

Green Composites. II. Environment-friendly, Biodegradable Composites Using Ramie Fibers and Soy Protein Concentrate (SPC) Resin

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Abstract: Fully biodegradable and environment-friendly green composite specimens were made using ramie fibers and soy protein concentrate (SPC) resin. SPC was used as continuous phase resin in green composites. The SPC resin was plasticized with glycerin. Pre-curing and curing processes for the resin were optimized to obtain required mechanical properties. Unidirectional green composites were prepared by combining 65 % (on weight basis) ramie fibers and SPC resin. The tensile strength and Young's modulus of these composites were significantly higher compared to those of pure SPC resin. Tensile and flexural properties of the composite in the longitudinal direction were moderate and found to be significantly higher than those of three common wood varieties. In the transverse direction, however, their properties were comparable with those of wood specimens. Scanning electron microscope (SEM) micrographs of the tensile fracture surfaces of the green composite indicated good interfacial bonding between ramie fibers and SPC resin. Theoretical values for tensile strength and Young's modulus, calculated using simple rule of mixture were higher than the experimentally obtained values. The main reasons for this discrepancy are loss of fiber alignment, voids and fiber compression due to resin shrinking during curing.

Keywords: Green composite, Ramie fiber, Soy protein concentrate, Tensile properties, Flexural properties

Introduction

Fiber-reinforced polymeric composites offer many advantages over conventional metals. High strength and modulus of advanced composites combined with their lower density results in high strength and modulus per unit weight. Their use can be seen in wide ranging applications from sports equipment to aerospace and from consumer goods to electronics. Majority of the composites available in the market today, however, are made from petroleum-based non-degradable polymers and fibers and designed for long term use. Composites made using two dissimilar materials are difficult to reuse or recycle. As a result, most of them end up in landfills at the end of their life. With the environmental concerns growing worldwide, the interest in developing environment-friendly and fully biodegradable composites, made from fully sustainable resins and fibers employing agricultural crops such as starch, protein and cellulose has risen sharply in recent years. These green composites can be safely discarded or composted at the end of their life without harming the environment.

Natural, plant-based cellulose fibers such as flax, hemp, jute, sisal, henequen and ramie are yearly renewable and abundantly available throughout the world. Many of these fibers have been investigated for use as reinforcement in both thermoplastic and thermoset matrix composites [1-20]. Mohanty *et al.* [11] have reviewed the structural aspects as well as the mechanical and physical properties of natural fibers for use in biodegradable and other composites. Many

of these fibers have low density and high toughness and acceptable specific strength and modulus. Moreover, the hollow cellular structure of some plant fibers provides good insulation against heat and noise [4]. For example, Joseph *et al.* [3,6] have used sisal fibers to develop fiber-reinforced polyethylene composites and showed their tensile strength increase with the fiber content up to 30 % and the fiber length of 6 mm. Pedro and Manuel [7] found that incorporating jute fibers in polyethylene resin to form composites increased the tensile strength of the composites by up to 50 %.

Among various biopolymers, soy protein has received considerable attention due to several advantages including the ability to form a network structure for use as resin, worldwide availability as well as the low cost [21]. Three main varieties of soy protein, soy protein concentrate (SPC), soy protein isolate (SPI), and soy flour (SF) are marketed commercially. Chemically, SPC contains 70 % protein whereas SPI contains about 90 % protein. SPC also has 18 % carbohydrates, 6 % ash and remaining is fiber and moisture. SF contains up to 55 % protein and 32 % carbohydrates. Soybean protein contains several amino acids such as glutamic acid, arginine, lysine, cystine and aspartic acid that contain reactive groups [21]. These groups can be effectively used for cross-linking and/or hydrogen bonding to improve the mechanical properties of soy protein resin. For example, the cystine acids form covalent sulphur cross-links under oxidative conditions [22]. Dehydroalanine formed from alanine, reacts with lysine and cystine to make lysinoalanine and lanthionine cross-links, respectively [22]. Amide-type of cross-links can also be generated from the reaction between asparagine and lysine [22]. All these reactions occur during the curing process resulting in a polymeric

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resin with moderate strength [22,23].

Pure soy protein polymer is very brittle when dry. Liang *et al.* [24] studied the suitability of soy protein polymer for manufacturing molded specimens. They noted that both SPC and SPI displayed rigid and brittle plastic properties, which make it difficult to process. Studies have shown that the mechanical properties of soy protein polymers depend on both their chemical formulation and the manufacturing process [24-28]. Recently, various forms of protein modification have been investigated including adjusting pH values and adding plasticizers or other cross-linking agents to improve its properties as well as its ability to be processed [17-19,24-35]. Thames and Zhou [28] used maleinized tung oil to cross-link SPI and improve its tensile properties. Fatty acids have been studied as plasticizers for zein, a protein obtained from corn, sheets [30], and stearic acid as an effective plasticizer for SPI resin [17]. Chabba and Netravali [18,19] modified SPC with glutaraldehyde to increase mechanical and thermal properties as well as moisture resistance and then to fabricate yarn and fabric reinforced composites.

