Flax Fiber Reinforced Arylated Soy Protein Isolate

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ABSTRACT: Soy protein plastics prepared by solution casting method can achieve the modulus of 20-50 MPa while that of soy protein plastics prepared by compression molding ranges from 50-100 MPa at high relative humidity (50 to 75% RH). On the other hand, modulus of natural fiber bundle varies between 650 and 1050 MPa. So the modulus of soy protein based plastics is relatively very less compared to that of natural fibers. It has been recently reported that arylation of soy protein in presence of 2,2-diphenyl-2-hydroxyethanoic acid (DPHEAc) leads to protein material with very high modulus in the range of 800 to 1100 MPa even at high relative humidity (50 to 75% RH). Water-mediated arylation by dip coating method is responsible for the high modulus of soy protein materials. Here, we are reporting damage-sensitive composites prepared from arylated soy protein (as brittle-matrix) and flax fabric. Bio-composites were successfully prepared by reinforcing soy protein isolate with different weight fractions (0.2 to 0.4) of woven flax fabric. Flax fabric reinforced soy protein isolate based composites were then arylated with 2,2-diphenyl-2-hydroxyethanoic acid (DPHEAc) for 4h to get arylated bio-composites. Characterizations of the arylated and non-arylated bio-composites were performed by thermo gravimetric analysis. Results indicated that arylated soy protein based composites displayed mechanical behaviour like brittle-matrix composites that differentiated them from non-arylated soy protein based composites which displayed mechanical behaviour like polymer-matrix composites. Scanning electron microscopy was also carried out to understand the nature of cracks and fractures suffered by the arylated soy protein composites when subjected to tensile tests.

1. Introduction

Composites include a wide variety of materials which can be tailored to desired properties for intended end use applications. In the past decades, many efforts have been made to investigate the suitability of natural fibers as a reinforcing component for soy protein based biopolymers.[1–2]

Brittle-matrix composites result from a combination of constituent brittle materials which ultimately ends up in a material which is no longer brittle but instead damage-tolerant. These kinds of materials are of interest for thermo-structural applications.[3] The matrix is less resistant to impact than the fibers in brittle-matrix composites. Integrity in these classes of composites is often maintained by fibers which provide strength to the material. It has been reported that cracking is the main cause of the damage in the brittle-matrix composites. In the past, structures or materials of the brittle-matrix composites have been designed by models of mechanical behaviour.[4,5]

Modulus of natural fiber bundle varies between 650 to 1050 MPa.[6] Soy protein plastics prepared by solution casting method show the modulus of 20-50 MPa[7] while soy protein plastics prepared by compression molding ranges from 50-100 MPa[1,8] under high relative humidity (50 to 75% RH). Hence, modulus of soy protein based plastics is very less compared to natural fibers. Recently, it has been reported that arylation of soy protein in presence of 2,2-diphenyl-2-hydroxyethanoic acid (DPHEAc) leads to a material with very high modulus in the range of 800 to 1100 MPa[9-11] even under high relative humidity (50 to 75% RH). Water-mediated arylation by dip coating method is responsible for the increase in modulus of soy protein material. This is attributed to the evolution of CO_2 and the formation of more stable compound such as diphenylhydroxymethane (DPHM) from DPHEAc.[9,10]

