

Biodegradable Soy Protein–Polyester Blends by Reactive Extrusion Process

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Received 24 October 2003; accepted 23 January 2004

Abstract: Blends of soy protein concentrate and biodegradable polyester (Estar Bio Copolyester, EPE) were prepared by using glycerol as a compatibilizing agent. Good miscibility was obtained only when the soy protein was initially combined with glycerol under high shear and at elevated temperatures in an extruder. Under these conditions, partial denaturing of the soy protein led to specific interactions between functional groups of the protein with the glycerol. The extrusion conditions and appropriate screw configuration were the critical factors affecting the reactivity of the protein and hence, the properties of the blends. Screws with large kneading blocks that produced high shear mixing were preferred and led to thermoplastic blends characterized by high elongation and high tensile strength. The morphology of these soy protein/polyester blends was studied by using environmental scanning elec-

tron microscopy (ESEM) and indicated good wetting of the soy protein particles within the polyester matrix. The thermal properties were studied by differential scanning calorimetry (DSC) and showed a lower degree of crystallinity and a continuous depression of the melting point of the polyester as the concentration of protein was increased. The possibility of using soy protein concentrate instead of the more expensive (higher purity) soy protein isolate in the preparation of biodegradable resins should lead to new commercial opportunities based on renewable, agricultural byproducts. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3231–3239, 2004

Key words: biodegradable; blends; compatibilization; morphology; polyesters; proteins; reactive processing; renewable resources; thermoplastics

INTRODUCTION

There is an increasing number of studies dealing with biodegradable compositions derived from agricultural products that are set to compete with polymeric materials derived from petroleum-based products for a variety of different applications. Many of these bio-based compositions are derived from soybean, an annual crop that is plentiful and not as costly to produce as most other crops.¹ Generally, soybeans contain about 40% meal (soy flour, soy isolate, and soy protein concentrate), about 20% oil, and the rest is cellulose, sugars, and crude fiber. Soybean meal is currently the more valuable component obtained from processing soybeans; however, the majority of it is used as a high-protein ingredient in livestock feed, whereas only a small portion of it is used in the preparation of protein concentrates and isolates for industrial applications. Thus, the relative abundance of soy protein, its moderate cost, the local and well-established production practices, as well as its biodegradability make soy protein an attractive source of raw material for the plastic industry. Furthermore, its use in biodegradable

resins will reduce environmental waste and will add value to agricultural products.

Soy protein is among several proteins that can be processed into films. It is available commercially in three different grades from soybean processing plants: soy isolate (about 90% protein content), soy protein concentrate (65–72% protein content), and soy flour (about 54% protein). The rest of the composition in each of these grades consists primarily of carbohydrates.² About 90% of the proteins in soybeans are dehydrated storage proteins with two major components: conglycinin (7S) and glycinin (11S).³ Conglycinin has an average molecular weight of 200,000, whereas glycinin has both acidic and basic subunits and an average molecular weight of 350,000 and 200,000, respectively.⁴ However, irrespective of the grade used, soy protein films are very brittle, have fairly low tear strength, poor tensile strength, and high water sensitivity. These problems must be addressed and resolved before it can be used in commerce.

Early studies^{5–7} of processing soy protein into useful materials describe incorporation of formaldehyde and other hardening agents followed by molding the resulting resins into disks. Although various translucent thermoplastic and thermoset resins were obtained, depending on the type of additives used, pH, and the water content, it was realized that water sensitivity and the brittle nature of the soy protein re-

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mained the two main problems that needed to be resolved before soy protein could be processed into useful products. Several approaches were taken to address these problems that include addition of various hardening and crosslinking agents, as described in these early studies: blending the soy protein with other polymers, and chemically⁸⁻¹¹ or enzymatically¹² modifying its structure to render it less hydrophilic. Of particular interest here is the blending approach with the use of small amounts of compatibilizing agents, as this approach is easier to scale-up into commercial process by using existing equipment. Since these early studies, many studies have been published using blends of soy protein with other biodegradable polymers in an attempt to enhance the mechanical properties and eliminate the water sensitivity problems of the protein. A few recent examples include blends with anhydride-modified polyesters,¹³ polybutylene succinate-*co*-adipate,¹³ starch,¹⁴ sodium alginate,¹⁵ carboxymethylated konjac glucomannan,¹⁶ polycaprolactone,¹⁷ and poly(ethylene-*co*-ethyl acrylate-*co*-maleic anhydride).¹⁸

It is generally agreed that highly purified grades of soy protein (e.g., soy isolate) are needed for fundamental studies related to understanding the structure of the protein or determining some specific interactions of it with other materials. However, it is preferred to use soy protein concentrate, which is less costly and more readily available, for applying the results into possible commercial applications. In this study, we report our results on a reactive extrusion process for producing a blend of soy protein concentrate and biodegradable Eastar Bio Copolyester.

