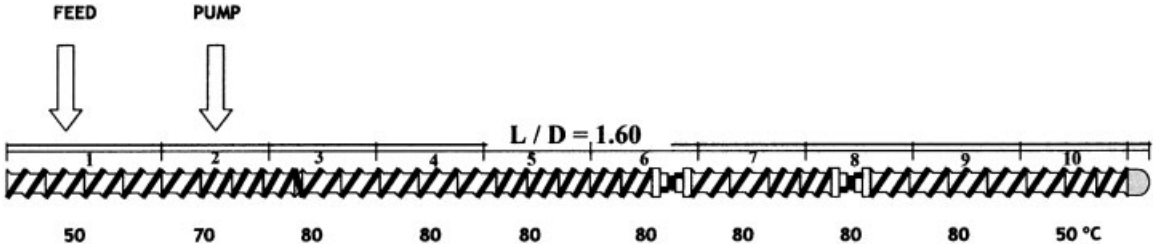


**Figure 1** Standard (St) screw configuration.

where $rpm_{max}$ = 550 rpm and $P_{max} = 10.5 \times 10^3$ W are characteristics of the extruder used in this study.

### Capillary rheometry

Rheometry measurements were conducted in a Rosand precision advanced capillary extrusion rheometer, at 130°C, using the extruded materials (in the form of pellets) with a moisture content of 20%.

The maximum shear stress values, $\tau_w$, were calculated from eq. (2):

$$\tau_w = \frac{(\Delta P \times R)}{2L} \quad (2)$$

where $\Delta P$ is the pressure measured at the capillary entrance, $L$ is the capillary length, and $R$ is the radius ($R$ = 1 mm).

The apparent shear rate at the wall, $\gamma_w$, was calculated using the conventional Rabinowitsch correction:

$$\dot{\gamma}_w = \left[ \left( \frac{3n+1}{n} \right) \times \left( \frac{\pi \times Q}{R^3} \right) \right] \quad (3)$$

where $Q$ is the volumetric flow rate and with $n$ is the pseudoplastic index.

The viscosity at a given shear rate was obtained from the ratio between the shear stress and the shear rate [eq. (4)]:

$$\eta(\gamma) = \frac{\tau_w}{\dot{\gamma}_w} \quad (4)$$

### Injection molding of soy thermoplastics

The extruded compounds (in the form of pellets) were molded into dumbbell ASTM tensile test bars (2 × 4 $mm^2$ of the cross-section), after being preconditioned (60°C and 24 h) until the respective moisture content reached the reference level of 12 to 14%. These specimens were molded using a DEMAG D25 NC IV under optimized and steady processing conditions, namely barrel temperatures ranging from 120 to 140°C.

A batch of the injection-molded specimens was submitted to a thermal treatment performed at 80°C during 24 h in an air-circulating oven ($24TTSI_{tp}$). Subsequently, the injection-molded samples were conditioned at 25°C and 60% relative humidity (RH) for at least 1 week before testing.

### Tensile testing and moisture content

The mechanical behavior of the produced soy specimens was assessed by means of tensile tests performed on a Zwick Z010 universal mechanical testing machine equipped with a 5 kN static load cell. The test crosshead speed was always 1 mm/min (corresponding to a strain rate of $6.67 \times 10^{-4}$ $s^{-1}$). The deformation data was obtained from a resistive extensometer. The $E$-modulus at 0.05–0.25% strain ($E_{0.05-0.25\%}$), the yield tensile strength ($\sigma_y$), and the strain at break ($\epsilon_b$) were evaluated. The tensile tests were performed in a controlled environment (20°C and 55% RH) equivalent to the atmosphere used for conditioning the specimens.

