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'Green' composites Part 1: Characterization of flax fabric and glutaraldehyde modified soy protein concentrate composites

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Fully biodegradable, environment friendly 'green' composites were prepared using glutaraldehyde (GA) modified soy protein concentrate (MSPC-G) and flax fabric. Soy protein concentrate (SPC) polymer has low tensile properties, poor moisture resistance and is brittle. SPC polymer with 15% glycerin, as an external plasticizer, exhibited fracture stress and Young's modulus of 17 and 368 MPa, respectively. SPC polymer was cross-linked with GA to increase its tensile properties and improve its processability as a resin to manufacture flax fabric-reinforced composites. GA reacts with the free amine groups in SPC to form crosslinks. MSPC-G showed 20% increase in fracture stress and 35% increase in Young's modulus as well as improved moisture resistance compared to SPC. Besides the mechanical properties, MSPC-G was also characterized for its thermal stability and dynamic mechanical properties.

Composite laminates, approximately 1 mm thick, were made using flax fabric and MSPC-G polymer. Composite specimens were prepared with two different orientations, namely, 0° or 90°. The laminates exhibited a Young's modulus of 1.01 and 1.26 GPa in the longitudinal and transverse directions, respectively. The experimental values were compared with the theoretical predictions using pcGINA© software and showed good agreement. The composite specimens also showed good adhesion between flax fabric and MSPC-G resin. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

The idea of making composites has been derived from nature itself. Nature offers composites in different forms such as wood from trees. Wood is a natural composite, with cellulose fibers acting as the reinforcement and lignin as the matrix [1]. Thus imitating the nature, humans have long been known to use composite materials for a variety of structural and non-structural applications. Composites offer several advantages over conventional polymers and plastics, such as higher strength and stiffness and better energy efficiency (on a total life cycle basis) [2]. However, most composites used at present are made using petroleum based resins and fibers. These composites offer excellent strength, stiffness and durability but do not degrade after their useful life for several decades. Increasing environmental awareness and strict government environmental laws have helped drive manufacturers towards 'greener' alternatives for conventional composites [3].

Natural plant based fibers such as ramie, flax, jute, hemp, bamboo etc. are currently being explored as cost effective biodegradable alternatives to glass fibers for composite manufacturing [3, 4]. Composites made using natural fibers and non-biodegradable resins, e.g., polypropylene and polyester, help in maintaining a balance between cost and environmental concerns [5]. However, they are only partially biodegradable and can neither return to an industrial metabolism nor to a natural metabolism after their useful life [3]. Fully biodegradable and environment friendly 'green' composites using plant based fibers and biodegradable resins can offer convenient solution to all these problems. Plant based natural fibers, mentioned above, are annually renewable and offer several other advantages including high specific properties and good thermal and acoustic insulation [6]. In comparison, it takes 20–25 years for trees to grow before usable wood can be obtained [3]. In the past several years, much research has been carried out to develop fully green composites using natural plant based fibers and biodegradable polymers such as poly(lactic acid) (PLA), poly(hydroxybutyrate-co-valerate) (PHBV), cellulose acetate, soy protein, corn pith, corn starch etc. [7–17]. In part 1 of the research

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presented here, plain woven flax fabric has been used as reinforcement for fabricating green composites with modified soy protein resin.

Flax is a bast fiber and is obtained from an annual plant, *Linum usitatissimum*, which is grown in temperate and sub tropical regions [18]. Flax fiber has higher degree of polymerization and crystallinity than cotton fiber which gives it a higher strength [19] and even in wet condition it is stronger than many other plant (cellulosic) fibers [20].

Woven fabric-reinforced composites offer several advantages over unidirectional composites. These include good stability in mutually orthogonal warp and weft directions, more balanced properties in the fabric plane and better impact resistance [21]. Woven fabric composites are known to exhibit better damage tolerance, higher toughness and subtle conformability [22]. These composites offer the advantage of lower fabrication costs and easier handling in production quality than tape laminates [23]. Research efforts have been made to develop woven fabric-reinforced composites using natural plant based fibers and biodegradable as well as non-biodegradable matrices [24–28].

Theoretical analysis of flax fabric reinforced composites in both longitudinal and transverse directions was carried out using pcGINA© software. pcGINA© is a "PC based Graphical Integrated Numerical Analysis" program that can be used to design and predict the properties of textile reinforced composites [29–31]. The software takes into account the fabric structure, thread spacings, yarn diameters, orientation of different fabric layers, layer thickness and resin properties to predict the composite tensile properties. It has the capability to calculate both mechanical and thermal properties of textile composites. Further details about the software can be obtained elsewhere [29–31].

Soy protein is commercially available as soy protein isolate (SPI), soy protein concentrate (SPC) and soy flour (SF). Chemically, SPI contains 90% protein while SPC contains 70% protein. SPC also has 18% carbohydrates, 6% ash and remaining is fiber and moisture. SF contains up to 55% protein and 32% carbohydrate. Soybean protein contains several amino acids such as glutamic acid, argenine, lysine, cystine and aspartic acid that have polar groups [32]. These groups can act as useful cross-linking and/or hydrogen bonding sites to improve the mechanical properties of soy protein polymer. In the present research SPC was modified with glutaraldehyde (GA) to increase its mechanical and physical properties, improve thermal stability, reduce its moisture absorption and improve its processability as a resin for composite fabrication. Several researchers have studied the crosslinking of GA with proteins [33–35] and confirmed the reaction mechanisms. Richard and Knowles [34] and Habeeb and Hiramoto [35] have proposed that GA reacts with the amino groups in protein to form cross-links. Blass *et al.* [33] showed that GA binds irreversibly with the ε-amino group of lysine. Thames and Zhou [36] used maleinized tung oil to cross link SPI and improve its tensile properties. Paetau *et al.* [37] have explored various acid treatments soy proteins to control the moisture absorption and thus improve their mechanical properties.