EXPERIMENTAL

Materials

Soy flour from Central Soya (Fort Wayne, IN) (Soyfluff 200W), characterized by a particle size of 90% smaller than 200 mesh, was used. Soy concentrate (SC) was also obtained from Central Soya (Procon 2000). It is characterized by a particle size of 94% smaller than mesh 100, maximum moisture content of 10%, and precipitated from pH = 4.5 solution. All the soy protein samples were dried at 50°C for 24 h before use.

Biodegradable polyester from Eastman Chemicals (Eastar Bio Copolyester) was used. This random copolymer is composed of adipic acid, terephthalic acid, and 1,4-butanediol. Glycerol was obtained from J. T. Baker and was used as received.

Process

The soy protein was initially mixed with glycerol (70 : 30) in a kitchen mixer for 30 min and then extruded in a corotating twin-screw extruder ZSK-30 (Werner & Plfei-

derer) to obtain an apparent homogeneous mass. Care was taken not to degrade the protein during the plasticization process and, thus, a flat temperature profile of 135–140°C was used. The screw speed was kept at 125 rpm with a torque of about 65%. A vent port was left open just before the die to remove any volatile materials. The extrudate was very brittle and was grounded in a BTP granulator. These granules were then extruded with the polyester to give the protein/polyester blend. A flat temperature profile was used in all runs (either 135 or 170°C); the screw speed was kept at 125 rpm with a constant torque of about 55%. All pellet materials were metered by using a gravimetric Acrison feeder. Powdered materials were added by using calibrated K-tron volumetric feeder. The protein/polyester extrudate was quenched in a water bath, wiped dry, and pelletized. The pellets thus obtained were further dried at 58°C for at least 24 h.

Films were prepared by using a Killion single-screw extruder equipped with a film cast line whereby the resin was melted at about 150°C and was extruded between the two nip rolls kept at below room temperature to inhibit melt crystallization. The draw ration and therefore the film thickness and orientation were controlled by the relative speed of the main rolls and winder rolls. Typically, the roller speed was kept at 400 rpm and the winder speed was between 50 and 60 rpm.

Tensile test specimens were prepared by injection molding (Cincinnati Milacron) by using a flat temperature profile ranging from 135 to 180°C.

CHARACTERIZATION

Mechanical properties

The mechanical properties were measured on a United Testing Systems machine model SFM-20. Prior to testing, all the samples were equilibrated at 25°C and 25% relative humidity for at least 40 h. The tensile bars and films were tested according to ASTM D638 and ASTM D882, respectively. Young's modulus, tensile strength, and elongation at break were determined by using a crosshead speed of 50 mm/min for tensile bars and 100 mm/min for the film samples. At least five identical samples were examined and the average and standard deviation were calculated from the results.

Morphology

A Phillips ElectroScan 2020 environmental scanning electron microscope was used to study the morphology of selected blends. The fractured surfaces (from the mechanical properties tests) were mounted on an aluminum disc. Micrographs were taken under accelerating voltage of 20 kV gas sensitive electron detector (GSED) from different areas to ensure coverage of typical features.

