Advanced 'green' composites

ANIL N. NETRAVALI *, XIAOSONG HUANG and KAZUHIRO MIZUTA

Fiber Science Program, Dept. of Fiber Science and Apparel Design, Cornell University, Ithaca, NY 14853-4401, USA

Abstract—Fully biodegradable high strength composites or 'advanced green composites' were fabricated using yearly renewable soy protein based resins and high strength liquid crystalline cellulose fibers. For comparison, E-glass and aramid (Kevlar®) fiber reinforced composites were also prepared using the same modified soy protein resins. The modification of soy protein included forming an interpenetrating network-like (IPN-like) resin with mechanical properties comparable to commonly used epoxy resins. The IPN-like soy protein based resin was further reinforced using nano-clay and microfibrillated cellulose. Fiber/resin interfacial shear strength was characterized using microbond method. Tensile and flexural properties of the composites were characterized as per ASTM standards. A comparison of the tensile and flexural properties of the high strength composites made using the three fibers is presented. The results suggest that these green composites have excellent mechanical properties and can be considered for use in primary structural applications. Although significant additional research is needed in this area, it is clear that advanced green composites will some day replace today's advanced composites made using petroleum based fibers and resins. At the end of their life, the fully sustainable 'advanced green composites' can be easily disposed of or composted without harming the environment, in fact, helping it.

Keywords: Advanced green composites; green composites; soy protein; plant-based resins; cellulose fibers.

1. INTRODUCTION

Fibers such as graphite, aramids, glass etc., are commonly used to fabricate high strength composites. These so called 'advanced composites' have replaced metals in many applications because of their excellent mechanical properties and low density giving them high specific strength and stiffness. Such weight savings are highly desirable for applications in aerospace to transportation to reduce weight and associated fuel consumption. Another distinct advantage of

---

*To whom correspondence should be addressed. E-mail: ann2@cornell.edu

composites is their ability to be engineered to obtain required properties in different directions by appropriate fiber placing in different layers of the laminated structure. Currently available advanced composites commonly employ resins such as epoxies, polyimides and polyetheretherketones. Most of these fibers and resins are derived from petroleum feedstock and do not degrade for several decades under normal environmental conditions [1]. Composites, particularly those that use thermoset resins, are impossible to reshape, recycle or reuse. While a small fraction of these composites are crushed into powder and used as filler or incinerated to obtain energy in the form of heat, most of them end up in landfills at the end of their life. In anaerobic conditions, such as those in landfills, the petroleum based composites may not degrade for several decades making that land unavailable for any other use. On other hand, incineration produces toxic gases and requires expensive scrubbers. Both incineration and dumping in landfills are environmentally undesirable as well as expensive. In the future these methods of disposing of composites are expected to get even more expensive as the pollution laws all over the world get stricter and the number of landfills decline. In addition, at the present rate of consumption the world petroleum reserves are estimated to last for the next 50 years or so only [1]. This may be exacerbated further as the world consumption of petroleum increases as the economies of the developing countries expand. As a result, there is great interest in developing 'green' composites using fully sustainable, biodegradable, environment-friendly and yearly renewable fibers and resins, particularly those derived from plants [2]. A variety of resins, e.g. starch, proteins, etc. and fibers, e.g. flax, ramie, kenaf, etc., have been used to fabricate green composites for many applications. In many cases, only one component of the composites, either the fibers or the resin, has been biodegradable. Such 'semi-green' composites have the same problem of disposal at the end of their life. Most such 'semi-green' or 'green' composites reinforced with plant-based fibers, yarns or fabrics have moderate tensile strengths and stiffnesses (modulii) in the range of 100 to 200 MPa and 1 to 4 GPa, respectively. As a result, their applications are restricted to only non-critical and non-load-bearing parts, such as packaging, casings, etc. They cannot be used in load-bearing structural applications where high strength and stiffness are required [3–14].

Composite properties depend on the properties of the constituents, i.e. the fibers and resins used. The strength and stiffness of the composites are directly a function of the reinforcing fiber properties which carry most of the load, and their volume content. The resin helps to maintain the relative position of the fibers within the composite and, more importantly, transfers the load from broken fibers to the intact fibers. As a result, fiber/resin interfacial properties are also important and have a significant effect on composite properties, including toughness and transverse fracture stress. In summary, to fabricate high strength composites all three factors, namely, fiber properties, resin properties as well as the fiber/resin interface characterisitcs are critical.