Lodha and Netravali [38, 39] recently showed that modifying SPI with stearic acid significantly improves the mechanical and thermal properties and reduces the moisture regain as compared to SPI. Rhim *et al.* [40–42] have also explored various ways of improving the SPI film properties using fatty acids and propylene-glycol-alginate. Their results suggest that incorporation of fatty acids resulted in thicker and whitish films and the film shrinkage was significantly lower. However, their research was not directed towards the use of soy protein for composite applications. As a result, they did not characterize the mechanical properties of the modified soy protein. A brief review of various efforts of soy protein modification is presented by Netravali [11].

Lodha and Netravali [7] used SPI as a resin in ramie fiber reinforced random, short fiber composites while Nam [43] used SPC and ramie fibers to make unidirectional composites with tensile strengths of up to 275 MPa. In the present research, modified SPC resin was reinforced with flax fabrics to form green composites.

2. Experimental procedures

2.1. Materials

ARCON® S, SPC powder was provided by Archer Daniels Midland Company, IL. Analytical grade glycerin and sodium hydroxide were obtained from Fisher Scientific, PA. Glutaraldehyde, 25 wt% solution in water, was obtained from Aldrich Chemical Company, WI. All chemicals were used as received, without any further treatment. Woven flax fabric, in bleached form, was provided by Sachdeva Fabrics Pvt. Ltd., New Delhi, India.

2.2. SPC curing and modification

SPC powder was processed to make it suitable as a resin for green composite fabrication. Similar processing technique has been used earlier for SPC [43]. SPC powder was mixed with distilled and deionized water in a beaker in 1:13 ratio (by weight) and 15% glycerin (by SPC weight) was added as a plasticizer. The solution was homogenized using a magnetic stirrer for 15 min and then the pH of the mixture was adjusted to 11 ± 0.1, using 1 N NaOH solution. SPC solution was again stirred for 15 min and then the beaker was transferred to a water bath maintained at 70°C. The solution was 'pre-cured' by stirring for an additional 30 min. The pre-cured solution was cast on Teflon® coated glass plates and dried in Fisher Isotemp oven at 35°C for 20 hrs to obtain polymer (resin) sheets. Finally, the dried soy protein resin sheets were cured by hot pressing in Carver hydraulic hot press, model 3891–4PROA00, at 120°C for 25 min under a pressure of 7 MPa.

GA was added to modify SPC by introducing additional crosslinking and increase the resin's tensile properties and thermal stability. Similar processing technique was used, as described above for SPC. However, to modify SPC with GA, SPC was mixed with distilled and deionized water in a ratio of 1:15 (by weight) and the predetermined amount of GA was added to SPC/glycerin mixture while in a water bath, after 27 min of pre-curing at 70°C and continued to stir. The pre-cured modified SPC (MSPC) resin was dried at room temperature and cured using the same curing cycle in the hot press, as described above for SPC. The cured SPC and MSPC resin sheets were conditioned at standard ASTM atmosphere (65% r.h. and 21°C) for 3 days before performing various tests.

2.3. Effect of GA content

To optimize the GA% needed for crosslinking SPC, effect of GA% on the tensile properties of cured MSPC resin sheets was studied. The GA content (25 wt% solution) was varied between 5 and 50% (w/w of SPC), while the glycerin content was kept constant at 15%. Tensile properties of SPC and MSPC polymers were characterized in accordance with ASTM D 882-97. Conditioned resin sheets were cut into rectangular specimens of 110 × 20 mm dimensions. Three thickness measurements were carried out along the length of each specimen, and the average of these values was used for calculating the fracture stress and Young's modulus. The tests were performed on an Instron tensile tester, model 1122, at a strain rate of 1 min^{-1} and a gauge length of 50 mm.

2.4. Effect of glycerin content

After optimizing the GA%, the effect of glycerin content on the tensile properties of MSPC resin was studied. Glycerin acts as a plasticizer for soy protein. To study the effect of plasticizer content on the tensile properties of MSPC resin, three different glycerin contents, 10, 15 and 20% were used. Specimens with less than 10% glycerin content could not be prepared because of excessive curling during air drying and were too brittle to be cured in the hot press. Tensile properties of the conditioned MSPC sheets were measured as described above in Section 2.3.

2.5. Thermogravimetric analysis of SPC and MSPC

Thermo-gravimetric analysis of conditioned SPC and MSPC resin sheets was carried out using TA Instruments, Thermo-gravimetric Analyzer (TGA, model 2050). The specimens were scanned in a nitrogen atmosphere from 25 to 350°C at a ramp rate of 10°C/min.

2.6. Dynamic mechanical analysis of SPC and MSPC

Dynamic mechanical properties of SPC and MSPC resin sheets were measured using TA Instruments Dynamic Mechanical Analyzer (DMA), model 2980, at Cornell Center for Materials Research (CCMR) facilities, using tension film clamps. Conditioned resin sheets were cut into rectangular specimens of 11 × 6 mm dimensions. The tests were performed at 5 μm amplitude and 1 Hz frequency. The specimens were scanned from 0 to 240°C at a ramp rate of 5°C/min, for both SPC and MSPC resins.

2.7. Geometrical characterization of flax fabric

Woven fabric was characterized for threads (warp/ends and weft/picks) per cm, thickness, warp and weft denier and crimp. Fabric specimens were conditioned at standard atmosphere for 3 days before performing the tensile tests.

Fabric thickness was measured using Sherman W. Frazier compressometer according to ASTM D 1777-96, using a circular presser foot, 9.525 mm in diameter. Twenty measurements were made at a pressure of 0.023 MPa to obtain an average value for the fabric thickness.