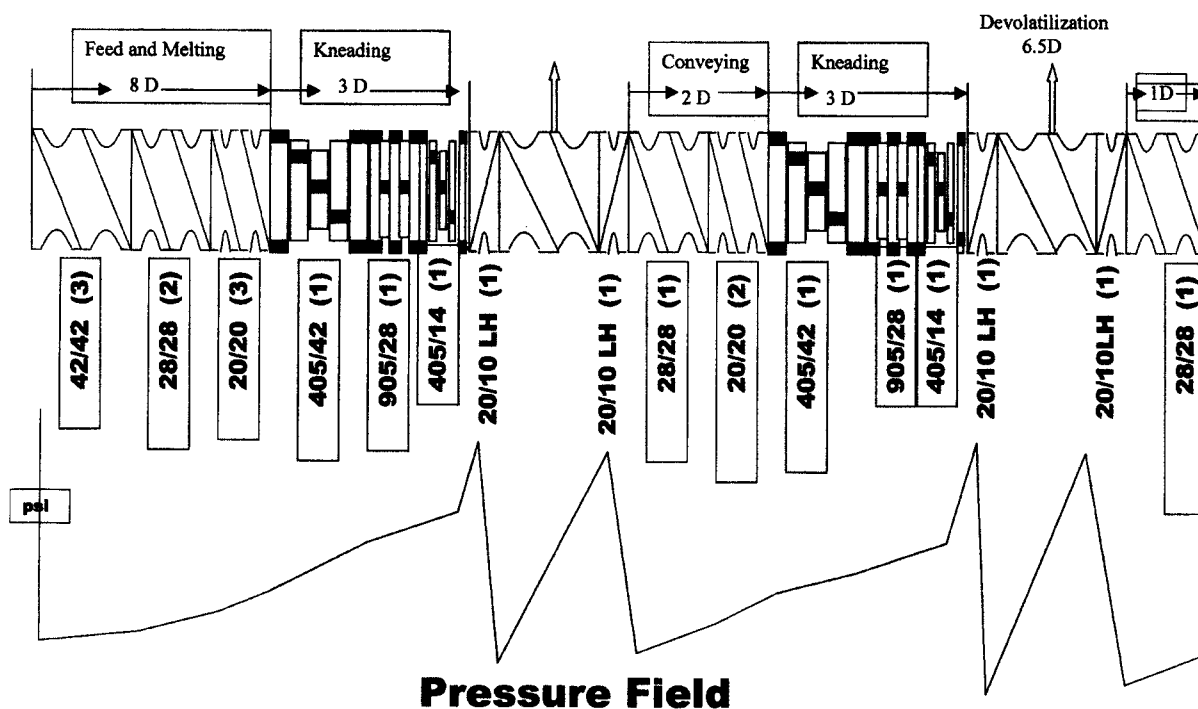


Figure 1 High kneading screw configuration.

Thermal analysis

Differential scanning calorimeter (DSC) model 2920 MDSC V2.6A (TA Instruments) was used to study the melting point depression. Samples were heated to 150°C and held at that temperature for 10 min to ensure complete melting and then cooled at a constant rate of 20°C/min. Alternatively, the samples were annealed between 40 and 70°C, quenched rapidly to -50°C, and then heated at 10°C/min to determine the melting point and the degree of crystallinity (area under the melting peak).

RESULTS AND DISCUSSION

Soy protein is among several proteins that are reported to be film forming by cast it from solution or by extruding it between two nip rollers. However, such films are brittle, have low tear strength, poor water resistance, and poor tear strength. One convenient method that was used to improve these properties was to blend soy protein with appropriate polymers. Because the chemical nature of a protein is a polyamide, composed of amino acids, it is inherently hydrophilic and thus incompatible with hydrophobic polymers or additives that are needed to reduce the water sensitivity of the blend. It was realized that the properties of such blends could be improved by incorporating a compatibilizing agent that resides on the polymer/protein interface.

The results of our studies show that the process conditions are critical to enhance the interactions between the protein and the compatibilizing agent (e.g., glycerol). Mixing at room temperatures or slightly above, even under high shear and extended period of time, was not sufficient. Best results were obtained by extruding glycerol and soy protein at high temperature by using a screw configuration with a high number of kneading elements, as shown schematically in Figure 1. The location of the kneading blocks along the screw undoubtedly has an effect on mixing, but was not optimized in this study.

Screws with lower kneading elements have higher conveying capacity, lower torque, and lower power requirements. Hence, such screw configurations are usually preferred from a productivity point of view. However, we observed that a higher number of kneading elements expanded the reactive zone whereby the high shear and high temperature caused denaturation of the protein and interactions with glycerol. Although the total throughput decreased when more kneading elements were used, it provided longer residence time and higher reactivity of the protein with glycerol. Attempts to increase the temperature beyond 140°C were not successful as they caused excessive thermal degradation of the soy protein during compounding.

Mechanical properties

The mechanical properties were greatly affected by the process used to incorporate the plasticizer (glyc-

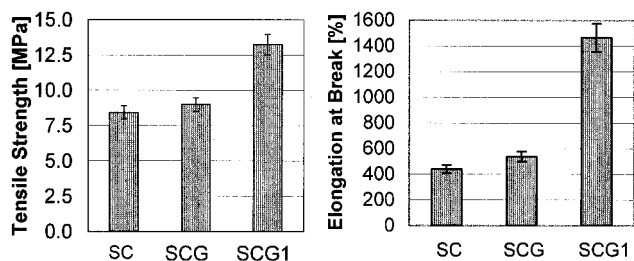


Figure 2 Effect of processing temperature using glycerol as a plasticizer. Samples were composed of 70 pph Eastar Bio Copolyester and 30 pph Soy protein SC : Soy concentrate (no glycerol). SCG: glycerol plasticized soy protein at RT; SCG1: glycerol plasticized soy protein at 135–140°C.

erol) into the protein, as shown in Figure 2. It is clearly evident that not adding glycerol or even mixing it in at room temperature is not as effective as adding the plasticizer under high shear and at an elevated temperature. The heat and the high shear are known to denature the protein, which most likely promoted intermolecular interactions with the plasticizer. It should be noted, however, that care must be taken not to degrade the protein under excessive heating or prolonged processing.

Attempts to use ethylene glycol instead of glycerol as a plasticizer were not successful as it was not possible to extrude it with the soy protein because of rapid rise in the torque even at very low feed rates.

As expected, the mechanical properties were highly affected by the composition of the blend as listed in Table I. As the content of the polyester in the blend was increased (and the soy protein was decreased), lower tensile strength and lower elongation at break were obtained.