After testing, specimens were milled using liquid $N_2$ and weighed into aluminium dishes for subsequent drying for 24 h in a vacuum oven at 40°C.[23] Moisture content (MC) was determined in triplicate for each type of material as percentage of the initial weight ($W_0$) lost during drying ($W_{0d}$):

$$MC = \left[ \frac{(W_0 - W_{0d})}{W_0} \right] \times 100 \quad (5)$$

### Total protein content

All the samples were ground using liquid $N_2$ and subsequently sieved with a mesh size of 1 mm. Fifty milligrams of protein samples were dispersed in a mixture of demiwater and concentrated $H_2SO_4$. After adequate digestion of the protein materials, carried out at 420°C during 50 min, the total protein content ($N_{tot}$) of the resulting solution was determined by Kjeldahl analysis and calculated as:

$$N_{tot}(\%) = \left[ \frac{V(\text{HCl}) \times 0.1 \times 14 \times 6.25}{W_d} \right] \times 100 \quad (6)$$

where, $V$ (HCl) is the volume of HCl 0.1 $M$ used during the Kjeldahl titration, 14 is the atomic mass of nitrogen (N), and 6.25 the Kjeldahl factor of soy. $W_d$ is the dry weight of the protein powder sample tested.

### Solubility tests

A 0.1% protein solution was prepared by dispersing about 50 mg of the protein powders in 45 g of demineralized water. The dispersion was magnetically stirred until complete dispersion of the powder (approximately 30 min). The pH values of the solutions were adjusted to the desired pHs (in the case, pHs of 3, 4, 5, 6, 7, and 9) using HCl 0.1 $M$ or NaOH 0.1 $M$. The solutions were again stirred for 1 h and the pHs verified and adjusted if necessary. When the pH values were stable, the total weight was brought to 50 g with additional water. Subsequently, the dispersions were centrifuged for 10 min at 13,500 rpm. The protein content in the supernatant was determined by Kjeldahl analysis as explained above. However, the digestion conditions were different for these liquid samples and composed of three steps: (1) 160°C for 1 h; (2)

260°C for another 1 h; and (3) 420°C for more than 50 min. The protein solubility at the different pHs was calculated according to:

$$\text{solubility}(\%) = \left(\frac{N_{\text{sup}}}{N_{\text{tot}}}\right) \times 100 \quad (7)$$

The protein content of the supernatant ($N_{\text{sup}}$) was calculated by eq. (8).

$$N_{\text{sup}}(\%) = \left[\left[\left[\frac{V(\text{HCl}) \times 0.1 \times 14 \times 6.25}{W_d}\right] \times 1000\right] \times 100\right] \quad (8)$$

$W_d$ is the weight of the supernatant tested. The $N_{\text{tot}}$ corresponds to the protein content of the dry samples used to prepare the dispersions and is calculated by eq. (6).

### Free amine group measurement

The free amine group content of the protein samples was determined using the OPA method.[24] An OPA solution was made by mixing 25 mL of 0.1 *M* sodium borate (pH 9.2), 2.5 mL of 20% (w/w) sodium-dodecyl sulphate (SDS), 40 mg of OPA (dissolved in 1 mL methanol), and 100 $\mu$L of $\beta$-mercaptoethanol. The final volume was adjusted to 50 mL with deionized water. To determine the degree of alkylation, an aliquot (50 $\mu$L: containing 2 g/L protein in sodium tetraborate buffer 0.0125 *M* + 2% SDS) was added directly to 1.0 mL of the OPA reagent in a cuvette. The solution was mixed rapidly and incubated for 2 min at room temperature before the absorbency was red at 340 nm against water. A calibration curve was previously established by using L-leucine as a standard.

### SDS-PAGE

Protein powder samples dissolved in a sample buffer (50 m*M* Tris-HCl pH 6.8, 4% SDS w/v, 12% glycerol, 2% $\beta$-mercaptoethanol w/v and bromophenol blue) were applied to the polyacrylamide gel. Samples were electrophoresed at 150 V using an II Dual Slab Cell (Bio-Rad Laboratories) with a 15% polyacrylamide gel and a stacking gel of 4% acrylamide. High molecular weight standards (phosphorylase b 94 kDa; bovine serum albumine 67 kDa; ovalbumine 43 kDa; carbonic anhydrase 30 kDa; soybean trypsin inhibitor 20.1 kDa; and $\alpha$-lactalbumine 14.437 kDa) from Pharmacia (Uppsala, Sweden) were used as protein references. The gels were stained with Serva Blue R for 45 min and destained using a solution of methanol : acetic acid : demiwater (4 : 1 : 5) for at least 3 h. After decoloration, the gel was dried in a coating dryer (Bio-Rad Laboratories) for 1 h at 60°C.