Warp and weft crimps were determined in accordance with modified ASTM D 3883-99. Since no tension device was available, crimp was removed by hand using extreme care. Yarn length was measured in the fabric and after removing the crimp. Yarn crimp is the change in length expressed as a percent, between the fabric length and the straightened yarn length [44]. Yarn crimp was calculated according to Equation 1 below [44].

$$\text{Crimp Percentage} = \frac{StraightenedLength - FabricLength}{FabricLength} \times 100 \qquad (1)$$

2.8. Tensile characterization of flax fabric

Flax fabrics were tensile tested according to ASTM D 5035-95 on Instron tensile tester, model 1122. Fabric specimens were raveled for tensile tests. Initially, 30 mm wide test strips were cut in the desired direction (warp or weft) and then the lengthwise yarns were removed from both edges until the specimen width was reduced to 20 mm. The same procedure was followed for test strips in both warp and weft directions. Twenty specimens were characterized in both warp and weft directions. Tensile tests were performed at a gauge length of 50 mm and a strain rate of 1 min^{-1}. Average fabric thickness was used for calculating the fracture stress and Young's modulus.

2.9. Preparation of flax fabric composites

Two dimensional (2D) flax fabric-reinforced composites were fabricated using MSPC resin. Composites were prepared with either all layers oriented at 0° (warp wise) or 90° (weft wise). Flax fabric strips, 25 mm wide and 130 mm long, were cut in desired direction (warp wise/longitudinal or weft wise/transverse). Four fabric strip layers were used for each composite specimen fabrication and weight of the fabric strips was recorded. Fabric strips were held under slight tension, using masking tape, in a glass container. Precured MSPC resin was poured over the fabric strips and allowed to stand for 15 min at room temperature. The resin impregnated fabric strips were transferred to Teflon® coated glass plates and more resin was applied in between layers using a paintbrush. Then the composite specimens were allowed to dry in an oven at 35°C for approximately 26 hrs. Care was taken to ensure that the specimens were neither totally dry nor completely wet before hot pressing. These specimens were then transferred into a mold. A mold-release agent was used, for easy removal of composites after curing. Curing was done in the Carver Hydraulic hot press at 120°C for 25 min at a pressure of 8 MPa. On completion of the curing cycle, the composite specimens of approximately 1 mm thickness were removed from the hot press and conditioned at standard ASTM atmosphere for 3 days prior to characterization of their properties. The fiber weight fraction in final composite specimen was calculated on the basis of final composite weight and initial weight of the fabric strips.

2.10. Tensile characterization of composites

Tensile properties of fabric-reinforced composites were characterized in accordance with ASTM D 3039/D3039M-00 using approximately 1 mm thick and 25 mm wide. Three thickness measurements were made along the gauge length of each specimen and the average of these values was used for calculating the fracture stress, fracture strain and Young's modulus. The tensile tests were performed on an Instron tensile tester, model 1122, at a strain rate of 1 min^{-1} and a gauge length of 50 mm. At least five specimens were tested to obtain average tensile properties.

Theoretical analysis of flax fabric reinforced MSPC composites in both longitudinal and transverse directions was carried out using pcGINA© software. pcGINA© is a "PC based Graphical Integrated Numerical Analysis" program that can be used to design and predict the properties of textile reinforced composites. The software is designed to calculate mechanical and thermal properties of textile composites. pcGINA© was created by Dr. Yasser Gowayed, and Mr. Larry Barowski, at Auburn University, U.S.A. with support from Pratt & Whitney, NASA Lewis and GE. The fabric structure, thread spacings, yarn diameters, orientation of different fabric layers, layer thickness and MSPC-G resin properties were specified into the pcGINA© software to predict the composite tensile properties. Further details and theoretical background of pcGINA© can be found elsewhere [29–31].

2.11. Flexural characterization of composites

Flexural properties of fabric-reinforced composites were characterized in accordance with ASTM D 790–99. Three thickness measurements were made along the length of each specimen and the average value was used for calculating the flexural stress, flexural strain and flexural modulus. The flexural tests were carried out on an Instron tensile tester, model 1122, at a crosshead speed of 2 mm/min and a span length of 30 mm. At least six specimens were tested to obtain the average flexural properties.

2.12. Fracture surface characterization of composites

The fracture surfaces of fabric-reinforced composites were observed under Leica scanning electron microscope (SEM), model 440X. All fractured specimens were sputter coated with gold-palladium to get good conductivity. SEM photographs of specimens tested in both longitudinal and transverse directions were taken to characterize and understand the failure mechanism of the composites. These photographs were also used for qualitative analysis of interfacial bonding between MSPC resin and flax fabric. All SEM photographs were taken at the CCMR facilities.

3. Results and discussion

3.1. Effect of GA% on MSPC tensile properties

Fig. 1 shows the effect of GA% (w/w of SPC) on the tensile properties of MSPC resin. As can be seen from Fig. 1, increasing GA% from 0 to 40% increased the fracture stress from 16.9 MPa to 19.9 MPa and Young's modulus from 368 MPa to 484 MPa. Further increasing GA% didn't improve the tensile properties any further. It should be noted from Fig. 1 that the change in slope for fracture stress and Young's modulus curves is lower up to 20% GA concentration and becomes steeper on further increasing the GA content. It is proposed that 30% and higher concentration of GA leads to sufficient crosslinking with SPC. The increase in tensile properties with GA addition can be attributed to the crosslinks formed by GA with SPC.

Richard and Knowles [34] and Habeeb and Hiramoto [35] have proposed that GA reacts with the amino groups in protein to form cross-links. Blass *et al.* [33] showed that GA binds irreversibly with ε-amino group of lysine. A possible crosslinking reaction between SPC and GA is shown in Fig. 2. Similar reaction scheme has been used by Matsuda and co-workers to explain the crosslinking between GA and gelatin [45].

Park *et al.* [46] showed that crosslinking SPI with GA increased the tensile strength from 8.3 to 14.9 MPa. They suggested that the covalent intermolecular and intramolecular crosslinking between soy protein and GA increased the mechanical properties of SPI/GA films.

It is also important to mention that adding GA to SPC changed the color of the resin from pale yellow to dark reddish brown. Similar color change has also been reported for SPI/GA films [46]. Based on these results, 40% GA, which gave highest strength, was selected as the optimum concentration for further MSPC resin characterization and composite fabrication.

