

Bio-film Composites Composed of Soy Protein Isolate and Silk Fiber: Effect of Concentration of Silk Fiber on Mechanical and Thermal Properties

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ABSTRACT: A novel, simple and totally recyclable method has been developed for the synthesis of nontoxic, biocompatible and biodegradable bio-composite films from soy protein and silk protein. Bio films are defined as flexible films prepared from biological materials such as protein. These materials have potential application in medical and food as a packaging material. Their use depends on various parameters such as mechanical (strength and modulus), thermal, among others. In this study, prepare and characterization of bio films made from Soy Protein Isolate (SPI) (matrix) and Silk Fiber (SF) (reinforcement) through solution casting method by the addition of plasticizer and crosslinking agent. The obtained SPI and SPI/SF composites were subsequently subjected to evaluate their mechanical and thermal properties by using Universal Testing Machine and Thermal Gravimetric Analyzer respectively. The tensile testing showed significant improvements in strength with increasing amount of SF content and the % elongation at break of the composites of the SPI/SF was lower than that of the matrix. Though the interfacial bonding was moderate, the improvement in tensile strength and modulus was attributed to the higher tensile properties of the silk fiber.

Key Words: Bio films, Soy protein isolate, Silk fiber, Tensile properties, Thermal stability, Interfacial bonding

1. INTRODUCTION

Petroleum-based plastics dominate today's plastics market because of their high strength, lightweight, low cost, easy processibility, and good water barrier properties. However, most of the synthetic polymers are not biodegradable. Synthetic biodegradable polymers, such as poly (lactic acid), poly caprolactone, and poly (hydroxy butyrate) have high production costs. With the increasing concerns of environmental pollution caused by non-biodegradable petroleum-based plastics, increasing efforts have been made to utilize the polymeric materials derived from agricultural products. In recent years, biodegradable and bio-based polymers have received extensive interest for plastic applications as an alternative to conventional petroleum-based plastics.

Owing to its sustainability, abundance, low cost and functionality, soy protein has attracted great research interest for

the development of environment-friendly protein materials with potentially good properties, such as regeneration, biocompatibility and biodegradability, etc. SPI has been widely used in hydrogel, adhesives, plastics, films, coatings, and emulsifiers [1-4], and it has also been reported as a promising material for biotechnological and biomedical utilization [5,6]. In recent years, many natural and renewable materials such as soy protein [7,8], wheat protein [9,10], polybutylenesuccinate [11] etc., and were utilized to make biodegradable films. Natural matrices are biodegradable, renewable and cheaper. Further, these materials are expected to lower the usage of synthetic polymers which are non-degradable and derived from precious depleting fossil fuels. But unfortunately, the natural matrices are brittle with low mechanical properties and are not suitable for packaging materials in their original form. In order to improve the mechanical properties, they are often reinforced with natural fibers/fabrics such as hemp [12-14], sisal,

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Alfa [15], kenaf [16], Hildegardia [17,18] etc. Due to their abundance and economics, protein matrices are preferred. But protein film formation is a complex process which involves three steps – (1) rupture of low energy intermolecular bonds; (2) rearrangement and orientation of polymer chains (shaping) and (3) formation of a three dimensional structure [19,20]. The inherent cohesiveness in Soy Protein Isolate (SPI) facilitates film formation [7]. As a plant-based polymer, soy protein (SP) has attracted to the authors as matrix owing to its abundance intensive research interest in nonfood industrial applications [22-25]. As the leftover from soybean oil crushing, soy meal is an agricultural residue. Soy meal can be grinded into soy flour (54% protein), or further purified into soy protein concentrate (SPC) (65-72% protein) and soy protein isolate (SPI) (90% protein). The United States is one of the major producers of soybeans in the world. Soybeans, a \$17.5 billion market in the United States, are mainly used for animal feeds. Soybeans contain approximately 42% protein, 20% oil, 33% carbohydrates, and 5% ash on a dry basis [26]. In addition to its use as a food ingredient, non-food applications of soy protein as polymeric materials have attracted increasing attention in recent years. The main attractive features of soy protein-based plastics are that they are biodegradable, environmentally friendly, and from an abundant renewable resource. Use of soy protein as a plastic material can be traced back to the 1930s. Broth and Mckinney studied the formaldehyde-hardened soy plastics and their compounding with the phenolic resin [27,28]. The formaldehyde-treated soy plastics compounded with phenolic resin were reported to display very low water absorption.