The applications of soy protein polymers include garbage and grocery bags [25], edible films [27,32], and adhesives in particleboard and plywood [31,34]. Several attempts to develop fully biodegradable green composites using natural fibers and soy protein polymers have also been made [13-19,28]. Thames and Zhou [28] and Lodha and Netravali [13,16] incorporated SPI with wood fibers and ramie fibers, respectively, to fabricate fully biodegradable composites using compression molding or hot pressing. Soy protein and wood and short ramie fibers were found to form a compatible system to yield composites of moderate strength for use in many applications.

In the present research, fully biodegradable and environment-friendly green composites were fabricated using ramie fibers and SPC resin. In the first part of this paper [20], we characterized ramie fibers and found them to have favorable tensile properties and thus suitable for reinforcement in green composites. To make the SPC resin easier to process and less brittle, glycerin was used as a compatible plasticizer and treatments combining an alkaline pH and a moderate temperature were used prior to the curing process. The effect of glycerin concentration and curing conditions on the mechanical properties of SPC resin were investigated. Unidirectional ramie fiber-reinforced soy protein composites were then prepared using hot pressing. The tensile and flexural properties of the composites in both longitudinal and transverse directions were compared with three common wood varieties. It is expected that these unidirectional green composites will find useful applications in secondary structural elements which are not primary load bearing parts. These will require moderate mechanical properties such as interior door panels or seat backs in automobiles or furniture parts, etc. Also, these composites can be easily disposed of in an environmentally sound way such as composting, rather than through landfill deposition or

incineration, thus completing the nature's ecological cycle without harming the environment.

Experimental

Materials

Ramie fibers were obtained in Seocheon-gun, Korea. The fiber specimens were between 600 and 1700 mm long. ARCON[®]S, a soy protein concentrate (SPC) in powder form, was obtained from Archer Daniels Midland Co., Illinois. Analytical-grade glycerin and sodium hydroxide (NaOH) were used for SPC processing.

SPC Resin Preparation

The SPC powder was mixed with distilled and deionized water at a ratio of 1:10. Glycerin was added as a plasticizer to overcome the resin brittleness. To study the effect of plasticization, glycerin was added to the mixture from 0 % to 60 % in steps of 10 %, based on SPC weight. The pH of the solution was then adjusted to 11 ± 0.1 using 1N solution of sodium hydroxide [29,36]. The mixture was homogenized by a magnetic stirrer for 10 minutes and then held for 30 min at 70 °C in a constant temperature water bath (pre-curing). The pre-cured soy protein solution was cast on Teflon[®] coated glass plates, and dried at room temperature for about 72 hours. The full 'curing' of the dried SPC specimens (resin sheets) was carried out by hot pressing at 80, 100, 120, and 140 °C for 2 hours under a pressure of 5 MPa.

Composite Preparation

Unidirectional fiber-reinforced composites were prepared using ten-gram batches of 100 mm long fibers. Small amounts of the fibers, in parallel bundle form, were soaked in pre-cured SPC solution containing 30 % glycerin. Excess solution was squeezed out. This process was repeated several times to obtain complete penetration of the SPC solution between the fibers. The wet fiber bundles were aligned on a Teflon[®] coated glass plate layer by layer to make a 100 mm × 100 mm sheet and dried for 48 hours at room temperature. For measurement of properties in the longitudinal direction, 10 mm wide specimens of these 'pre-cured' sheets were prepared. The dried sheet was then placed between two 150 mm × 150 mm stainless steel plates and hot pressed (cured) in an automated Carver laboratory press, model Auto M-D at 120 °C and 5 MPa pressure for 2 hours. The plates with cured composites were removed from the press and allowed to cool down. The fiber content of the composites was calculated based on the final weight of the dry composite and the weight of the fibers used in composite fabrication.

Tensile Properties of SPC Resin

The tensile properties of SPC resin were measured using an Instron tensile testing machine (Model 1122) according to ASTM D 882-97. Pre-cured and cured resin sheets were cut

into 90 mm × 10 mm strips after conditioning at 21 °C and 65 % RH for 24 hours. An average of the five thickness measurements was used for the calculation. The gauge length of 50 mm and the crosshead speed of 50 mm/min (strain rate of 1 min⁻¹) were used for all tests.

Mechanical Properties of Ramie/SPC Composites

Tensile and flexural properties of ramie/SPC unidirectional composites were investigated according to ASTM D 3039/D3039M-00 and ASTM D 790-99, respectively. Tensile tests performed in both parallel (longitudinal) and perpendicular (transverse) directions relative to the fiber axis. Tensile properties including ultimate tensile strength (tensile strength), Young's modulus, fracture strain and energy to break were measured. For tensile measurements in the transverse direction, the cured composite sheets were cut into 10 mm wide strips. Wooden tabs were glued on two sides at the two ends of the specimens to avoid slippage and jaw breaks. The average thickness of the specimen was obtained from five measurements along the gauge length of each specimen. A gauge length of 20 mm and a crosshead speed of 1 mm/min (strain rate of 0.05 min⁻¹) were used. Five successful tests were conducted to obtain average tensile properties.

Flexural strength, flexural modulus and flexural strain were obtained from the three-point bending tests. For this test composite specimens of 30 mm × 10 mm were prepared. The crosshead speed was set at 1 mm/min and the span length was 20 mm. Five successful tests were conducted to obtain average flexural properties.

The mechanical properties of composites were compared with those of pure SPC resin and with the tensile and flexural properties of bass, cherry and walnut wood specimens [10].