## RESULTS AND DISCUSSION

### Specific mechanical energy input (SME)

The extrusion of soy thermoplastics was characterized by relatively low values of the specific mechanical energy input (250–350 kJ/kg) (Table I). This fact proves the relatively easy processability (with low energy requirement) of this type of materials by conventional techniques, when compared with other proteins, such as collagen.[25]

The pH decreasing effect (from 7 to 4), over the solubility of the protein was clear (Table I). Due to the fact that at pH 4, the protein is near its isoelectric point (pI = 4.5) and presents an almost zero net charge and a lower interaction with water molecules, the processability of the melt required more mechanical energy, resulting in an increase of the SME (~100 kJ/kg).

During crosslinking with glyoxal, an increase in the SME (~50 kJ/kg) was also found (Table I). This effect was mainly due to the higher melt viscosity, reflected by a higher extruder torque, caused by the increase of chemical bonds within the protein structure.

### Rheological behavior

Figure 2 presents the flow curves of $SI_{tp}$ and 0.6X-$SI_{tp}$ with 20% moisture content, obtained by capillary rheometry.

The $SI_{tp}$ presented a shear-thinning behavior typical of the thermoplastic melts. The 0.6X-$SI_{tp}$ presented a higher viscosity than $SI_{tp}$ (except for very low shear rates), which explains the need for a higher specific mechanical energy input during extrusion (see earlier). However, for higher residence times at higher temperatures (>80°C), 0.6X-$SI_{tp}$ suffers additional crosslinking and starts to present a thermoset-like behavior. This behavior inhibited the measurement of the shear viscosity at high shear rates for this compound, as observed in Figure 2.

### Tensile properties

The types of interactions between polypeptide chains, namely the level at which crosslinks are established (intra- and intermolecular), are very important parameters that determine the tensile properties of soy plastics.

#### Glyoxal crosslinking

Crosslinking of soy thermoplastics with glyoxal resulted in materials with decreased tensile strength (22.2 MPa for $SI_{tp}$ and 15.5 MPa for 0.6X-$SI_{tp}$), as