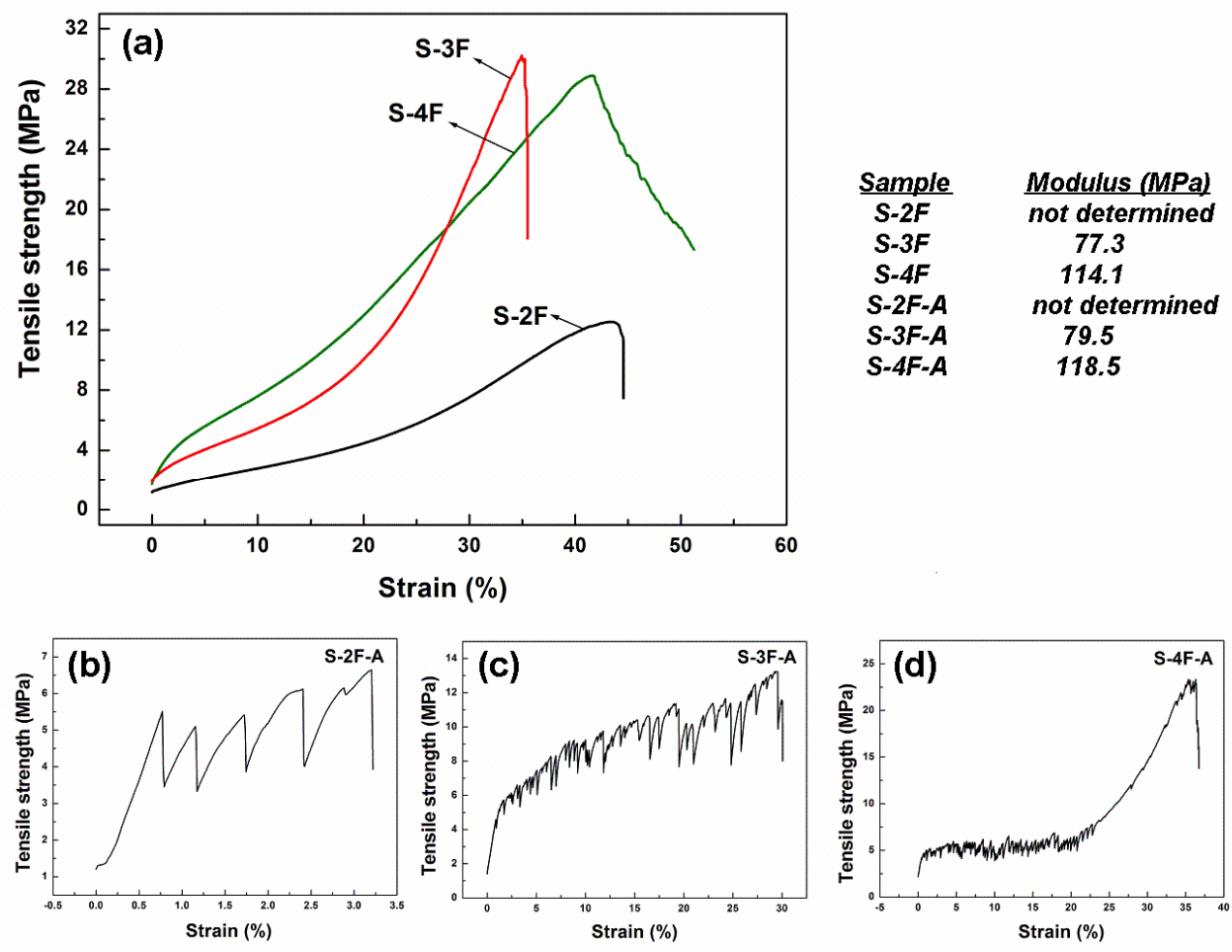
In this paper we are reporting damage-sensitive composites prepared from arylated soy protein (as brittle-matrix) and flax fabric. The composites were characterised by the mechanical and thermal properties. Morphology of the arylated composites is also evaluated to show the presence of cracks confirming the brittle-matrix behaviour.

2. Experimental Section

2.1 Materials

Soy protein isolate (SPI) containing 90.27% of protein on dry basis was purchased from Zhenghou Ruikang Enterprise Co., Ltd. (Zhengzhou, China). Thiodiglycol (TDG) (bp:164-166 °C, mol wt:122.19, and density:1.182 g/cm^3) and DPHEAc (mp:149-151 °C, mol wt:228.25) were purchased from Sigma-Aldrich and used as received. Flax woven fabric: 180 g/m^2 was purchased from Libeco, Belgium with 19 threads/ cm in warp and 21 threads/cm in weft. The tensile strengths of the fabric in warp and weft, as provided by the supplier, are 835.4 N/cm and 1181 N/cm, respectively. Sodium hydroxide was purchased from Minema Chemicals, South Africa.

In the first stage, a resin was prepared by mixing SPI with 30% of TDG (w/w) for about 1h in 0.025 M NaOH solution having pH ~9.5–10. Here, TDG acts as plasticizer. To prepare the composites, flax fabrics were wetted in the SPI resin and then dried in an oven at 50 ^{o}C for 24h to get the composite sheets. The effect of the weight content of flax fibers (20–40 wt%) on the properties of composites was evaluated. The composites reinforced with 20, 30, and 40 wt% of the flax fabric were designated as S-2F, S-3F, S-4F, respectively. These composites were then immersed in DPHEAc solution (0.5% w/v) for 4h to get arylated composites, coded as S-2F-A, S-3F-A and S-4F-A.[10] Subsequently, the arylated composites were taken out and put between two steel plates fixed by binder clips to prevent



Sample	Modulus (MPa)
S-2F	not determined
S-3F	77.3
S-4F	114.1
S-2F-A	not determined
S-3F-A	79.5
S-4F-A	118.5

Fig 1. Tensile stress-strain curves for non-arylated (a) and arylated (b-d) soy protein composites.

2.2 Preparation of the arylated soy protein composites

dimensional instability of the arylated composites.[10]

2.3 Characterizations

Scanning electron microscopy (SEM) images of the surfaces and cross-sections of the composites were taken on FEI Quanta 200 (Eindhoven, The Netherlands) electron microscope at an accelerating voltage of 20kV. The crosssections of samples for SEM characterization were prepared by freezing them in liquid nitrogen before fracturing. Gold sputtering was not required for the preparation of the sample in this instrument. Thermogravimetric analysis (TGA) of approximately 5 mg dried films was carried out at a heating rate of 10 °C min^{-1} between room temperature and 700 °C in nitrogen atmosphere on a TG-IR interface (Perkin Elmer, Buckinghamshire, UK).

The tensile strength, elongation at break, and the Young's modulus (E) of the composites were measured on an Instron 3369 testing machine at a strain rate of 10 $mm.min^{-1}$ according to ASTM D882 (E) in weft direction. The films tested were 110 mm × 15 mm (length × width) in dimensions. The clamping length for each specimen on each jaw was 15 mm. An average value from five replicates of each sample was taken for each of the tests mentioned above.