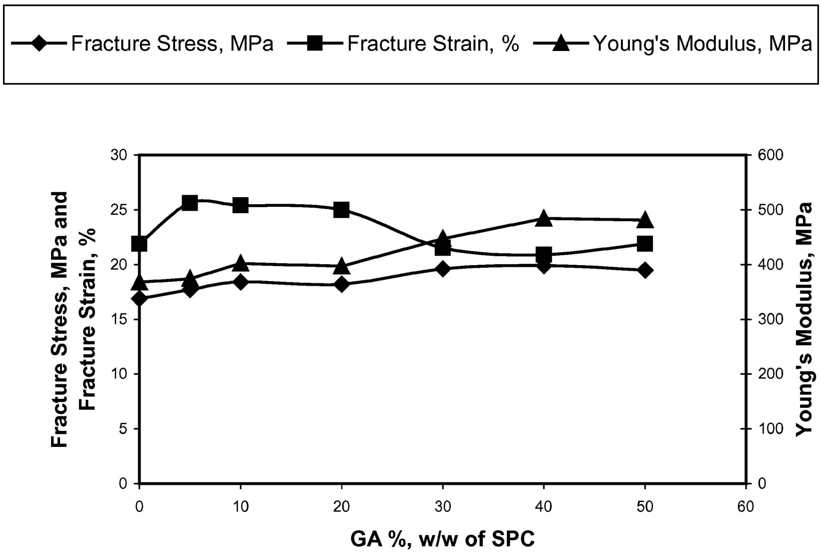


Figure 1 Effect of GA% on the tensile properties of MSPC resin with 15% glycerin.

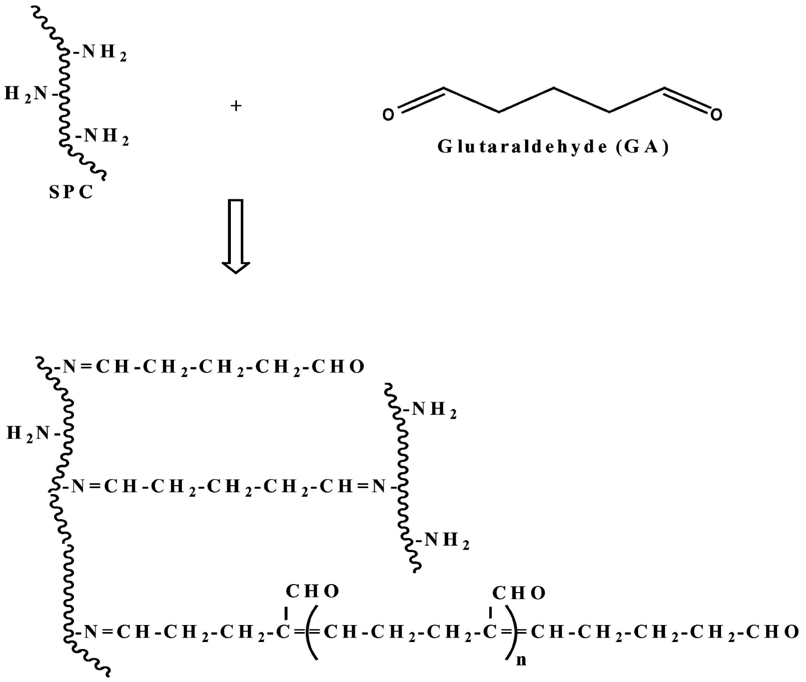


Figure 2 Reactions between SPC and GA.

3.2. Effect of glycerin content on MSPC tensile properties

Fig. 3 shows the effect of glycerin content on the tensile properties of MSPC resin. MSPC resin with less than 10% glycerin could not be cured, due to the excessively brittle nature of the unplasticized resin. Zhang *et al.* [47, 48] and Nam [43] also reported similar processing problem with the unplasticized soy protein resin. As expected, increasing glycerin content from 10 to 20% increased the fracture strain from 10.5 to 32.5%. It also reduced the fracture stress and Young's modulus from 26.8 to 14.7 MPa and 755 to 267 MPa, respectively. All these results indicate that glycerin has a good plasticizing action with SPC, leading to reduced brittleness and increased plasticity. Glycerin has been reported to increase the flexibility and extensibility of soy protein plastics by reducing the interaction between protein molecules [7, 48]. Zhang *et al.* [49] also studied the effect of glycerin content on the tensile strength and breaking elongation of soy dreg-GA sheets and reported similar trend.

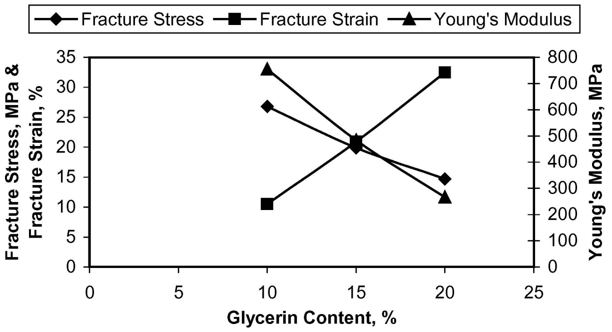


Figure 3 Effect of glycerin content on the tensile properties of MSPC resin.

TABLE I Effect of glycerin content on the moisture content of SPC and MSPC resins

Glycerin (%) (w/w of SPC)	Moisture content of SPC (%)	Moisture content of MSPC (%)
10	13.7	13.5
15	15.0	13.9
20	16.6	15.1

3.3. Moisture absorption by SPC and MSPC resins

Table I summarizes the effect of glycerin content on the moisture content of SPC and MSPC resins. It is evident from Table I that reducing the glycerin content reduces the moisture content of both SPC and MSPC resins. The free volume theory [50] explains that an external plasticizer (glycerin in this case) increases the free volume of the polymer system by increasing the number of chain ends. Increased free volume decreases the glass transition temperature (T_g) of the system making it easier for the moisture to diffuse in. In addition, water molecules are attracted to hydroxyl groups present in glycerin. This is also clear from the fact that glycerin is freely miscible in water.