Fracture Surface Characterization

Fracture surfaces of the composites, both longitudinal and transverse directions, were characterized, after tensile tests, using a scanning electron microscope (SEM), Leica model 440X.

Results and Discussion

Tensile Properties of SPC Resin

Effect of Curing Temperature

To prepare SPC resin, glycerin was used as a plasticizer and the pH was maintained at 11. Soy protein has an isoelectric point between 4.5 and 5 pH when the molecules fold up into globular form and become insoluble in water. The alkaline pH is known to help to unfold the soy protein molecules and thus allow them to dissolve in water. Under the same conditions bridges created between the protein molecules helps to stabilize and thus strengthen the network [29,36]. Along with the alkaline treatment, moderate heating (pre-curing) was also used to denature soy protein resulting in unfolding of the

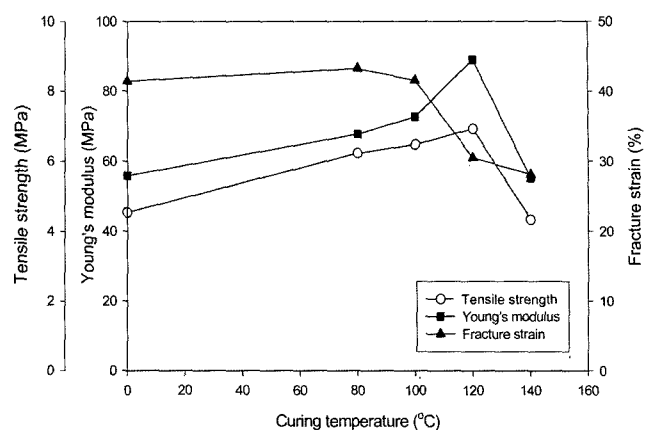


Figure 1. Effect of curing temperature on the tensile properties of SPC resin.

protein molecules [37].

Tensile properties of SPC resin plasticized with 30 % glycerin, after hot pressing (curing) for 2 hours at 80, 100, 120, and 140 °C were compared with the pre-cured SPC resin properties. The effect of curing temperature on the SPC resin tensile properties is presented in Figure 1. The fracture strain is highest for specimens cured at 80 °C but decreases for those cured at higher temperatures. It is also clear that the tensile strength and Young's modulus increased with the curing temperature and reached a maximum of about 7 MPa and 90 MPa at 120 °C, respectively and decreased thereafter. Properties of soy protein resin are highly related to its structures and amino acid residue. Soy proteins are composed of 18 amino acids. Some groups on amino acids such as the amino, carboxyl and sulfhydryl groups, are relatively reactive and may form cross-links upon heating [22]. The disulphide cross-link, which is the most common type of cross-links, is formed from two cysteines [22]. The dehydroalanine (DHA) residues formed from alanine by loss of side chain beyond β -carbon atom can react with lysine to form lysinoalanine cross-links. DHA can also react with cystine to form lanthionine cross-links. In addition, asparagine and lysine may also react to form amide-type cross-links [22]. These cross-links are important in maintaining the three dimensional structure of protein molecules. Cheftel *et al.* [23] reported that thermal treatment in alkaline pH promotes intra- as well as inter-molecular cross-links between soy proteins. It is presumed that heat-induced cross-linking contributed to increased tensile strength and modulus of the SPC resin. Similar observations have also been reported for SPI films by Gennadios *et al.* [27]. At 140 °C, however, all mechanical properties decreased. After curing, SPC resin films were yellowish and translucent. However, at the curing temperature of 140 °C, the resin color changed from yellow to darker brown as a result of degradation.

The fracture strains of pre-cured and cured SPC resin were high, ranging from 28 % to 43 %. Liang *et al.* [24] reported the fracture strains of SPI, as high as 120 % to 215 % depending

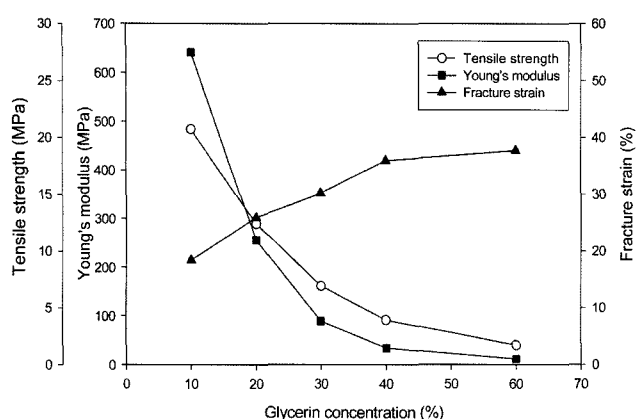


Figure 2. Effect of glycerin concentration on the tensile properties of SPC resin.

on the amount of plasticizer. As the curing temperature increased, the fracture strain of the SPC resin decreased due to increased cross-linking.

These results suggest that the optimum curing condition for SPC resin is 120°C for 2 hours. These parameters were used to process ramie fiber-reinforced SPC resin composites.

Effect of Glycerin Concentration

As mentioned earlier, glycerin was added as a plasticizer to SPC resin to reduce its brittleness and prevent chipping and cracking during handling. The effect of glycerin, ranging from 10 % to 60 %, on the tensile properties of SPC resin, was characterized and is presented in Figure 2. Pure SPC resin, without glycerin, was too brittle to test.