Natural fibers are largely divided into two categories depending on their origin: plant based like jute and animal based like silk. By reinforcing various natural fibers/fabrics (NF), environmental friendly composites are made [29]. A lot of work has been done by many researchers on the composites based on both natural and synthetic fibers [30]. In the last decades, a growing interest in NF reinforced composites is observed because of their high performance in terms of excellent mechanical properties, processing advantages, good chemical resistance, etc [31]. Silk fibers from silkworms have been used in textiles for nearly 5000 years. Silks are fibrous proteins, which are spun into fibers by a variety of insects and spiders [32]. They have repetitive protein sequences. The mechanical properties of silk fibers consist of a combination of high strength, extensibility, and compressibility [33,34]. Silk fabrics are mainly produced in China and India. Annually large amounts of waste silk fibers (WSFs) are generated in silk industries in these two countries. Further, as the consumers of silk fabrics are more especially in India, lots of old used fabrics are going as waste. In order to add value to the waste generated and to achieve higher tensile properties for the SPI composites, we have selected waste silk fabrics (SF) as reinforcement [35].

The effect of fabric loading on the tensile properties and thermal stability of SPI/SF composites was studied.

The combination of SPI and SF would be an attractive method to develop new biodegradable films by drawing advantages of the SPI and SF components and minimize their disadvantages. To the best of our knowledge, there are no reports on the properties of SPI/SF blend films so far. This partly stimulated research data might be useful for new biodegradable film preparations.

2. MATERIALS AND METHODS

2.1 Materials

All chemicals used were of analytical grade and high purity. Soy protein powder was purchased from Honeyville Food Products, Salt Lake City Utah, USA. As per the manufacturer's data, SPC supplied consisted 90% protein, 4% fat, about 5% ash and 1% remaining unknown constituents. Glutaraldehyde solution 25% Laboratory reagent grade purchased from SD fine chemicals limited, Mumbai, India. We purchased glycerol about 98% pure from MERCK chemicals, Ahmadabad, India. We obtained WSFs from the silk industries in Dharmavaram town of Anantapur district, Andhra Pradesh, India. Deionized water was used throughout the study.

2.2 Modification of SF

Cocoons of the mulberry silkworm were boiled for 1 hr in a 0.02 M aqueous sodium carbonate solution and then rinsed carefully with cold and hot water to remove the sericin proteins. The alkali treated SFs were washed with diluted mild soap for 2 to 3 minutes and later rinsed with distilled water thoroughly to remove grease and dirt. The dried fibre were cut to the mould size and weighed.

2.3 Composite Preparation and Processing

The required amounts of SP powder and glycerol (10 wt% of SP) were mixed with 20 times (by wt. of SP) distilled water. Proteins are soluble in high alkali medium [22]. The protein molecules dissociate and unfold when the pH of the protein solution is raised in the range of 8-12. These changes enhance the formation of near s-s bonds between the aligned protein polypeptide chains [10]. In the present work, we optimized and adjusted the pH of the solution to 10 by adding required amounts of 1 N NaOH solution. Glutaraldehyde (20 wt% of WPI) was added to this mixture as a crosslinker [36,37]. The cleaned and dried fibers were dipped in the SP solution until they were impregnated with SP. Then the dipped fabrics were stacked as 1(S/S-1), 2(S/S-2), 3(S/S-3) and 4(S/S-4) layers and each set was placed on Teflon coated glass molds and allowed to dry at room temperature for 48 hours. The stacked sheets were then cured at 120°C and 2 MPa pressure for 20 min. This procedure was repeated for matrix also.