3. Results and Discussions

3.1 Mechanical properties of the composites

Non-arylated soy protein film shows tensile strength of 4.6 MPa with elongation at break of 214%. Tensile strength of the soy protein film reported here is low and percentage elongation at break is very high due to the fact that the protein films are prepared by solution casting method where water also acts as plasticizer in addition to plasticizer (TDG) that has been added.[7,12] Fig. 1a shows the mechanical properties of the non-arylated composites. Tensile stress and modulus increase with the increase in weight fraction upto 30% of the flax fabric. Thereafter there is a decrease in tensile stress for composites containing 40% flax fabric with the increase in tensile modulus as shown in Fig. 1a. There is a decrease in percentage elongation at break due to flax fabric. This class of composite can be termed as damage-insensitive.

Arylated soy protein film shows tensile strength of 18.6 MPa with elongation at break of 2%. Hence arylation of soy protein leads to brittle-matrix. Figs. 1(b-d) show the mechanical properties of arylated soy protein composites. For S-2F-A and S-3F-A the maximum load on the composites is the same as that of matrix alone, the composites continue to carry the decreasing load after the peak. The post peak resistance is primarily provided by pulling out of fibers from the cracked surface. Although no significant increase in tensile strength of the arylated soy protein composite is observed. A considerable increase in the toughness of S-3F-A composite in comparison to S-2F-A is noticed. In S-4F-A, even after the cracking of the matrix, the composite continues to bear tensile load; the peak stress is greater than that of the matrix alone. During the inelastic range in S-4F-A multiple cracking of the matrix, fiber debonding and step occur. Thus in the arylated composites, there is a clear evidence of stick-slip mechanism which is perhaps dominating and it prevents easy deformation of the reinforced film.

3.2 Thermal properties of the composites

The thermal stability of the arylated and non-arylated composites determined by thermogravimetric analysis in nitrogen atmosphere is shown in Fig. 2. The thermal degradation of all the non-arylated samples in presence of TDG as plasticizer experiences a two-stage mass loss i.e., T_{max1} for the temperature range 200–300 °C and T_{max2} for the temperature range 300–400 °C. Here T_{max} represents the temperature at which mass loss is maximum. T_{max1} is attributed to the loss of plasticizer and T_{max2} is attributed to the degradation of soy protein and fabric. On the other hand arylated soy protein composites show one stage mass loss. T_{max1} peak in arylated soy protein

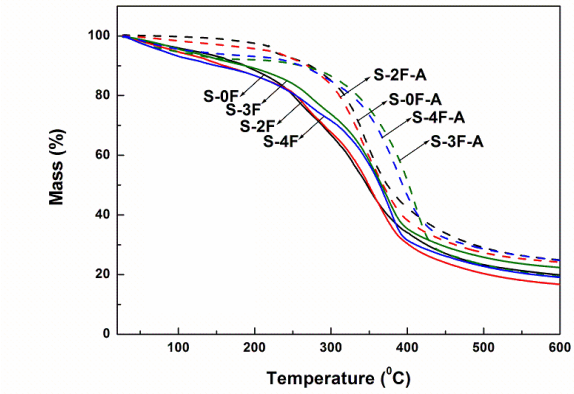


Fig 2. TGA curves for arylated and non-arylated soy protein composites.

composites either disappeared or was of very low intensity as reported earlier.[9] More importantly, the mass loss observed in arylated composites between 200-300 °C also decreased. T_{max2} peak increased from 338 °C for S-0F-A to 390 °C for S-3F-A, indicating the thermal stability of the composites increases and was found to be optimum for 30% flax fabric. The char yield at 700 °C for the arylated composites was higher than non-arylated samples.

3.3 Morphology

Surface morphology of the non-arylated composites after tensile tests shows the homogeneous surface while arylated composites show the cracks after tensile tests (Fig. 3).

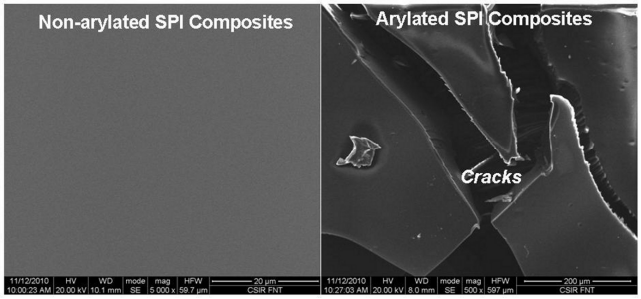


Fig 3. Surface morphology of arylated and non-arylated soy protein composites. after being subjected to tensile tests.

4. Conclusions

Flax fabric reinforced soy protein composites, either arylated or non-arylated, showed better mechanical and thermal properties compared to neat soy protein. Results from the mechanical properties indicated the generation of brittle-matrix behaviour for the arylated soy protein composites and is well confirmed by the presence of cracks on the surface of the arylated composites as evidenced from SEM. In the arylated composites, there is a clear evidence of stick-slip mechanism which is perhaps dominating and it prevents easy deformation of the reinforced film.

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