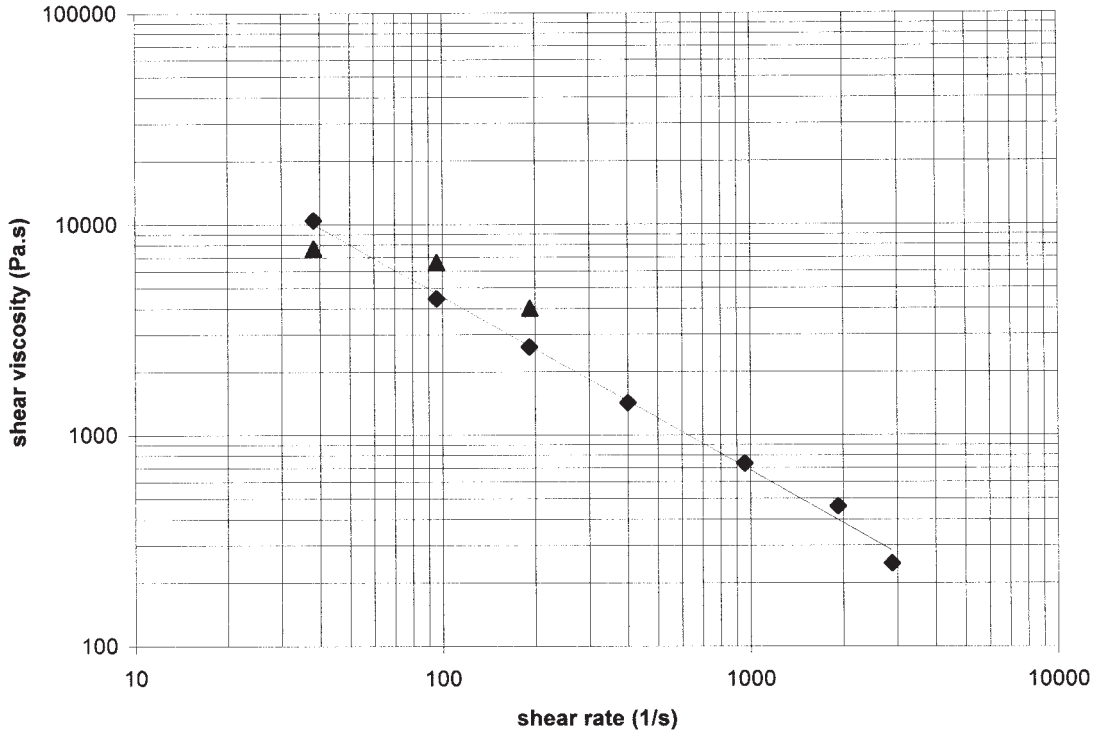


**Figure 2** Flow curves for thermoplastic soy ($SI_{tp}$, ◆) and soy crosslinked with glyoxal (0.6X-$SI_{tp}$, ▲) at 103°C and 20% moisture content.

presented in Table II. The stiffness of the materials also decreased with the increase of the crosslinking degree, from 1436 MPa for $SI_{tp}$ to 1229 MPa for 0.6X-$SI_{tp}$ (Table II). This is consistent with the previously reported results for dermal sheep collagen crosslinked with glutaraldehyde.[26,27] During extrusion, the probability of glyoxal (a relatively small dialdehyde molecule, Mw 58.04 g/mol) to crosslink through two amine groups of soy located on two adjacent chains is apparently smaller than that to crosslink through two amine groups presented along the same chain. As a consequence, the covalent bonds were predominantly introduced within the polypeptide chains and not between them (intramolecular crosslinking). This type of crosslinking does not inhibit the melt processing cycle but results in a reduced chain mobility (with higher difficulty to unfold and align during the extrusion process), and consequently, in a higher sensitivity to thermal degradation (see earlier). The above referred decrease in stiffness and strength may be a direct result of the thermomechanical degradation occurred during processing.

### Heat treatment

The tensile properties of soy thermoplastics as a function of the heat treatment are also presented in Table II. A significant increase of ~90% in stiffness was found, with an $E_{0.05-0.25\%}$ increment from 1436 MPa for $SI_{tp}$ to 2698 MPa for 24TT$SI_{tp}$. Simultaneously, the

**TABLE II**
**Mechanical Properties of Soy Protein-Based Plastics**

| Glyoxal (%)[a] | Heat treatment[b] (time/h) | pH of extrusion | $\sigma_y$ (MPa) | $\varepsilon_b$ (%) | $E_{0.05-0.25\%}$ (MPa) | MC (%) |
|---|---|---|---|---|---|---|
| 0 | 0 | ~7 | 22.2 ± 2.3 | 1.8 ± 0.3 | 1436 ± 56 | 5.2 ± 0.1 |
| 0.3 | 0 | ~7 | 20.7 ± 1.4 | 1.9 ± 0.2 | 1241 ± 83 | 5.4 ± 0.1 |
| 0.6 | 0 | ~7 | 15.5 ± 2.1 | 1.3 ± 0.2 | 1229 ± 38 | 5.5 ± 0.1 |
| 0 | 24 | ~7 | 30.2 ± 3.7 | 1.1 ± 0.2 | 2698 ± 269 | 5.2 ± 0.1 |
| 0 | 0 | ~4 | 21.0 ± 2.2 | 2.3 ± 0.4 | 1217 ± 159 | 5.5 ± 0.2 |

[a] w/w % based on protein.
[b] All heat treatments performed at 80°C. $E_{0.05-0.25\%}$: E-modulus at 0.05–0.25% strain; $\sigma_y$: yield tensile strength; $\varepsilon_b$: strain at break.