As can be seen from Figure 2, the tensile strength and Young's modulus of the SPC resin decreased and the fracture strain increased as the glycerin concentration was increased. As mentioned earlier glycerin acts as a plasticizer. Also, being hydrophilic glycerol attracts water, further plasticizing the SPC resin. In addition, since glycerin has three hydroxyl groups and an asymmetric structure, its interactions with polypeptide chains are complex, leading to a less organized network [38]. At concentrations of up to 30 % the plasticization effect is significant. At concentrations above 40 %, the slopes of the curves for all tensile properties decreased i.e. the effect of additional glycerin was not as marked. This is believed to be due to aggregation of glycerin molecules, reducing its plasticization efficiency. In this study, 30 % glycerin was selected for the processing condition for ramie

fiber/SPC resin composites, because the resin with less than 30 % glycerin showed shrinkage and shape deformations, e.g. warping, as the moisture evaporated during curing.

Mechanical Properties of Unidirectional Ramie/SPC Green Composites

Tensile Properties

Unidirectional green composites were prepared using ramie fibers and soy protein concentrate (SPC) resin with 65 % fiber content by weight. Tensile strength, Young's modulus, fracture strain and energy to break of green composites both in longitudinal and transverse directions, are presented in Table 1. Unreinforced SPC resin properties are also included in Table 1 for comparison. As can be expected for unidirectional composites, the longitudinal tensile strength of 271 MPa is over 35 times the tensile strength of 7.4 MPa in the transverse direction. In general, the measured transverse tensile strength of the composite should be comparable to the fiber/resin interfacial strength or the resin tensile strength. However, in the present case there are two other factors that affect the transverse fracture. The first one is simply due to the ramie fibers for which fibril separation is easy [20]. This can reduce the transverse tensile strength. The other factor is that since the fibers were hand laid, the composites are not fully unidirectional. Some fibers that are at an angle to the longitudinal axis can increase the transverse fracture of the composites. In addition, these composites were hard to cut and could have been weakened because of the significant

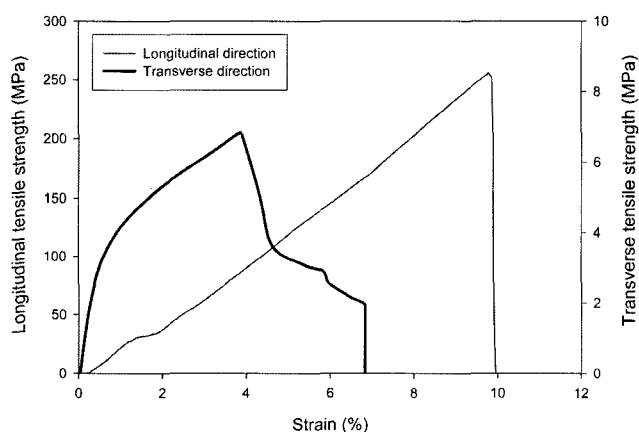


Figure 3. Typical tensile strength vs. strain plots of ramie fiber/SPC composite.

Table 1. Tensile properties of the green composites in longitudinal and transverse directions and the SPC resin

Materials	Direction in measurement	Tensile strength (MPa)	Fracture strain (%)	Young's modulus (GPa)	Energy to break (J)
Green composite*	Longitudinal	271 (8.6)**	9.2 (18.3)	4.9 (17.3)	3.9 (23.4)
	Transverse	7.4 (27.5)	5.3 (22.5)	0.9 (30.3)	0.1 (37.5)
SPC resin		6.9 (6.7)	30.2 (10.7)	0.1 (4.8)	0.2 (25.0)

*65 % fiber volume fraction, ** numbers in parentheses show the percent coefficient of variation for each measurement.

amount of stress applied during specimen cutting. The tensile strength and Young's modulus of the composite in the longitudinal direction were found to be significantly higher compared to those of pure SPC resin, as can be expected.

Typical tensile strength-strain plots of the green composites in both longitudinal and transverse directions are shown in Figure 3. The strength-strain plot in the longitudinal direction is linear, whereas in the transverse direction the plot is non-linear. This difference indicates that the fracture mechanisms in two directions, as can be expected, are different. The longitudinal fracture of the composite is mostly generated from fiber fracture, whose fracture has also shown a linear behavior [14]. The non-linear fracture in the transverse direction may be attributed to matrix failure or longitudinal fiber splitting rather than fiber/matrix interfacial debonding, because SPC resin tensile strength is lower than the interfacial shear strength (IFSS) between ramie fiber and SPC resin. The plot also indicates the possibility of fiber pull-out since the fiber orientation, as mentioned earlier, was not perfect because of the hand lay up of fibers. The IFSS values were obtained to be 23 MPa for unplasticized SPC and 15 MPa for SPC resin containing 30 % glycerin [15]. The fracture strains of the composite in both directions were significantly lower than that of the SPC resin since it is mainly controlled by the fiber fracture, longitudinally or in transverse direction by fibril splitting.