It can also be seen clearly from the data in Table I that MSPC resin has lower moisture content than SPC resin. This can be attributed to the crosslinks formed by GA with amine groups of SPC making the system tighter by reducing the free volume. Also, since some of the amine groups are consumed in the crosslinking reaction the MSPC is less polar than SPC. Based on these results and ease of resin processing, SPC resin with 40% GA and 10% glycerin, henceforth referred to as MSPC-G, was selected as the optimum blend content for composite fabrication.

3.4. Thermogravimetric properties of SPC and MSPC-G

Fig. 4 shows the typical TGA thermograms for SPC containing 10% glycerin and MSPC-G resins, in a nitrogen atmosphere. As can be seen from Fig. 4, MSPC-G resin is more stable than SPC resin. The SPC resin starts to decompose, as indicated by the increased weight loss, around 235°C whereas the MSPC-G resin starts to degrade around 270°C. The improved thermal stability of MSPC-G resin can be attributed to the crosslinks formed by GA with SPC. In addition, it can be seen from the plot, the MSPC-G resin is highly stable up to 120°C with minimal weight loss, the processing temperature for fabric-reinforced composites. The weight loss up to 120°C can be attributed to the loss of moisture from the specimen. Vaz *et al.* [51] who studied the thermal behavior of SPI also found SPI to be stable up to 100°C.

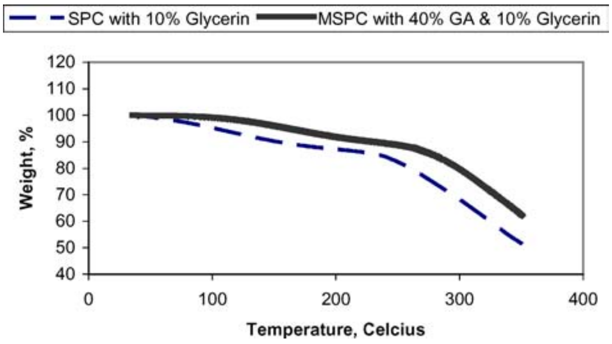


Figure 4 TGA thermograms for SPC and MSPC-G resins.

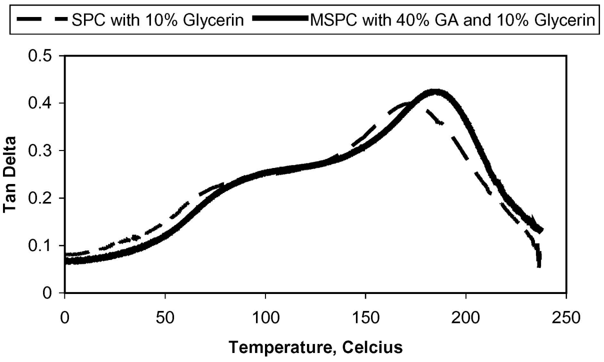


Figure 5 Variation in tan δ with temperature for SPC and MSPC-G resins.

3.5. Dynamic mechanical properties of SPC and MSPC-G

Fig. 5 shows the tan δ curves for SPC containing 10% glycerin and MSPC-G resin. It is evident from the plots that SPC resin shows the glass transition temperature (T_g) at 173°C and the β transition at 80°C, while MSPC-G resin shows T_g at 185°C and the β transition at 89°C. These values are comparable to those obtained by Zhang *et al.* [47, 48]. Thus, crosslinking GA with SPC improved the thermal stability of the SPC resin and increased the T_g by 12°C.

Figs 6 and 7 show the plots for storage (E') and loss (E'') moduli for SPC resin containing 10% glycerin and MSPC-G resin, respectively. As can be seen from Fig. 6, the E' value for SPC resin at 25°C is 1.9 GPa. Comparative values for epoxy and polycarbonate are 1.20 and 0.93 GPa, respectively [52]. Wang *et al.* [53] also reported E' value for dry soy protein plastic to be 1.76 GPa. They attributed the high storage modulus value for soy protein to two main factors [53]. First, the crosslinking effects resulting from charge-charge and dipole-dipole interactions between amino acid side chains. Second, the 7–10% (by volume) nano sized spherical protein particles present in soy protein matrix,

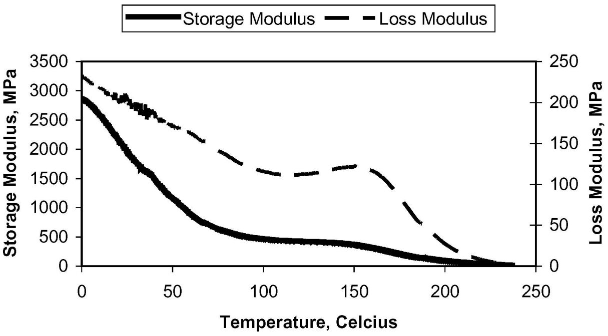


Figure 6 Variation of storage and loss moduli with temperature for SPC resin with 10% glycerin.

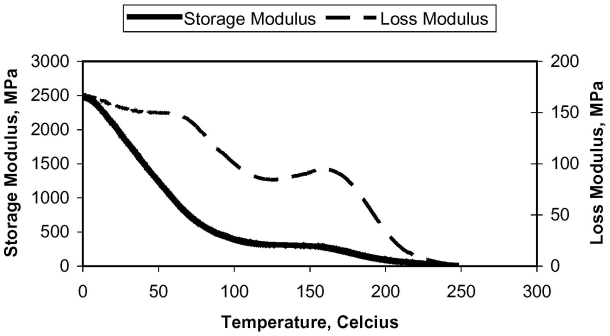


Figure 7 Variation of storage and loss moduli with temperature for MSPC-G resin.

which might act as filler and toughen the soy protein matrix [53].

It can be seen from Fig. 7 that the storage modulus value for MSPC-G resin at 25°C is 2.0 GPa. The higher storage modulus can be attributed to the crosslinks formed by GA with SPC. Zhang *et al.* [49] also showed that crosslinking soy dreg with GA improved the storage modulus of soy dreg/GA sheets. It can also be observed from Figs 6 and 7, the storage modulus decreases continuously with an increase in temperature and unlike synthetic polymers; the drop in the storage modulus at T_g is not catastrophic. Similar results have also been reported, by other researchers, for soy protein [47, 48].