2.4 Measurement of Mechanical Properties

The tensile test was performed according to ASTM D638 standard using Universal Testing Machine INSTRAN 3369 at a crosshead speed of 5 mm/min and gauge length 50 mm and the test were performed at 28°C. Average and standard deviation of five specimens for each sample were tested and the tensile strength and tensile modulus were expressed as:

$$\text{Tensile strength (MPa)} = p/bh \quad (1)$$

$$\text{Tensile modulus (MPa)} = \sigma/\epsilon \quad (2)$$

Where, P = Pulling force (N), b = Specimen width (m), h = Specimen thickness (m), σ = Stress (N/m²) and ϵ = Strain

2.5 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) measurements of SP and SP/SF composites were carried out on DSC-TGA Q600 (TA instruments) under nitrogen atmosphere (flow rate 50 mL/min) at a heating rate of 20°C/min using approximately 11 mg of sample weight.

3. RESULTS AND DISCUSSION

In the present study, the fibre content in the composites was reported as weight fraction. The average thickness of the matrix was found to be 0.1 mm whereas that for composites with fabric weight fraction of 0.13(S/S-1), 0.25(S/S-2), 0.37(S/S-3) and 0.5(S/S-4) was found to be 0.3, 0.6, 0.9 and 1.2 mm respectively. The chemical composition of the SPI/SF composite is presented in Table 1.

3.1 Mechanical Properties

The tensile parameters of the matrix and the composites of SPI/SF are presented in Fig. 1. From the figure it is evident that the tensile strength (Fig. 1a) and modulus (Fig. 1b) were higher than for the matrix and increased with fibre content. This improvement can be attributed to two factors - tensile properties of the fibers and the interfacial bonding between the fibers and SP. The cocoon silk fibers have higher tensile strength and modulus but lower % elongation at breaks [39]. Accordingly, the SPI/SF composites possessed higher tensile strength and modulus but lower % elongation at break. The maximum improvement in tensile strength and modulus of

Table 1. Formulations and composition of the soy protein isolate/ silk fiber composite

S.No	Soy Protein (gm)	Glycerol (gm)	Glutaraldehyde	Weight fraction of Silk fiber
SP	5	1	3	0.0
S/S-1	5	1	3	0.13
S/S-2	5	1	3	0.25
S/S-3	5	1	3	0.37
S/S-4	5	1	3	0.50