The results of the tensile measurements indicate the importance of the interactions between the various components in the blend and impact of the processing conditions on affecting these interactions. It is apparent that glycerol is intimately incorporated into the soy protein only under high temperature and shear encountered in the extrusion process as a result of some irreversible denaturing of the protein structure. The importance of this step needs to be emphasized as it was clearly noted by changing the screw configuration. It was observed that the tensile strength and the elongation at break were improved when the kneading zone was increased. Although screws with lower kneading capabilities have higher conveying capacity, lower torque, and lower power requirements (thus are usually preferred from a productivity perspective), they provide better mixing and ultimately higher mechanical properties.

Previous studies concluded that the mechanical properties of the blends are greatly affected by the composition but most were limited in composition to resinous materials having elongation at break of less

than 10%.^{18,19} It is to be expected that the tensile strength and Young's modulus would decrease as the content of the soy protein in the blend is reduced. However, it is always desirable to enhance the toughness of the blend by maintaining high tensile strength and high elongation. The tensile strength of the blend composed of Eastar Bio Copolyester : soy protein concentrate (60/40 EPE : SPI) was 9.9 MPa and 750% elongation at break compared with blends of 60 : 40 soy protein isolate and poly(ethylene-co-ethyl acrylate-co-maleic anhydride) that had tensile strength of 5.6 MPa and less than 30% elongation at break. Similarly, a blend of soy protein isolate and maleated ethylene-propylene copolymer had a tensile strength of 6.4 MPa²⁰ and a blend of soy protein isolate and carboxymethylated konjac glucomannan had a tensile strength of about 35 MPa and ultimate elongation around 20%.¹⁶ The difference is undoubtedly related to the mechanical properties of the soy protein grade (e.g., soy concentrate versus soy protein isolate) and the mechanical properties of the other components in the blend [EPE versus poly(ethylene-co-ethyl acrylate-co-maleic anhydride) or maleated ethylene-propylene copolymer] but also due to the degree of compatibility and homogeneity of the blends. The latter are usually derived from the type of compatibilizer and the preparation process.

It is apparent from the current study that incorporating the compatibilizer (e.g., glycerol) with the soy protein under high shear and high temperature prior to blending it with the copolyester had a significant effect on the properties. A significant increase in the tensile strength and the elongation at break was noticed only when the glycerol was initially extruded with the soy concentrate and then, in a second step, this modified soy protein was blended with the Eastar Bio Copolyester. It is interesting to note that a similar two-step approach did not prove advantageous¹⁹ to blends prepared from soy protein isolate and poly(vinyl alcohol). Evidently, the conditions in the extrusion that we used were more effective than in the previous study. It is realized that a one-step process has an obvious advantage over a multistep process in terms of product throughput, energy consumption, time, and ultimately cost. However, both steps (the protein plasticization and the blending with the Eastar Bio

TABLE I
Effect of EPE : PSC Ratio on the Mechanical Properties

| EPE (wt %) | PSC (wt %) | Tensile (MPa) | Elongation (%) |
|------------|------------|---------------|----------------|
| 40 | 60 | 4.58 ± 0.07 | 10 ± 1 |
| 50 | 50 | 6.07 ± 0.06 | 76 ± 12 |
| 60 | 40 | 9.93 ± 0.24 | 754 ± 49 |
| 70 | 30 | 13.38 ± 0.14 | 1499 ± 45 |

EPE: Eastar Bio-polyester; PSC: plasticized soy protein.