3.6. Geometrical characterization of flax fabric

Flax fabric used in this research had 17 threads/cm in both warp and weft directions. Fabric thread spacing controls the openness of the fabric structure, which affects the resin penetration through different fabric layers in the fabric-reinforced composites. The fabric used in this study had a regular structure (cover factor of 0.68), allowing easy penetration of resin through different fabric layers in the composite. Cover factor is the ratio of the area occupied by yarns in the fabric to the total fabric area. Lower the fabric cover factor, higher is the fabric porosity or openness.

The fabric thickness was measured at a pressure of 0.023 MPa using a 9.525 mm diameter circular foot. The average fabric thickness was found to be 0.39 mm. Fabric thickness affects the number of fabric layers required to fabricate the composite specimen of desired thickness.

Warp and weft yarns develop crimp (waviness) due to the interlacing between them during the weaving operation on a loom. The fabric used in this research had warp and weft crimps of 10.7 and 1.5%, respectively. When the fabric is put under tension, the yarns initially loose their crimp in the longitudinal direction to become fully extended. This consequently leads to even higher crimp in the transverse direction, which leads to the 'crimp interchange' [44]. The crimp significantly affects the Young's modulus of the fabric as well as composites as the force needed to straighten the yarns is much smaller than that needed to stretch the yarns. As a result, higher the crimp value, lower is the initial modulus in that direction.

TABLE II Tensile properties of flax fabric

Test direction	Fracture stress (MPa)	Fracture strain (%)	Young's modulus (MPa)
Longitudinal	33.3	17.7	513
[Warp]	(6.3)*	(6.2)	(7.0)
Transverse	41.2	7.1	1018
[Weft]	(10.1)	(7.8)	(10.7)

*Figure in parenthesis are CV%.

3.7. Fabric tensile properties

Tensile properties such as fracture stress, Young's modulus and fracture strain for the flax fabric in both longitudinal (warp) and transverse (weft) directions are summarized in Table II. As can be seen from Table II, the fracture stress and Young's modulus values of the fabric in the longitudinal and the transverse directions are different. The fabric has higher strength and stiffness in the transverse direction, as compared to the longitudinal direction. This difference is attributed to the difference in the warp and the weft yarn diameters (or denier) and crimps, which also leads to different fracture strain values in the two directions. For most fabrics weft crimp is higher than warp crimp. However, the fabric used in this study was designed to give higher crimp in warp yarns. A *t*-test was performed to test whether the difference in the tensile properties in the longitudinal and transverse directions was significant or not. It was found that the difference in the tensile properties in the longitudinal and transverse directions was highly significant at 95% confidence level.

3.8. Tensile properties of composites

Fabric-reinforced 'green' composites had a fiber weight fraction of 45% and an average thickness of 1.1 mm. Table III summarizes the tensile properties of fabric-reinforced 'green' composites in both longitudinal and transverse directions. Fig. 8 shows typical load displacement plots for flax fabric-reinforced composites in both longitudinal and transverse directions. As can be seen from Table III, the composite has higher Young's modulus in the transverse directions, while the fracture strain is higher in the longitudinal direction. This is attributed to higher Young's modulus and lower fracture strain of the fabric in the transverse direction. However, the difference between the fracture stress values in

TABLE III Tensile properties of flax fabric reinforced MSPC-G composites

Test direction	Fracture stress (MPa)	Fracture strain (%)	Young's modulus (GPa)
Longitudinal	50.3	21.0	1.01
[Warp]	(10.3) *	(8.6)	(10.0)
Transverse	55.7	7.8	1.26
[Weft]	(17.4)	(30.9)	(24.2)

*Figures in parentheses are CV%.

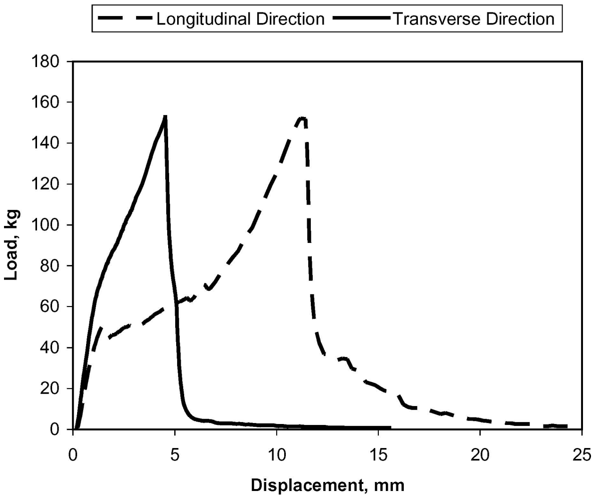
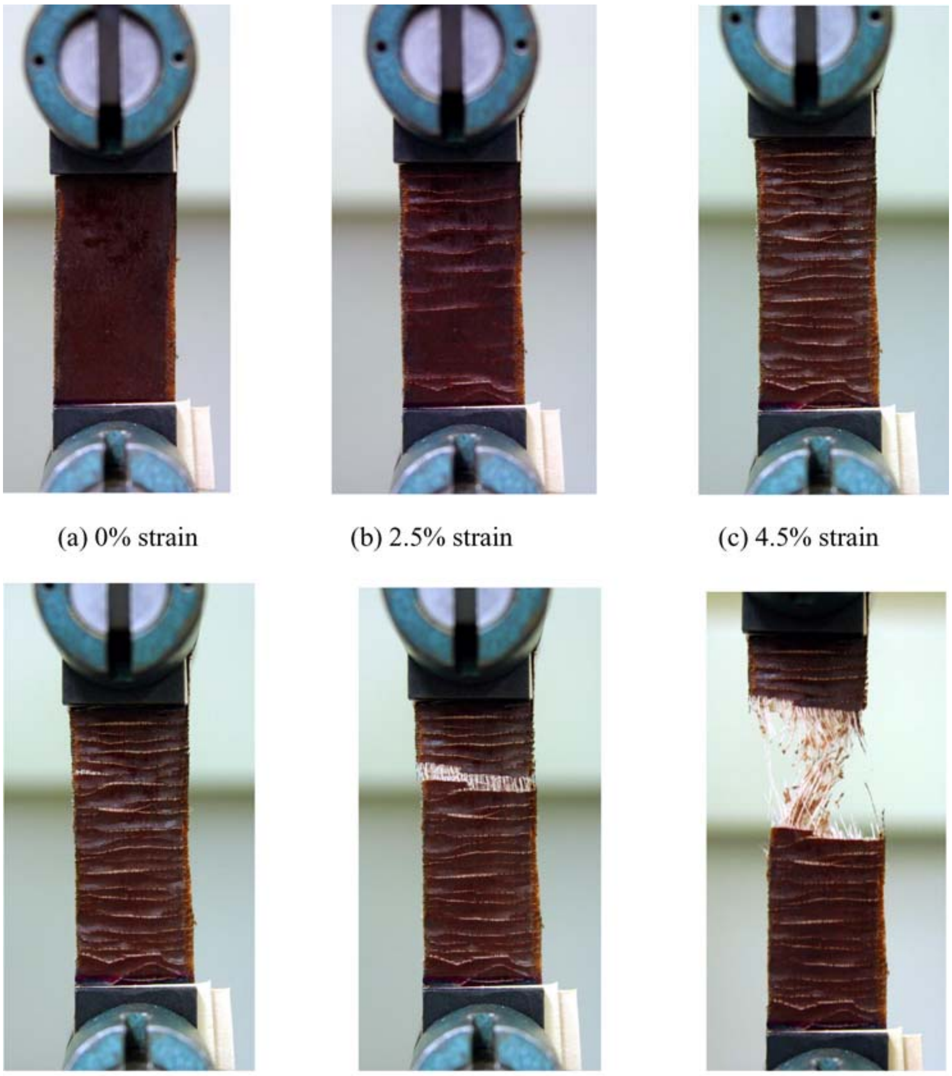