The high tensile strength and Young's modulus of the green composite, in the longitudinal direction, can be directly attributed to the tensile properties of the ramie fibers. In the first part of this paper [20], we have observed the favorable physical properties of ramie fibers including the tensile strength of 627 MPa and Young's modulus of 31.8 GPa. This reinforcement effect depends on the matrix ductility that provides the resistance to crack propagation and effective stress transfer mechanism [39]. The load carrying capability of the fibers, P_f , has been shown to be a function of the elastic modulus ratio E_f/E_r between the fiber and the resin according to equation (1) below

$$\frac{P_f}{P_c} = \frac{E_f/E_r}{(E_f/E_r) + V_r/V_f} \quad (1)$$

where P_f is the load carried by the fibers for a given load applied on the composite, P_c ; E_f and E_r represent the Young's moduli of fiber and resin, respectively; and V_f and V_r are the fiber and resin volume fractions, respectively [40]. In general, higher the E_f/E_r ratio, higher will be the load carried by the fibers. In this study, the high compliance of SPC resin and the high Young's modulus of the ramie fiber result in a high modulus ratio. Ramie fibers thus provide effective reinforcement to SPC resin.

The mechanical properties of the composites are also strongly dependent on the interfacial bonding between the fiber and the resin. Nam and Netravali [15] have shown that ramie/SPC have high interfacial shear strength, whose value

was determined to be 22.8 MPa without glycerin by the microbond technique. This high interfacial adhesion was attributed to the strong hydrogen bonding between soy protein that contain hydroxyl, carboxyl and amino groups and sugar units in cellulose, hemicellulose and pectin of ramie fiber that contain hydroxyl groups. The high interfacial shear strength is also a result of the mechanical bonding provided by the rough fiber surface and low viscosity of the SPC solution which can occupy the valleys present within the rough surface. The strong interfacial bonding is expected to allow efficient load transfer from broken fibers to intact fibers and enhance the strength of the composites in the longitudinal direction. At the same time, however, the composites tend to become more brittle as the fracture strain is controlled by the fibers. However, it is possible to engineer the fiber/resin interfacial characteristic by treating fiber surfaces depending on the specific application. Nam and Netravali [15] were able to tailor the interfacial bonding behavior by ethylene plasma treatment on the ramie fiber to reduce the brittleness and improve toughness of the composite.

Theoretical Analysis

Theoretical calculations of the tensile strength and Young's modulus in the longitudinal direction were carried out using the simple rule of mixtures [41] as shown in equations (2) and (3):

$$\sigma_c = \sigma_f V_f + \sigma_r V_r \quad (2)$$

$$E_c = E_f V_f + E_r V_r \quad (3)$$

where σ_c , σ_f and σ_r represent the tensile strength values of the composite, fiber and resin, respectively and E_c , E_f and E_r are the Young's modulus of composite, fiber and resin, respectively. The tensile strength and Young's modulus values for composite, SPC resin and fiber specimens were experimentally obtained. The calculated values of tensile strength and Young's modulus of the composites with 65 % fiber weight content are 410 MPa and 20.7 GPa, respectively. The experimental tensile strength and modulus values of 271 MPa and 4.9 GPa, respectively, are much lower than the theoretical values. This discrepancy is believed to be primarily attributed to the imperfect fiber alignment, fiber bending, compression, presence of fiber ends within the gauge length as well as voids within the resin and at the fiber/resin interface. While the imperfect fiber alignment and bending are primarily due to the hand lay up of the fibers and not being able to maintain them straight and under stress, the SPC resin shrinkage occurs during drying and curing, as it loses significant amount of moisture. This resin shrinkage affects the composite performance in two different ways: first the fibers embedded are compressed longitudinally and second the shrinkage creates significant amount of stress at the fiber/resin interface. The longitudinal shrinkage affects the composite modulus adversely and the

stresses at the interface affect the tensile strength. At high curing temperature of 120°C, the moisture in the resin and fiber vaporizes creating voids. These voids could be small and may not be visible to human eyes. Voids in composites have been reported to result in significant reduction in tensile strength as a result of creating stress concentration points [42]. As noted by Tang *et al.* [43], even though pressure is applied during the curing process to minimize void content, complete elimination of voids from composites may not be possible for all fiber/resin systems. If the effect of voids on the mechanical properties is considered, a good approximation of the experimental results from the theoretical model will be possible. Garcia-Zetina *et al.* [44] used a correction factor that takes into account the void content to predict the strength of a composite made of polyester resin and short natural fibers, and found that the correction factor is dependent on the fiber volume factor. In the present case, obtaining void content was difficult. Lodha and Netravali [13] also observed lower Young's modulus of ramie fiber/SPI resin composites having various fiber lengths and contents when comparing with the theoretical prediction from Zweben's model. This was attributed to the high variability of fiber tensile strength, distribution, fiber orientation as well as voids. Plastic deformation of resin and imperfect interface between fiber and resin due to poor resin wetting, which are not considered in the theoretical model, may also contribute to the discrepancy of experimental values from theoretical values.

Theoretical calculations are also based on fibers being continuous, i.e., there are no ends in the composites. In the present case, since ramie fibers are short, there are several ends within the gauge length. This also is a factor in getting lower tensile strength and Young's modulus values.