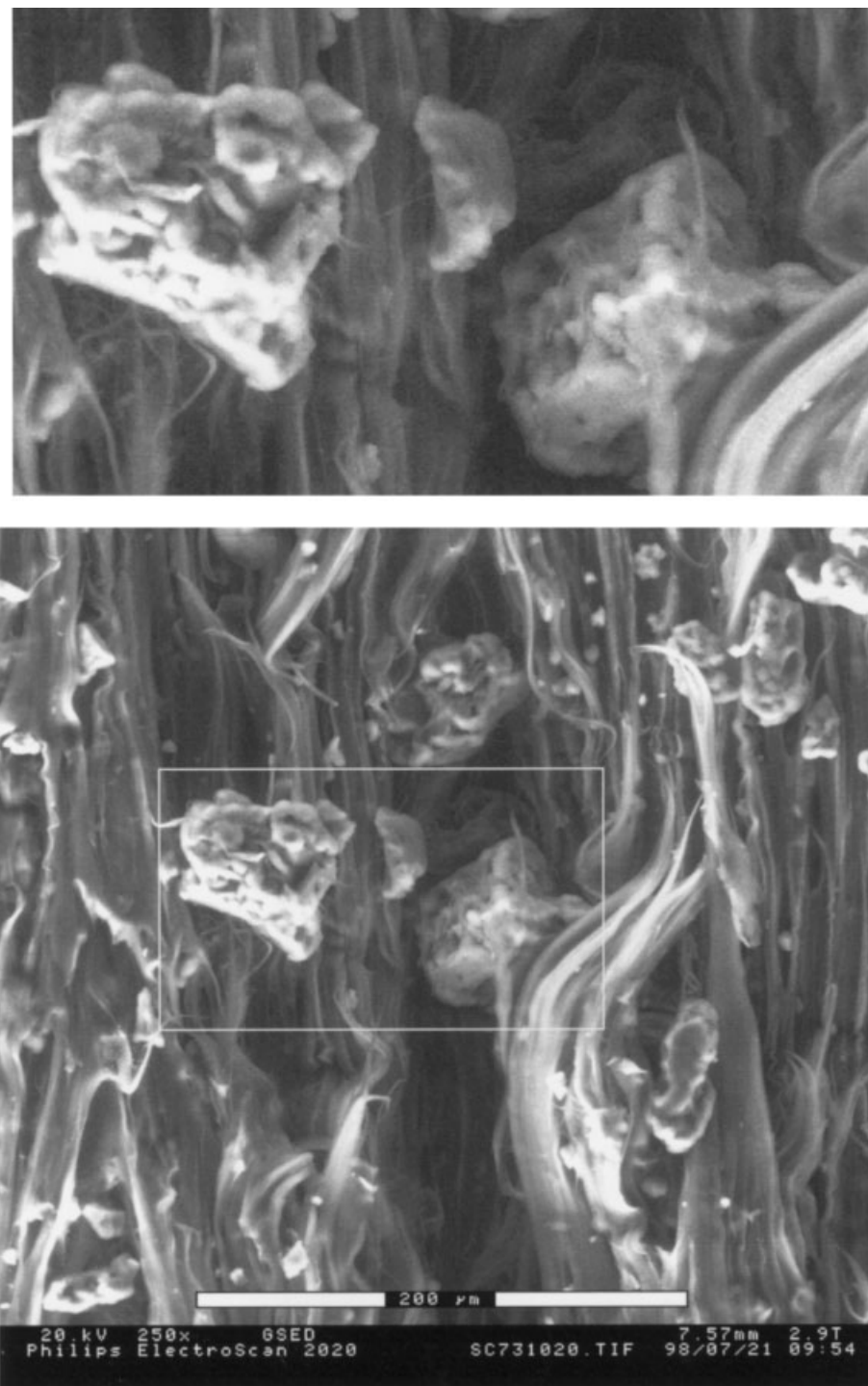


Figure 3 SEM photograph of EPE : SPC blend (70 : 30) plasticized with glycerol at RT.

Copolyester) can be combined into a single operation by using two extruders in a T-configuration, thereby producing the blend in a continuous process.

Morphology

Powder of soy concentrate is composed of irregularly shaped particles several hundred micrometers in size

with relatively large particle size distribution. Significant secondary aggregation of the particles occurs if the soy is exposed to moisture, due to its hydrophilic nature. These particles are clearly visibly embedded in the Eastar Bio Copolyester when the soy protein was not thoroughly wetted by glycerol prior to its blending with the polyester (Fig. 3) as was the case when the soy protein and glycerol were not pre-reacted and