Figure 8 Typical load displacement plot for flax fabric reinforced MSPC-G composites.

longitudinal and transverse directions was not found to be significant. Fig. 9 shows photographs of a typical tensile fracture sequence of the flax fabric-reinforced composite in the longitudinal direction. As can be clearly seen from Fig. 9 that the resin starts to fail (crack) at strains below 2.5%. The load is then transferred to the fabric layers in the longitudinal direction. This is clear in Fig. 8 where a shoulder can be seen in the load displacement plot of composite tested in the longitudinal direction. This is due to the difference in the fracture strain values of the resin (10.5%) and the flax fabric (17.7%) in the longitudinal direction. Although the resin fracture strain is 10.5%, high local strains due to the straightening of yarns can result in resin (composite) cracking at much lower strain values. In the transverse direction there is not much difference in the fracture strain values of the resin (10.5%) and the fabric (7.1%), the slope change in the plot (Fig. 8) is not as dramatic. However, one can still see the inflection point (shoulder) in the plot where resin starts to fracture, in the transverse direction as well. A *t*-test was performed to test the significance between the differences in the composite tensile properties in the longitudinal and transverse directions were significant or not. At 95% confidence level, it was found that the differences in the fracture strain and Young's modulus values were significant while the difference in the fracture stress values in the two directions was not significant. This is clearly due to the difference in the fracture


(a) 0% strain (b) 2.5% strain (c) 4.5% strain

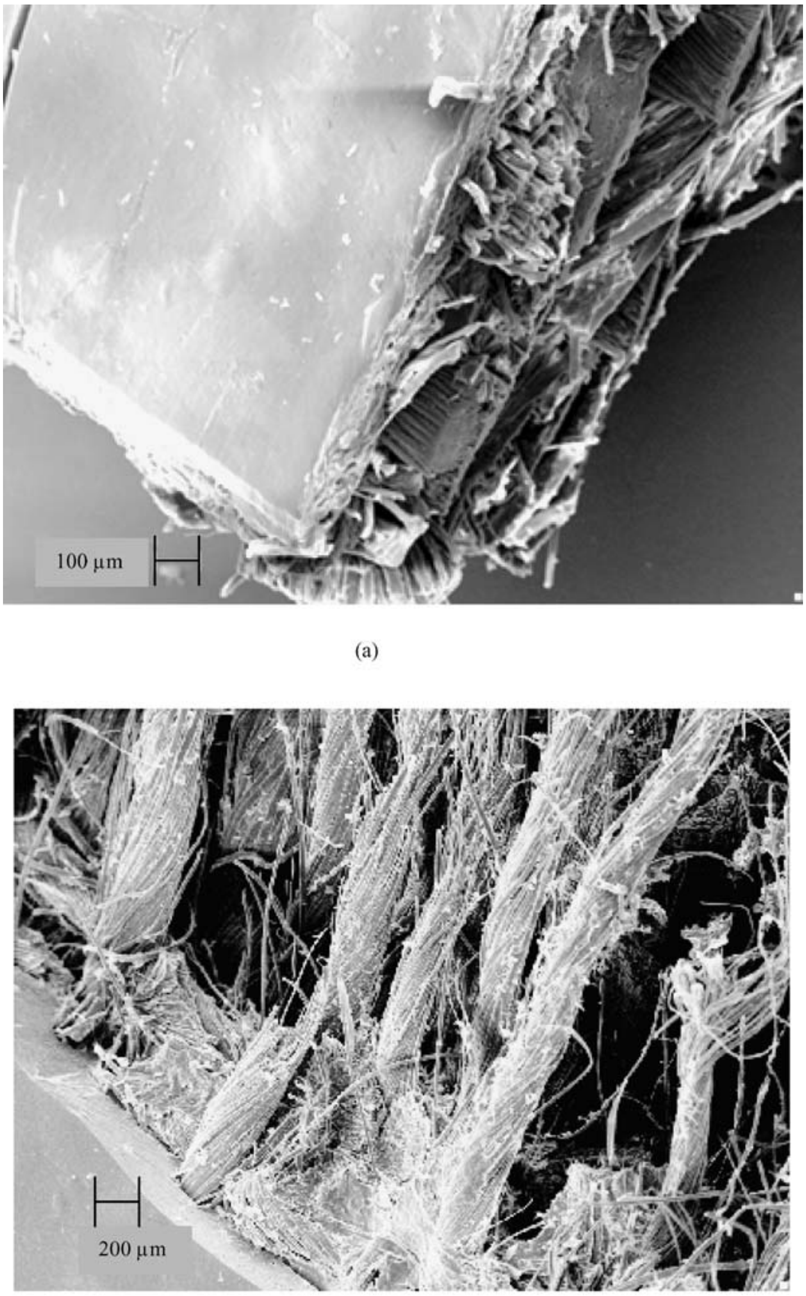
(d) 10% strain (e) 20% strain (f) 24% strain