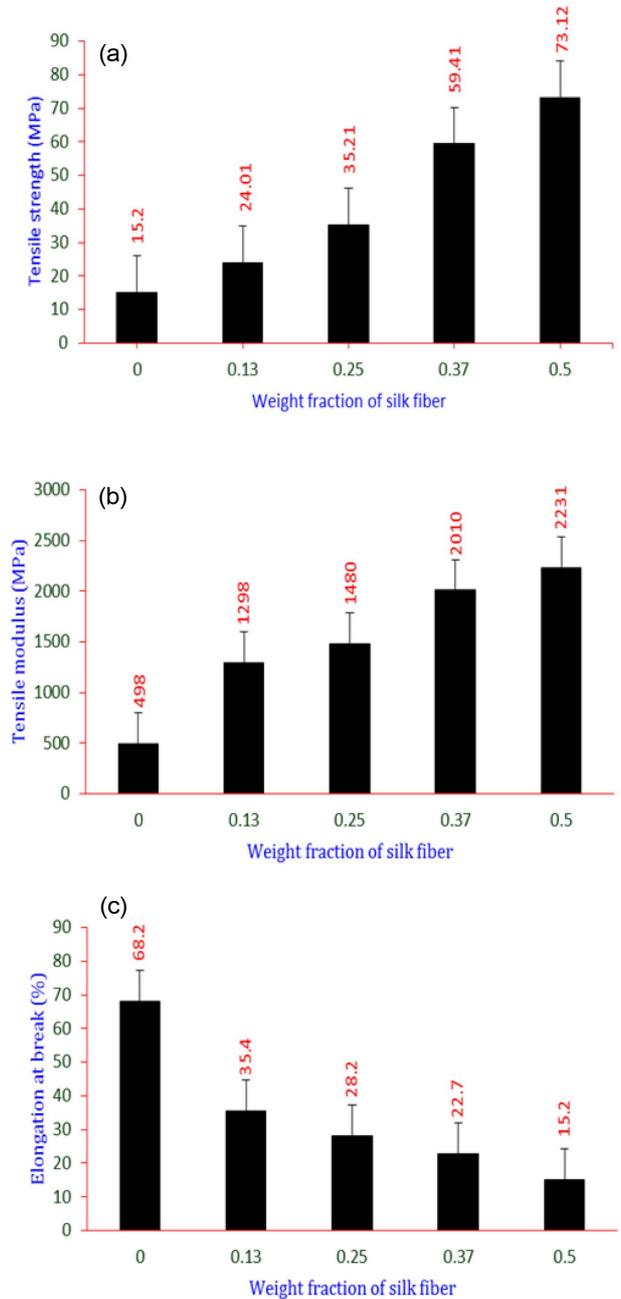


Fig. 1. Tensile properties of SP/SF composites (a) Tensile strength; (b) Tensile Modulus and (c) %Elongation at break

the composites over matrix has for the maximum possible fabric weight fraction of 0.5. The biaxial orientation of the fibers in the present composites might be another factor for higher improvement in tensile strength and modulus and decrease in the % elongation at break of SPI/SF composites.

3.2 Thermogravimetric Analysis

In order to probe the effect of fibre on the thermal stability of the SPI/SF composites, their primary thermograms were recorded and presented in Fig. 2. From Figure it is evident that

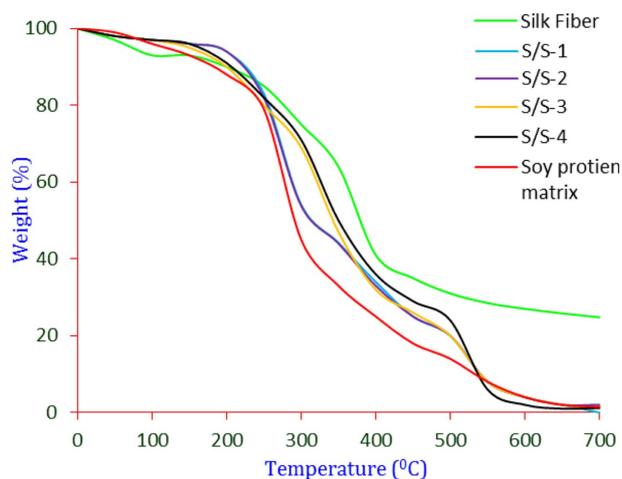


Fig. 2. Thermo grams of Soy Protein Isolate, Silk fiber and SPI/SF composites with different fiber weight fractions

the silk fabric had higher thermal stability and the matrix the least. Further the thermal stability of the SPI/SF composites lied between that of the fabric and the matrix and increased with increasing fibre content. Further, the moisture content of the fabric was ~7%. However, for the matrix and composites it reduced to ~3% due to the crosslinking reaction. Thus the SPI/SF composites possessed thermal stability than the SPI matrix.

4. CONCLUSIONS

Natural fibers are considered as potential replacement for man-made fibers in composite materials although natural fibers have advantages of being low cost and low density. In this study fully biodegradable composites were developed from SPI with SF. using glycerol as the plasticizer and glutaraldehyde as the crosslinking reagent. The effects of SF loading on the tensile properties were studied. The tensile strength and modulus were improved with increasing fabric content whereas the % elongation at break decreased. Though the interfacial bonding was moderate; the increase in tensile strength and modulus of the composites was mainly attributed to the higher tensile properties of the SF. Thermogravimetric analysis shows that the decomposition temperatures of SPI/SF is higher compared with that of the pure matrix and the thermal stability of the composites increased slightly with fabric content. In addition to biodegradable, these composites are considerable as renewable resources, environmentally friendly.

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