Comparison of Green Composite Properties with Common Wood Varieties

Table 2 presents the tensile and flexural properties of the ramie fiber/SPC resin green composites in longitudinal and transverse directions. Properties of three common wood

varieties, bass, cherry and walnut corresponding in grain (longitudinal) and perpendicular to grain (transverse) directions are also reported for comparison. The data for the wood was obtained from the work done by Luo and Netravali [9]. Like the unidirectional composites, wood specimens also exhibit anisotropic behavior with high tensile and flexural tensile strengths in the grain direction and low tensile and flexural tensile strengths in the transverse (to grain) direction.

It can be seen that the green composites exhibited much higher tensile strength of over 270 MPa in the longitudinal direction than the wood samples, all of which tensile strengths of lower than 140 MPa. In the transverse direction, the tensile strength of the green composite was comparable to that of all wood specimens. Like the tensile strength, the flexural strength of the green composites in the longitudinal direction was also significantly higher than that in the transverse direction. Typical flexural load vs. displacement curves in longitudinal and transverse directions for green composites are shown in Figure 4. Compared to the wood specimens, the green composites exhibited higher flexural strength in the longitudinal direction, but the flexural strength values in the transverse direction are comparable. It is interesting to note that the

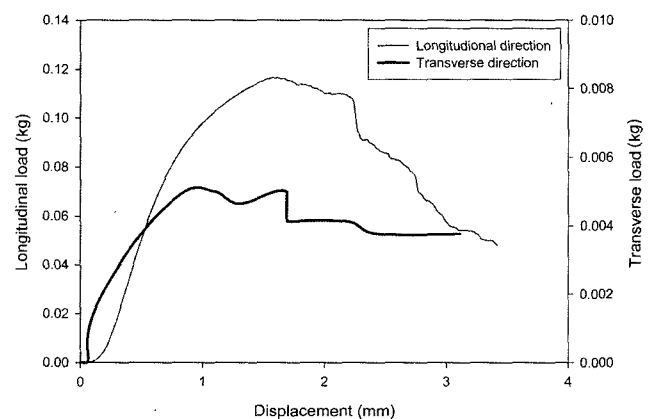


Figure 4. Typical flexural load vs. displacement curves of ramie fiber/SPC composite.

Table 2. Tensile and flexural properties of green composite and three different wood varieties

Materials	Direction	Strength (MPa)		Modulus (GPa)		Strain (%)	
		Tensile	Flexural	Young's	Flexural	Tensile	Flexural
Green composite*	Longitudinal	271 (8.6)**	234 (6.4)	4.9 (17.3)	12.4 (9.3)	9.2 (18.3)	3.1 (6.3)
	Transverse	7.4 (27.5)	18 (18.9)	0.9 (30.3)	0.85 (9.4)	5.3 (22.5)	2.8 (19.3)
Basswood	Grain	117 (20.1)	93 (7.7)	4.8 (24.8)	8.9 (9.6)	3.2 (25.3)	1.5 (7.2)
	Perpendicular to grain	4.8 (45.7)	9.2 (26)	0.34 (29.1)	0.29 (17.1)	1.9 (52.1)	4.3 (15.2)
Cherry wood	Grain	124 (55.6)	143 (13.9)	3.5 (19.1)	9.1 (23.2)	3.6 (39.7)	2.2 (10.5)
	Perpendicular to grain	9.5 (23.1)	18.7 (27.3)	0.64 (14.1)	0.88 (33.9)	1.9 (18.8)	2.5 (19.6)
Walnut wood	Grain	139 (18.2)	133 (8.4)	2.9 (6.9)	6.9 (6.2)	5.5 (27.6)	2.8 (16.9)
	Perpendicular to grain	9.4 (40.5)	18.9 (23.8)	0.96 (14.5)	1.2 (9.7)	1.1 (17.9)	1.7 (29.6)

*65 % fiber volume fraction, **numbers in parentheses show the percent coefficient of variation for each measurement.

strength of AISI 1020 steel is between 240 to 280 MPa. With the steel density around 7.84 g/cc, the green composites (about 1.4 g/cc) developed here are about 5.5 times stronger than 1020 steel on per weight basis.

The Young's modulus of green composites was comparable to wood specimens in both longitudinal and transverse directions. On the other hand, the flexural modulus of the green composites was significantly higher than those of wood specimens in the longitudinal direction, but comparable in the transverse direction.

The fracture strains for the green composites were higher than those for woods in longitudinal and transverse directions, but the flexural strains were comparable with those of woods in both directions. The relatively high strain of the composite can be explained by the ductility of SPC resin plasticized with glycerin. The wood specimens failed catastrophically in the three-point bending test [9], but such failure was not observed in the composite measurements.

A point to note is that the wood is derived from grown

plants which needs about 25 years for full growth. The green composites, however, are fabricated using fibers and resins that are yearly renewable. Also, the properties of the green composites may be easily manipulated in different directions as desired, by using layered structure and varying fiber orientation in each layer. For naturally occurring woods that is not an option. A third difference is that different shapes can be obtained by molding the composites which would be difficult to obtain with wood.

Fracture Surface

In order to further investigate the fracture behavior of the green composites, the fractured surfaces after tensile testing in longitudinal and transverse directions were observed. Figure 5(a) and (b) show the fracture surfaces of green composites in longitudinal and transverse directions, respectively. The longitudinal fracture surface shows that most fibers broke at the fracture surface and these fractured fibers were held together by SPC resin. This behavior confirms the strength-strain plot shown in Figure 3. This brittle fracture behavior also confirms the strong fiber/SPC resin interfacial bonding, which is a result of a highly polar nature of both ramie fiber and SPC resin, and their good mechanical interlocking. The good penetration of low viscose SPC resin between the fibrils has been observed by SEM, showing high interfacial area in bonding [15]. For the weak interfacial bonding, generally, fibers are pulled out from the matrix with no resin adhering to the fibers [9,12].