Many natural and synthesized biodegradable resins are currently commercially available for fabricating green composites [2]. Some of the most common ones are poly(lactic acid), proteins, starches, polyhydroxyalkanoates and their copolymers, etc. Most of these are obtained either from plant sources or through bacterial fermentation processes. Within the commercially available materials, soy protein, perhaps, is the least expensive and most widely available material in the world. It is commercially available in three forms: defatted soy flour (SF), soy protein concentrate (SPC) and soy protein isolate (SPI). The SF contains about 55% protein whereas SPC and SPI contain about 72% and 90% protein, respectively. The rest is carbohydrates, minerals, soluble fibers, ash, etc. Soy proteins contain 18 different amino acids including some containing carboxyl groups (glutamic acid and aspartic acid) and some containing amino groups (lysine and arginine). In addition, there are other amino acids that contain polar hydroxyl groups (serine, threonine, tyrosine). The amino acids are connected through peptide (amide) bonds to form polypeptide chains. The reactive groups on the amino acids can be utilized to chemically modify soy proteins and improve their properties. Soy protein has an isoelectric point between 4.5 to 5 pH. At the isoelectric point soy protein is insoluble in water. However, away from the isoelectric point, in either direction, the soy protein molecules open up and become more soluble in water. This opening of the molecules allows the reactive groups to be exposed making it easier for them to undergo chemical reactions for any modifications. Many researchers have modified soy protein to improve its mechanical properties [3–6, 10–25]. Some of the most common ways of improving soy based resin properties include blending with other polymers, cross-linking, forming an interpenetrating network (IPN) or semi-IPN structure and addition of nano-particles such as nano-clay to form nano-composites [6, 24–29]. All these modifications have been shown to result in improvements in various properties of the resins. The present research also suggests that the incorporation of microfibrillated cellulose (MFC) can significantly improve the resin properties to an even greater extent than those obtained by the use of nano-clay particles because of its high aspect ratio.

Recent developments in both resins and high strength cellulosic fibers have been significant and should allow the development of high strength 'advanced green composites' with significantly better mechanical properties [6, 12–23]. Many other properties such as physical and thermal properties as well as specific properties such as fire retardancy, vibration damping, impact strength, antimicrobial, gas barrier, water resistance, etc., can also be improved at the same time to widen the application range of green composites. In this paper, modifications of soy protein carried out in two steps: (1) to form an interpenetrating network like (IPN-like) structure by blending with polysaccharides that cross-link by themselves and (2) to further modify them using nano-clay and MFC to significantly improve their mechanical properties, are discussed. The mechanical properties of these resins were comparable or better than the most commonly used DGEBA based epoxy resins. These modified SPC resins were reinforced with high strength liquid crystalline

(LC) cellulosic fibers to fabricate 'advanced green composites'. The same modified resins were also reinforced to fabricate composites using E-glass and Kevlar® 49 (Kevlar®) fibers for comparison. The comparison of the mechanical properties suggest that the high strength green composites have excellent mechanical properties and could be used for many load-bearing applications. In the future, with further progress achieved with respect to green resins and fibers, it should be possible to obtain even stronger and tougher advanced green composites.

2. EXPERIMENTAL

In the present research SPC was modified four different ways. SPC powder was obtained from Archer Daniels and Midland Co., Illinois, USA, Cloisite® clay used in this study was obtained from Southern Clay, Products, Texas, USA and MFC was obtained from Daicel Chemical Industries, Ltd., Japan. Liquid crystalline cellulose (LC cellulose) fibers were provided by Dr. H. Boerstoel, Teijin Twaron BV. The Kevlar® fibers were obtained from DuPont, Delaware, USA, and the E-glass fibers were obtained from Owens Corning, Illinois, USA, and had only water size. Polycarboxylic acid (PCA) was obtained from Sigma Aldrich Co., St. Louis, MO, USA. The four different resin compositions prepared in this research are given below. All numbers in parenthesis are weights based on SPC weight taken as 100.

(1) SPC (100) + MFC (40) + glycerol (10)

(2) SPC (100) + PCA (50) + glycerol (8)

(3) SPC (100) + PCA (50) + glycerol (15) + clay (7)

(4) SPC (100) + PCA (50) + glycerol (15) + MFC (40)

To prepare the SPC resin, SPC powder was mixed with water and glycerol (plasticizer). The mix ratio of SPC:water was 1:15 by weight. After homogenizing the mixture for 15 min, it was transferred to a water bath maintained at 75°C for 30 min (pre-curing). The stirring was continued during this period. For characterizing the resin properties, the pre-cured resin was cast into sheets, dried in an air circulating oven kept at 35°C and hot pressed (cured) at 120°C under a pressure of 8 MPa. To make the PCA modified resins, the PCA was dissolved in water at 80°C and then added to the SPC solution before pre-curing. MFC and nano clay suspensions were prepared separately and added during pre-curing, in required proportions to prepare the modified SPC resins. The drying and curing processes were same as described for the pure SPC resin. The cured resin sheets had thicknesses between 0.12 and 0.15 mm. The resins were characterized for their tensile properties using Instron universal testing machine (model 5566) as per ASTM D 882-02. The specimen gauge length and test strain rate were 50 mm and 1 min^{-1}, respectively. Five specimens were tested for each resin to obtain average values.