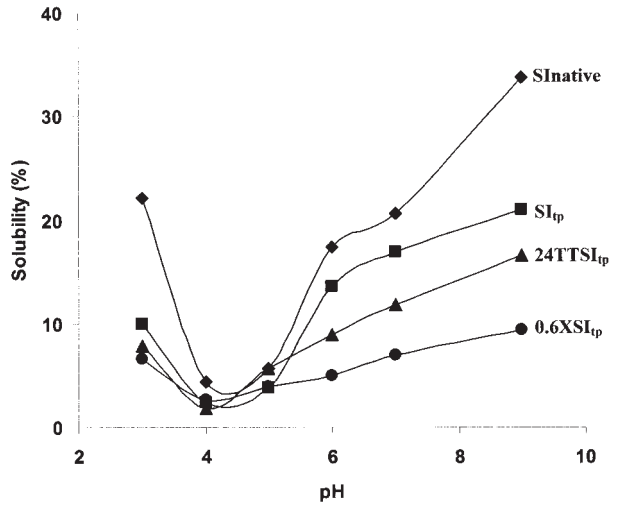


**Figure 3** Solubility profiles at different pHs of: native soy (◆) and soy-based plastics: (i) $SI_{tp}$ (■) (ii) $24TTSI_{tp}$ (▲); and (iii) 0.6X-$SI_{tp}$ (●).

tensile strength increased and the strain at break decreased in about 40%. Thermal treatment resulted in the production of highly stiff and brittle soy plastics. This effect was mainly attributed to the formation of disulfide linkages, hydrogen bonds, hydrophobic interactions, and also amine crosslinks during the heat treatment.[13,28] Due to the formation of disulfide and hydrogen bonds, heat treatment introduces linkages not only within but also between the polypeptide chains (intra- and intermolecular crosslinking). As the heat treatment is only performed after the processing cycle, an eventual thermomechanical degradation of the protein matrix is avoided and, consequently, a reduction in the mechanical performance is not detected.

## Solubility

The solubility profile of soy protein isolate at various pHs is shown in Figure 3.

A reduction in the protein solubility with the pH level was observed. The minimum solubility was found between pH 4 and 5, and a subsequent resolubilization of the protein at pHs lower than 4. Higher protein solubility (greater than 25%) was observed at pH values greater than 8 compared to the acidic pH values at which the protein solubility's were around 20%. The solubility of these materials is known to vary considerably with pH,[29] because above or below the isoelectric point proteins have either a positive or a negative charge, which enhances solubility. So, at the isoelectric point, pH 4.5 in the case of soy protein isolate, the net charge is zero, resulting in the association of molecules and on the consequent reduced solubility.

The pH effect on the solubility was also evaluated for the other compounds ($SI_{tp}$, $24TTSI_{tp}$, and 0.6X-$SI_{tp}$) being the respective profiles presented in Figure 3.

All the curves evidence a similar type of pH dependence, with a minimum at the isoelectric point (pH 4.5). However, this curvature is attenuated as the material's solubility is decreased. This decrement arises from the crosslinking occurred in the protein structures in result of the different operations and treatments performed. So, the materials with lower solubility have higher crosslinking degrees, as revealed by the free amine groups content listed in Table III.