In the transverse fracture, it is seen that the ramie fibers separated from each other with resin still adhering to the fibers. Fibrillation can also be seen in some fibers. This shows that the fracture of composites in the transverse direction occurred by fiber/matrix interface, matrix failure, or fiber fibrillation depending on the local situation. The strength-strain plot in Figure 3 confirms that after the main fracture some of the fibers that are misaligned continue to get pulled out or fracture. Also, close observation of broken fiber fragments in the SEM micrograph reveals that the fibers are separated into fine fibrils of different lengths. These observations indicate that fibril separation behaves like defects in the composites. It may, therefore, be important to use finer diameter fibers where fibrillation may not be a significant problem. As mentioned earlier, the voids within the resin or at the fiber/resin surface can affect the mechanical performance of the composites. However, they are difficult to locate from the SEM micrographs.

Conclusion

In this research, fully biodegradable, environment-friendly, green composites were fabricated using ramie fibers and SPC resin and their mechanical properties were investigated. The conclusions drawn from experimental analyses can be summarized as follows:

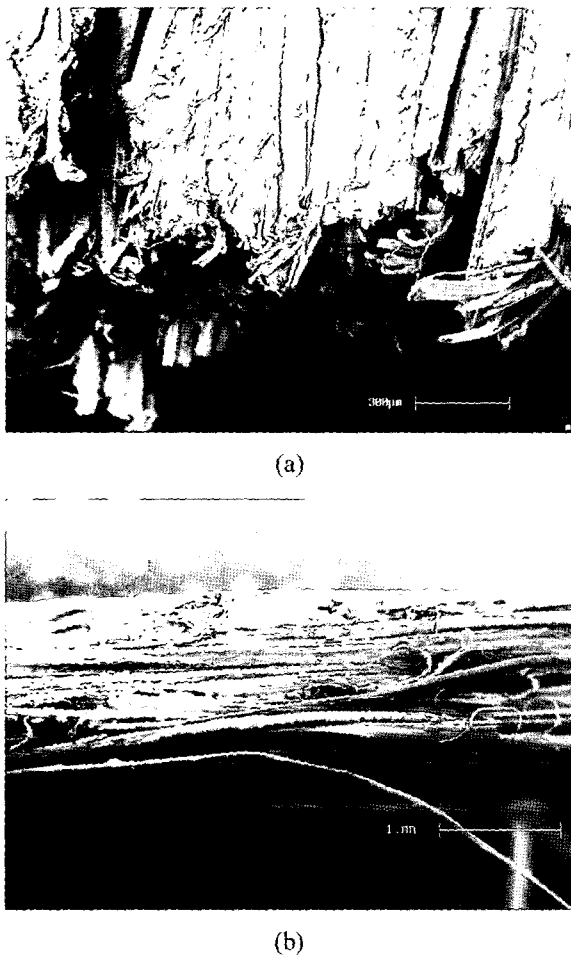


Figure 5. SEM photomicrographs of the fracture surfaces of ramie fiber/SPC composites, fractured (a) in the longitudinal direction and (b) in the transverse direction.

1) As the curing temperature increased, the tensile strength and Young's modulus of the SPC resin increased and the fracture strain decreased as a result of higher cross linking. However, curing above 120°C, decreased the tensile properties as a result of thermal degradation of the resin.

2) Addition of glycerin to SPC resin decreased its tensile strength and modulus, while increasing the fracture strain due to plasticization.

3) Optimum properties of SPC resin were obtained with 30 % glycerin and a curing at 120°C for 2 hours. Under these conditions, SPC resin had an average tensile strength of 6.9 MPa, Young's modulus of 0.1 GPa and a fracture strain of about 30 %.

4) The experimental values of tensile strength and modulus, in the longitudinal direction of the composite, were lower than the theoretical values. This is primarily due to fiber misalignment, longitudinal compression and bending as well as shrinkage of the SPC resin and presence of voids in the composite specimens.

5) The green composites had significantly higher tensile and flexural properties in the longitudinal direction than some of the commonly used wood specimens. However, in the transverse direction, the values were comparable to the wood specimens. The tensile properties of the composites in the longitudinal direction were controlled by the fibers, whereas, the properties in the transverse direction were dominated by resin, fiber/resin interface and longitudinal fiber splitting.