Figure 9 Photographs showing typical tensile fracture sequence of flax fabric reinforced MSPC-G composite in the longitudinal direction.

strain values of MSPC-G resin and the flax fabric in the longitudinal direction. Because of this difference, as can be seen from Fig. 8, the composite specimens take higher load values in the transverse direction.

Mohanty *et al*. [25] fabricated biodegradable composites using alkali treated jute fabric and Biopol^{TM}. They reported a tensile strength factor (ratio of the tensile strength of composite to that of pure polymer) of approximately 1.55 for alkali treated jute fabric-reinforced composites. The tensile strength factors for the composites fabricated in this study are 1.88 and 2.07 in the longitudinal and transverse directions, respectively. Thus the composites fabricated in this study show superior properties, without any chemical modification of the fabric. This can be attributed to better bonding between the MSPC-G resin and flax fabric, due to the polar nature of both. The superior bonding between cellulose fibers and soy protein resin has been confirmed in many earlier studies [11, 38, 43, 54].

Theoretical predications of Young's modulus and fracture stress of flax fabric-reinforced MSPC-G composites in both longitudinal and transverse directions was carried out using pcGINA© software [29–31]. The fabric structure, thread spacings, yarn diameters, orientation of different fabric layers, layer thickness and MSPC-G resin properties were specified into the pcGINA© software to predict the composite tensile properties. More details and theoretical background of pcGINA© can be found elsewhere [29–31]. The fracture stress value predicted using pcGINA© for both longitudinal and transverse directions was 48.4 MPa, because of the same number of threads in both warp and weft directions. The Young's modulus values predicted using pcGINA© in the longitudinal and transverse



(a)

(b)

Figure 10 SEM photograph of the flax fabric reinforced MSPC-G composite tensile fracture surface.

TABLE IV Flexural properties of flax fabric reinforced MSPC-G composites

Test direction	Flexural stress (MPa)	Flexural strain (%)	Flexural modulus (MPa)
Longitudinal	26.8	6.6	526
[Warp]	(14.0)*	(8.4)	(14.9)
Transverse	34.6	7.1	610
[Weft]	(8.2)	(9.2)	(16.6)

*Figures in parentheses are CV%

directions were 1.09 and 1.11 GPa, respectively. The experimental fracture stress and Young's modulus values in the longitudinal and transverse directions for flax fabric-reinforced MSPC-G composites are summarized in Table III. It can be seen that the experimental values match closely with the predictions made using pcGINA©.

3.9. Flexural properties of composites

Table IV summarizes the flexural properties at yield including, flexural stress, flexural strain and flexural modulus for flax fabric-reinforced composites. As can be seen from Table IV, the composite specimens have a flexural stress values of 26.8 and 34.6 MPa and flexural modulus of 526 and 610 MPa, in the longitudinal and transverse directions, respectively. The difference in flexural properties in the transverse and longitudinal directions was found to be significant at 95% confidence level.

The higher flexural properties in the transverse direction can be attributed to the higher fabric fracture stress and Young's modulus and lower fracture strain in the transverse direction. Mwaikambo and Bisanda [27] reported the flexural strength and the flexural modulus of cotton/kapok-polyester composites to be nearly 36.5 and 525 MPa, respectively for 45% fiber volume fraction. These values are comparable to the values obtained in this research also. However, the cotton/kapok-polyester composites are not fully biodegradable as in the present case.

3.10. Fracture surface characterization of composites

Figs 10a and b show the SEM photographs of the flax fabric-reinforced MSPC-G composite tensile fracture surfaces. As mentioned earlier in Section 2.9, the composites were fabricated with four fabric layers. The fracture surface in Fig. 10a clearly shows different fabric and resin layers. It can also be seen from Figs 10a and b that most of the yarns fractured in a brittle manner. This correlates to the brittle failure exhibited in the Figs 8 and 9. It can also be seen from Figs 9 and 10a and b that some MSPC-G resin is adhering to the yarn surface. This is in spite of the resin being brittle which fractures during testing as a result of yarn straightening. In the present case both warp and weft yarns had very high twist. This, unfortunately, prevents resin from penetrating the yarns. As a result, the fractured resin pieces fall off during the test. However, as mentioned earlier several earlier studies have shown excellent bonding between the resin and the fibers [11, 38, 43, 54].

4. Conclusions

Soy protein concentrate was successfully crosslinked with GA and the modified resin showed improved tensile properties such as fracture stress and Young's modulus. MSPC-G resin showed improved thermal stability and the glass transition temperature increased by 12°C. MSPC-G resin also exhibited reduced moisture content than SPC resin. Flax fabric and MSPC-G resin were used to fabricate fully biodegradable, environment friendly 'green' composites. These 'green' composites showed good tensile and flexural strength in both longitudinal and transverse directions. Also, the theoretical predictions of composite tensile properties made using pcGINA© showed good agreement with the experimental values. These 'green' composites also showed good bonding between flax fabric and MSPC-G resin. Composite strength and bonding can be further improved by various chemical and surface modifications of the flax fabric and MSPC-G resin.

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