The effect of the amount of disulphide linkages on the solubility should also be considered. These chemical bonds, present in higher degree in the thermal-treated materials ($24TTSI_{tp}$) also contribute for the reduction of solubility. However, their total amount is apparently not enough to overcome the higher degree of crosslinking achieved by the glyoxal treatment of the soy materials (0.6X-$SI_{tp}$). In fact, disulphide linkages, which result from the reactions between cysteine residues of soy, are expected to occur in small extension because the percentage of cysteine residues in soy is only about 1%.[10,30]

## SDS-PAGE

SDS-PAGE patterns of soy isolate and soy-based plastics were obtained to examine the molecular weight distribution of the proteins after extrusion, heat curing, and crosslinking with glyoxal (Fig. 4).

**TABLE III**
**Crosslinking Degree of Soy Protein-Based Plastics**

| Glyoxal (%)[a] | Heat Treatment[b] (Time/hs) | Free-$NH_2$ Groups after Extrusion (%) | Free-$NH_2$ Groups after injection molding (%) |
|---|---|---|---|
| 0 | 0 | 100 | 97.6 |
| 0.3 | 0 | 71.4 | 66.3 |
| 0.6 | 0 | 59.3 | 55.9 |
| 0 | 24 | 83.8 | 72.2 |

[a] w/w % based on protein.
[b] All heat treatments performed at 80°C.

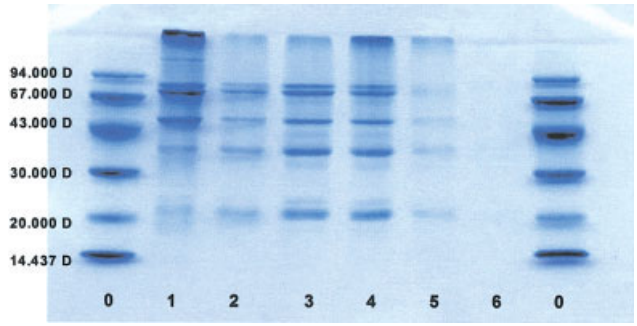


**Figure 4** SDS-PAGE analysis for native soy protein (lane 1); and soy-based plastics: (i) $SI_{tp}$ (lane 2); (ii) $SI_{tp}$ extruded at pH-4 (lane 3); (iii) $24TTSI_{tp}$ (lane 4); and (iv) $03.X\text{-}SI_{tp}$ (lane 5), and $0.6X\text{-}SI_{tp}$ (lane 6).

SDS-PAGE of the soy isolate extract revealed a band at the higher molecular weight region (>94 kDa) that was absent in the $SI_{tp}$. Another clear difference was the density of the molecular weight distributions between soy isolate and the respective plastics. Soy isolate presented a higher density of molecular weights greater than 30 kDa (Fig. 4, line 1). On the contrary, soy plastics (Fig. 4, lines 2 to 6) showed only fractions of specific molecular weights, namely of ~35, ~45, and ~67 kDa. This suggests the possibility of protein aggregation during the thermomechanical action of the processing stages.[27] $24TTSI_{tp}$ samples (Fig. 4, line 4) revealed a higher intensity of the specific bands described above. This indicates that heat treatment induces even more aggregations within the protein molecules, leading also to decreased solubility, as it was also explained earlier. Relative to the glyoxal-crosslinked samples ($0.3X\text{-}SI_{tp}$ and $0.6X\text{-}SI_{tp}$; Fig. 4, lines 5 and 6), the general intensity of the global patterns was less intense than for the other samples. This feature was already expected, and is due to the aggregation of the protein by crosslinking through amine and sulphydryl groups. Consequently, these materials showed a decreased solubility.

## CONCLUSIONS

In general, the soy plastics proved to be very versatile materials, easily processed by conventional melt-based technologies, presenting interesting mechanical performance and a pH-dependent solubility. Based on these characteristics, soy plastics present promising potential to be used in the production of pH-triggered devices, such as carriers for controlled release of bioactive agents.