References

- B. V. Kokta, R. Chen, C. Daneault, and J. L. Valade, *Polym. Compos.*, **4**, 229 (1983).
- C. Pavithran, P. S. Mukjerjee, M. Brahmakumar, and A. D. Damodaran, *J. Mater. Sci.*, **26**, 455 (1991).
- K. Joseph, S. Thomas, C. Pavithran, and M. Brahmakumar, *J. Appl. Polym. Sci.*, **47**, 1731 (1993).
- The Corporate Units in the Daimler-Benz Group, *Daimler-Benz High Tech Report*, **2**, 1 (1995).
- A. K. Mohanty and M. Misra, *Polym-Plast. Technol. Eng.*, **34**, 729 (1995).
- K. Joseph, S. Thomas, and C. Pavithran, *Polymer*, **37**, 5139 (1996).
- J. H. Pedro and D. J. A. Manuel, *J. Appl. Polym. Sci.*, **65**, 197 (1997).
- M. Wollerdorfer and H. Bader, *Industrial Crops and Products*, **8**, 105 (1998).
- S. Luo and A. N. Netravali, *J. Mater. Sci.*, **34**, 3709 (1999).
- S. Luo and A. N. Netravali, *Polym. Composite.*, **20**, 367 (1999).
- A. K. Mohanty, M. Misra, and G. Hinrichsen, *Macromol. Mater. Eng.*, **276**, 1 (2000).
- S. Luo and A. N. Netravali, *J. Adhes. Sci. Technol.*, **15**, 423 (2001).
- P. Lodha and A. N. Netravali, *J. Mater. Sci.*, **37**, 3657 (2002).
- S. Nam, M.S. Thesis, Cornell University, Ithaca, 2002.
- S. Nam and A. N. Netravali, *J. Adhes. Sci. Technol.*, **18**, 1063 (2004).
- P. Lodha and A. N. Netravali, *Polym. Compos.*, **26**, 647 (2005).
- P. Lodha and A. N. Netravali, *Compos. Sci. Technol.*, **65**, 1211 (2005).
- S. Chabba and A. N. Netravali, *J. Mater. Sci.*, **40**, 6263 (2005).
- S. Chabba and A. N. Netravali, *J. Mater. Sci.*, **40**, 6275 (2005).
- S. Nam and A. N. Netravali, *Fibers and Polymers*, **7**, 372 (2006).
- Y.-P. Ly, L. A. Johnson, and J. Jane, "Biopolymers from Renewable Resources" (D. L. Kaplan Ed.), p.144, Springer, New York, 1998.
- T. E. Creighton, "Proteins: Structure and Molecular Properties", 2nd ed. p. 1, Freeman, New York, 1993.
- J. C. Cheftel, J.-L. Cuq, and D. Lorient, "Food Chemistry" (O. R. Fennema Ed.), pp.245, 279, 289, 336, and 343, Marcel Dekker Inc, New York, 1985.
- F. Liang, Y. Q. Wang, and X. S. Sun, *J. Polym. Eng.*, **19**, 383 (1999).
- J. J. Kester and O. R. Fennema, *Food Technol.*, **40**, 47 (1986).
- I. Paetau, C. Z. Chen, and J. L. Jane, *Ind. Eng. Chem. Res.*, **33**, 1821 (1994).
- A. Gennadios, V. M. Ghorpade, C. L. Weller, and M. A. Hanna, *Trans. ASAE*, **39**, 575 (1996).
- S. F. Thames and L. Zhou "Proceedings of the International Conference on Composites Engineering-5", Las Vegas, p.887, 1998.
- A. Gennadios, A. H. Brandenburg, C. L. Weller, and R. F. Testin, *J. Agric. Food Chem.*, **41**, 1835 (1993).
- H. M. Lai, G. W. Padua, and A. H. Wei, *Cereal Chem*, **74**, 49 (1995).
- X. Z. Sun and K. Bian, *J. Am. Oil. Chem. Soc.*, **76**, 977 (1999).
- J. W. Rhim, A. Gennadios, A. Handa, C. L. Weller, and M. A. Hanna, *J. Agric. Food Chem.*, **48**, 4937 (2000).
- F. Ayhllon-Meixueiro, C. Vaca-Garcia, and F. Silvestre, *J. Agric. Food Chem.*, **48**, 3032 (2000).
- X. Q. Mo, J. Hu, X. S. Sun, and J. A. Ratto, *Ind. Crop. Prod.*, **14**, 1 (2001).
- X. Q. Mo and X. Z. Sun, *J. Am. Oil. Chem. Soc.*, **78**, 867 (2001).
- N. S. Hettiarachchy, U. Kalapathy, and D. J. Myers, *J. Am. Oil. Chem. Soc.*, **72**, 1461 (1995).
- X. Z. S. Sun, H. R. Kim, and X. Q. Mo, *J. Am. Oil. Chem. Soc.*, **76**, 117 (1999).
- J. Gueguen, G. Viroben, P. Noireaux, and M. Subirade, *Ind. Crop. Prod.*, **7**, 149 (1998).

39. R. N. O'Brien and K. Hartman, *J. Polym. Sci. Part C Polymer Symposium*, **34**, 293 (1971).
40. B. D. Agarwal and L. J. Broutman, "Analysis and Performance of Fiber Composites", p.15, John Wiley & Sons, New York, 1980.
41. D. Hull, "An Introduction to Composite Materials", pp. 36-38, Cambridge University Press, Cambridge, 1981.
42. B. D. Harper, G. H. Staab, and R. S. Chen, *J. Compos. Mater.*, **21**, 280 (1987).
43. J. M. Tang, W. I. Lee, and G. S. Springer, *J. Compos. Mater.*, **21**, 421 (1987).
44. F. Garcia-Zetina, E. Martinez, A. Alvarez-Castillo, and V. M. Castano, *J. Reinf. Plast. Comp.*, **14**, 641 (1995).