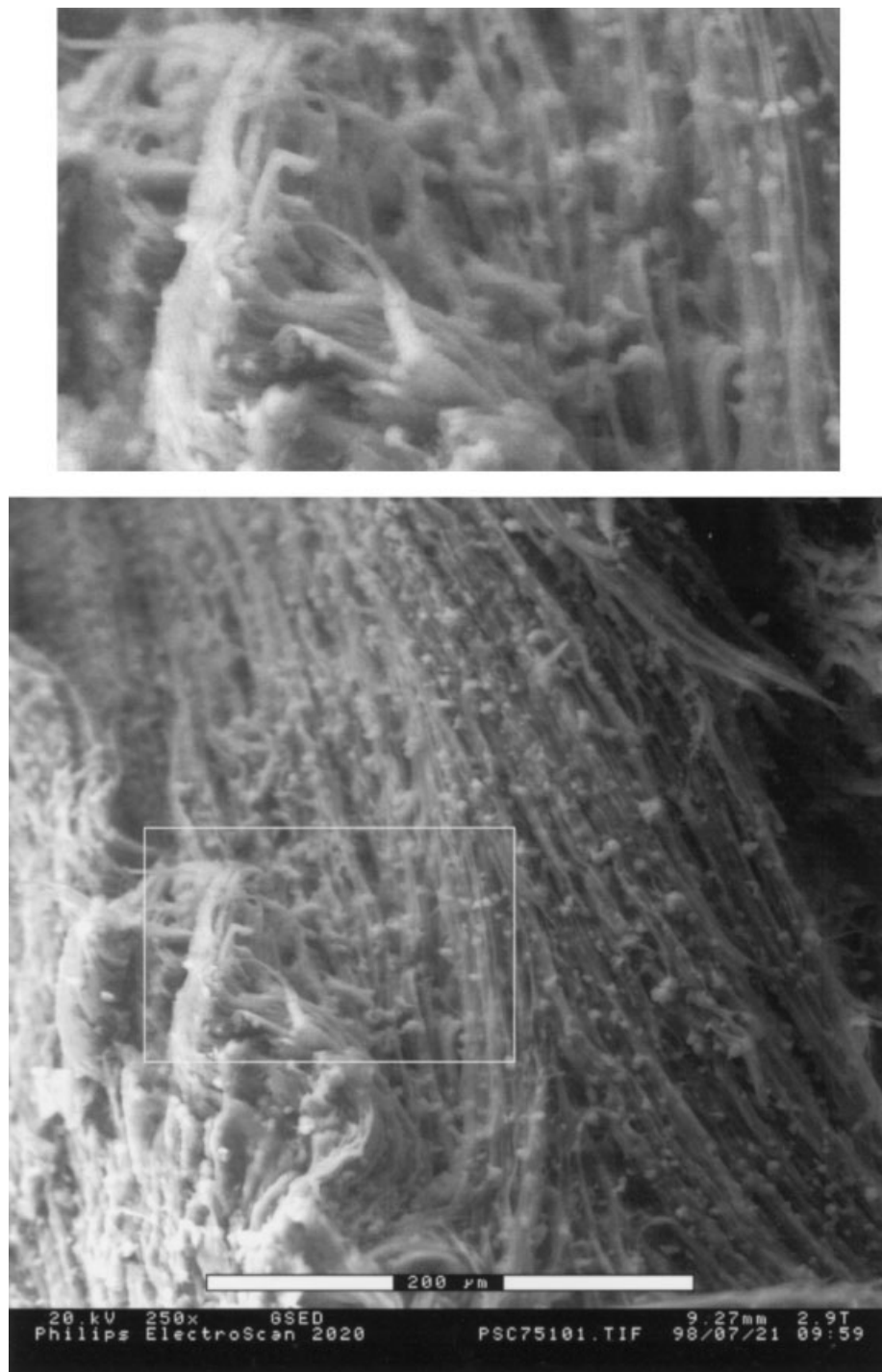


Figure 4 SEM photograph of EPE : SPC blend (70 : 30) plasticized with glycerol at 135°C.

extruded together with the Eastar Bio Copolyester. Under these conditions, the morphology of this blend indicates poor compatibility and consists of distinct soy protein particles not wetted by the polyester matrix. Furthermore, the sharp edges of the particles appear to indicate that they are crystalline and thus not affected by the glycerol. In the absence of interactions between the polyester matrix and the large, ag-

gregated soy protein particles, the polyester carries the mechanical load with no contribution from the soy protein.

On the other hand, extruding the soy protein with glycerol at elevated temperatures (above 135°C), before blending it with the Eastar Bio Copolyester, led to good wetting of the protein by the glycerol, resulting in a more homogeneous morphology (Fig. 4). The soy

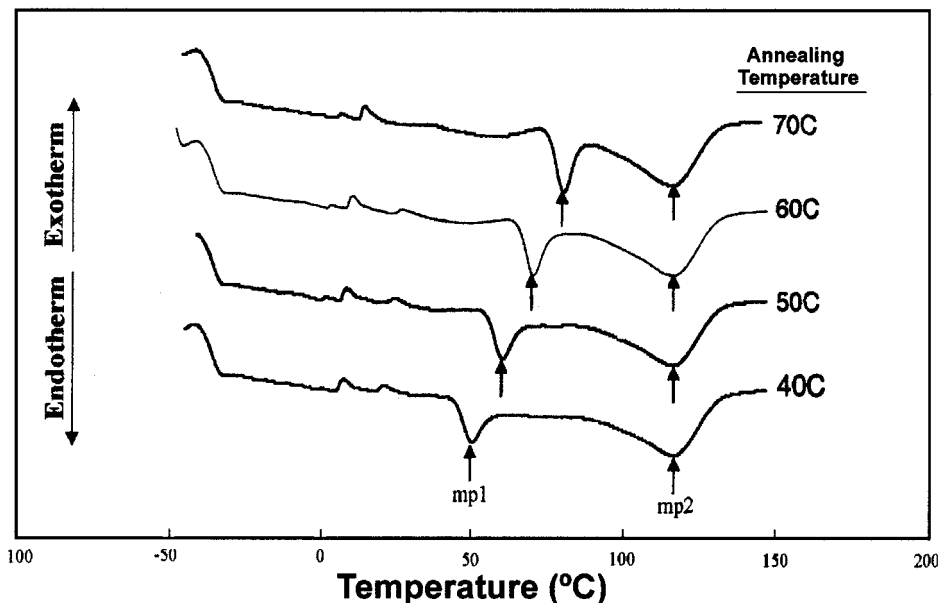


Figure 5 Melting point endotherms for various annealing temperatures.

protein particles are noticeably much smaller and less distinct. It is also observed that the soy particles are coated by the polymer matrix with much less discrete interface and their surface has no sharp edges. Indeed, the mechanical properties of the blend prepared under these conditions are much improved, indicating the soy protein particles act to reinforce the polyester matrix.