## References

1. Schilling, C. H.; Babcock, T.; Wang, S.; Jane, J. J Mater Res 1995, 10, 2197.
2. Paetau, I.; Chen, C.-Z.; Jane, J. J Environ Polym Degrad 1994, 2, 211.
3. Otaigbe, J. U.; Adams, D. O. J Environ Polym Degrad 1997, 5, 199.
4. Cuq, B.; Gontard, N.; Guilbert, S. Polymer 1997, 38, 2399.
5. Lai, H. M.; Padua, G. W.; Wei, L. S. Ceram Chem 1997, 74, 351.
6. di Gioia, L.; Cuq, B.; Guilbert, S. Ceram Chem 1998, 75, 514.
7. Marquie, C.; Aymard, C.; Cuq, J. L.; Guilbert, S. J Agric Food Chem 1995, 43, 2762.
8. Johnson, L. A.; Myers, D. J.; Burden, D. J. US Inform 1992, 3, 282.
9. Sheard, P. R.; Mitchell, J. R.; Ledward, D. A. J Food Technol 1986, 21, 627.
10. Ferreira, S. H. P.; Arêas, J. A. G. J Food Sci 1993, 58, 378.
11. Paetau, I.; Chen, C.-Z.; Jane, J. Ind Eng Chem Res 1994, 33, 1821.
12. Wang, S.; Sue, H.-J.; Jane, J. J Mater Sci Pure Appl Chem 1996, A33, 557.
13. Cheftel, J. C.; Cuq, J.-L.; Lorient, D. In Amino-Acids, Peptides and Proteins; Fennema, O. R., Ed.; Marcel Dekker Inc.: New York, 1985, p. 245.
14. Friess, W. Eur J Pharm Biopharm 1998, 45, 113.
15. Wong, S. S. Chemistry of Protein Conjugation and Cross-Linking; CRC Press: Boca Raton, FL, 1991.
16. Golomb, G.; Schoen, F. J.; Smith, M. S.; Linden, J.; Dixon, M.; Levy, R. J. Am J Patol 1987. 127, 122.
17. Huang-Lee, L. L. H.; Cheung, D. T.; Mimni, M. E. J Biomed Mater Res 1990, 24, 1185.
18. van Luyn, M. J. A.; van Wachem, P. B.; Olde Damink, L.; Dijkstra, P. J.; Feijen, J.; Nieuwenhuis, P. Biomaterials 1992, 13, 1017.
19. Weadock, K.; Olson, R. M.; Silver, F. H. Biomater Med Dev Artif Org 1983, 11, 293.
20. Khor, E. Biomaterials 1997, 18, 95.
21. Finley, J. W. In Protein Quality and the Effects of Processing; Phillips, R. D.; Finley, J. W., Eds.; Marcel Dekker Inc.: New York, 1989; p 1.
22. Gogoi, B. K.; Choudhury, G. S.; Oswalt, A. J. Food Res Int 1996, 29, 505.
23. ISO 62. Plastics—Determination of Water Absorption; International Organization for Standardization, 1980.
24. Bertrand-Harb, C.; Nicolas, M.-G.; Dalgalarrondo, M.; Chobert, J. M. Sci Alim 1993, 13, 577.
25. Goissis, G.; Piccirili, L.; Goes, J. C.; Plepis, A. M. D.; Das Gupta, D. K. Artif Organs 1998, 22, 203.
26. Olde Damink, L. H. H.; Dijkstra, P. J.; van Luyn, M. J. A.; van Wachem, P. B.; Nieuwenhuis, P.; Feijen, J. J Mater Sci Mater Med 1995, 6, 460.
27. Rault, I.; Frei, V.; Herbage, D.; Abdul-Malak, N.; Huc, A. J Mater Sci Mater Med 1996, 7, 215.
28. Rangavajhyala, N.; Ghorpade, V.; Hanna, M. J Agric Food Chem 1997, 45, 4204.
29. Gennadios, A.; Bradenburg, A. H.; Weller, C. L.; Testin, R. F. J Agric Food Chem 1993, 41, 1835.
30. Cheftel, J. C.; Cuq, J.-L.; Lorient, D. In Food Chemistry; Fennema, O. R., Ed.; Marcel Dekker Inc.: New York, 1985; p 245.