The composition of the blends (e.g., the ratio of Eastar Bio Copolyester to the soy protein concentrate) had no significant effect on the morphology other than the obvious increase in the number of soy particles. No cracks were noticed in any of the samples as was the case with other brittle blends.^{19,21}

It is important to note, however, that if the processing temperature was higher than 160°C, a noticeable degradation of the protein was observed and although good wetting with the matrix was still observed, the mechanical properties were generally poor.

Thermal analysis

Annealing Eastar Bio Copolyester with no additional soy protein at different temperatures showed dual melting peaks (Fig. 5) corresponding with the two major segments of the copolymer having different crystal species. It was observed that the lower melting point (mp1) is linearly proportional to the annealing temperature and shifts from 50 to 80°C as the annealing temperature is increased from 40 to 70°C. On the other hand, the upper melting point (mp2) was unaffected by annealing within this range and remained constant at 118°C (Fig. 6).

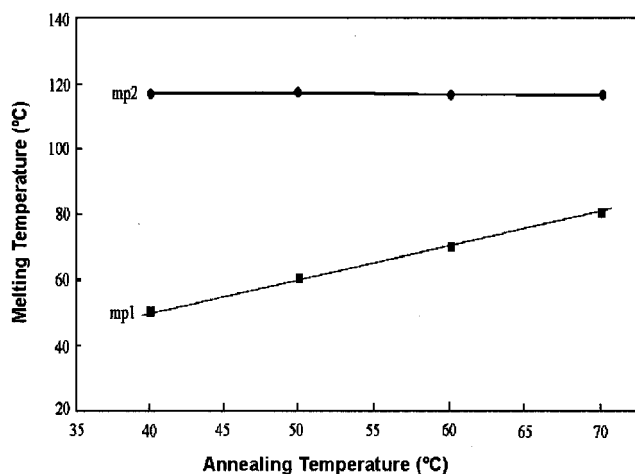


Figure 6 The effect annealing temperature on melting temperature.

DSC scans of the soy protein/Eastar Bio Copolyester blends showed the two melting peaks of the polyester components with no evidence of melting of soy protein crystals. Furthermore, the thermal properties of the blends were affected by their composition and the thermal history (annealing) of the samples. Most noticeable was the depression of the higher melting point (mp2) as the concentration of soy protein in the blends increased while the lower melting point (mp1) was not affected and remained constant, as shown in Figure 7 for the blends that were annealed at 50°C. Similar behavior was observed for all other blends annealed at different temperatures. The depression of the higher melting point (mp2) was always linearly

proportional to the composition and ranged between 112 and 118°C, whereas the lower melting point (mp1) remained constant irrespective of the composition. However, the temperature of the lower melting point was determined by annealing conditions as shown in Figure 6.

It is generally agreed that the crystal size affects the melting point and poorly defined, small crystals would have a somewhat lower melting point than otherwise identical large crystals. Accordingly, increasing the annealing temperatures from 40 to 70°C led to the development of larger crystals corresponding to mp1 but had no apparent effect on mp2, whereby interactions of soy protein with these crystals were responsible for the depression in mp2.

The enthalpy of fusion was calculated from the area under the melting peaks based on the sample weight and is plotted in Figure 8 as a function of the annealing temperature for a blend composed of 70 : 30 Eastar Bio Copolyester : soy protein. Similar characteristics were observed for the other blends in this study. It is apparent from these data that the enthalpy, which is proportional to the degree of crystallinity of mp1, is much lower than mp2, indicating that the majority of the crystalline phase consists of the higher melting point crystals. Furthermore, the enthalpy corresponding to mp1 is constant and independent of the annealing temperature, whereas the enthalpy corresponding to mp2 is inversely proportional to the annealing temperature and continuously decreases with an increase of the annealing temperature. Because the crystalline phase in the samples consists mainly of the upper melting point crystals (mp2), the overall degree of crystallinity in these blends also decreases as the annealing temperature is increased.

The overall degree of crystallinity also decreases as the soy protein content in the blend is increased (Fig. 9). Although the data are somewhat scattered, it is

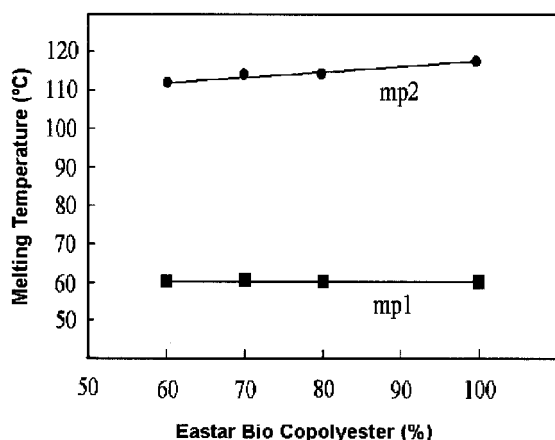


Figure 7 The effect of Eastar Bio Copolyester content on melting temperature.

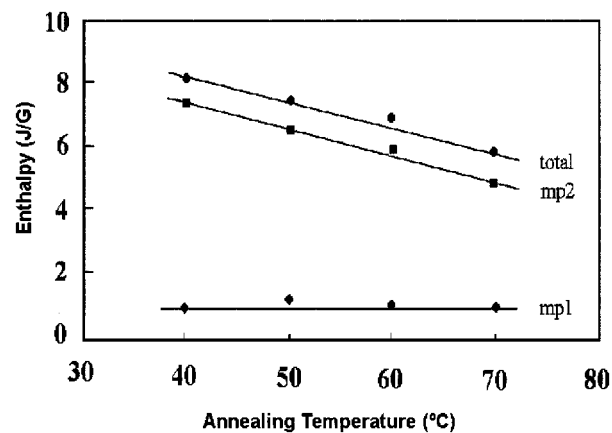


Figure 8 The effect of annealing temperature on enthalpy.

clearly observed that the degree of crystallinity of the polyester is reduced due to interactions of the soy protein with the polymer matrix. The effect of annealing temperature is not as clear because of the experimental error associated with these experiments but appears to indicate that lowest crystallinity is obtained at the highest annealing temperature.

It is interesting to note that the degree of crystallinity was observed to decrease in other blends containing soy protein and the melting point of the polymer matrix remained nearly constant, provided good interactions were obtained between the soy protein and the polymeric matrix.¹⁸ Apparently, the high shear and high temperature conditions that were used to incorporate the compatibilizer (glycerol) in the first step led to some denaturing of the protein and provided interactions between the alcohol groups and the functional groups on the protein (amine and carboxylic groups). These interactions were then sufficient to improve the compatibility of the hydrophilic protein within the hydrophobic polyester matrix. However, the data further indicate that these interactions were not sufficiently strong to drastically change the thermal properties of either the protein or the polyester, as would be the case in compatible blends.

CONCLUSIONS

A series of soy protein concentrate and biodegradable polyester (EPE) blends as prepared by using glycerol as a compatibilizer. It was observed that the blending process greatly affected the compatibility and subsequently the mechanical properties, morphology, and thermal behavior of these blends. Best results were obtained when the glycerol was incorporated initially with the protein in an extruder that provided the high shear and high temperature that are needed to partially denature the protein structure and enable it to interact with the glycerol. The protein/glycerol was

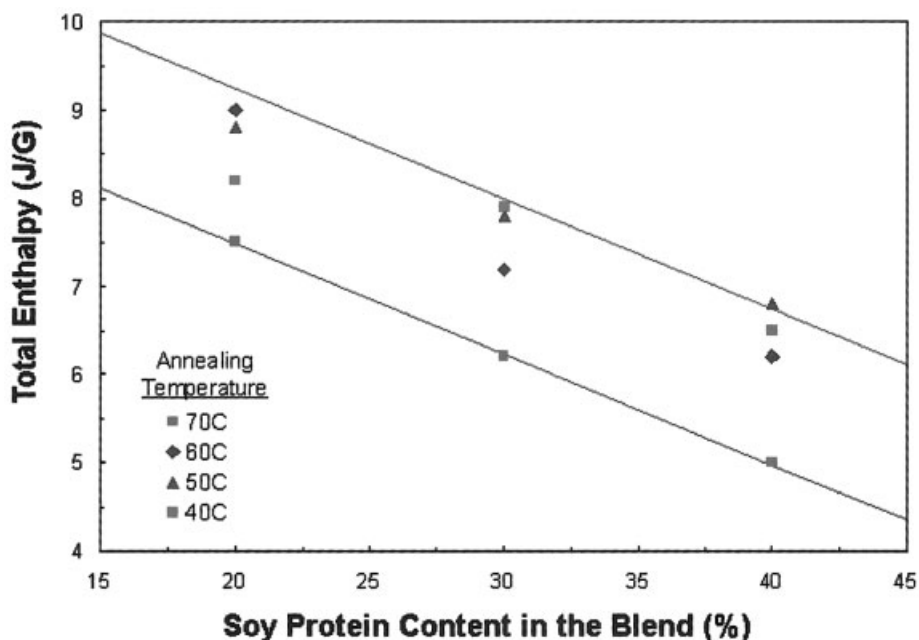


Figure 9 The effect of soy protein content in the blend on total enthalpy.

then blended with a biodegradable polyester (EPE) to yield various compositions whereby the protein particles are wetted by the polymer matrix and act as a reinforcing agent. The good miscibility of soy protein in the polyester matrix greatly improved the mechanical properties of the blends leading to tough materials having high tensile strength and high elongation at break. Provided good miscibility was attained, the thermal history of the samples (annealing at various temperatures) further affected the melting points and the degree of crystallinity of these blends.

It is important to note that this study was conducted by using soy protein concentrate, which is readily available and lower in cost compared with soy protein isolate. Moreover, the data indicate that under appropriate processing conditions even this low-grade protein can be compounded to yield low-cost, biodegradable materials that could replace low-density polyethylene products.

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