All three fibers, LC cellulose, Kevlar® and E-glass, were also characterized for their tensile properties. All fibers were obtained in the form of tows. The diameters of LC cellulose and Kevlar® fibers were between 10 and 12 µm whereas the glass fibers were about 20 µm diameter. The tensile tests were carried out on individual fibers using the same Instron testing machine as per ASTM D 3822-01. The gauge length and strain rate were 50 mm and 0.5 min^{-1}, respectively. Twenty fibers were tested for each fiber type to obtain average values.

The microbond technique [30–32] was used to characterize the fiber/resin interfacial shear strength (IFSS) between all three fibers and four resins. To prepare specimens, a small microbead (microdrop) of the pre-cured resin was placed on the fiber using a fine metal wire. The resin microdrop was dried and cured at 105°C in an air-circulating oven for 10 min. Specimens were then conditioned at 21°C and 65% for 12 h. The IFSS test was performed using the same Instron universal testing machine. The diameter (d) of the fiber and the embedded length (l) were measured using an optical microscope. The schematic and the procedure of the microbond test are explained in detail elsewhere [30–32]. To perform the test, microvise was kept at the bottom in place of the bottom jaws. The top end of the fiber was gripped in the top jaw of the Instron such that the microdrop was about 0.2 mm below the open microvise plates. The microvise plates were brought closer so as to just touch the fiber. The fiber was then pulled at a crosshead speed of 0.5 mm/min until the microdrop was sheared. Twenty microbead tests were conducted for each condition to obtain average IFSS values. The force, F, required to shear the microdrop from the fiber was measured and the average IFSS (τ) was calculated using equation (1) shown below.

$$\tau = \frac{F}{\pi \times d \times l}.$$ (1)

These conditions were slightly different than the ones used in fabricating composites, particularly that the hot pressing could not be used for the microbeads which would flatten out to thin paper like sheet. Also, while the composites were cured at 120°C, the microbead specimens were cured at 105°C. This was due to the very small size of the microbead which dries much faster. Higher temperatures or longer times were seen to degrade the microbead (resin).

To prepare unidirectional fiber reinforced composites, the filament tows (LC cellulose, Kevlar® or E-glass) were wound around a metal frame and soaked in the pre-cured resin solutions. Winding was done such that two layers of parallel-aligned filaments were wound so as to get composites of approximately 1 mm thickness. The soaking of filaments in the pre-cured resins was done such that maximum possible impregnation was obtained. However, in the case of the glass fibers, it was observed that the resin did not adhere well since these fibers did not have any coupling agent or were not treated. After soaking, the composite specimens were dried in an air circulating oven at 35°C for 24 h. The fiber weight fraction in the final composites was calculated on the basis of final dry composite weight and initial weight of the filaments used. All composites had 40 ± 2% fiber

volume fraction which was calculated based on the resin and fiber densities. All resin and composite specimens were conditioned at 21°C and 65% relative humidity for 5 days before characterizing their mechanical properties. The actual composite specimen thicknesses were 0.5 mm, 1.0 mm and 0.6 mm for Kevlar®, glass and LC cellulose fibers, respectively. The specimens were tension tested using the same Instron universal testing machine. The gauge length and strain rate were 50 mm and 1 min^{-1}. The flexural properties of the composites were characterized using three-point bending test as per ASTM D 790-02 using the same Instron universal testing machine. The specimen span length was 25 mm and the crosshead speed was 0.16 mm/min. At least 6 composite specimens were tested to obtain average tensile properties. The moisture content in cured resins was obtained using moisture/volatiles tester (C. W. Brabender Instruments, Inc., Model SAS) as per ASTM D 1576-90. One test was done per specimen to obtain the moisture content.

3. RESULTS AND DISCUSSION

3.1. Properties of the modified SPC based resins

The tensile properties, density and the moisture absorption of the four modified SPC based resins are presented in Table 1. It can be seen that all resins show good tensile properties. The high fracture stress and Young's modulus values of these resins are comparable to the commonly used DGEBA based epoxy resins. It should be noted that all resins contained some amount of glycerol as plasticizer. The densities of these resins are comparable to epoxies as well. The SPC resin modified with MFC (#1) has the best fracture stress (76 MPa) and modulus (2.75 GPa). This is presumably the effect of high strength and aspect ratio of the MFC. The cellulose molecules in the MFC are highly oriented and crystalline. The strength of the cellulose crystals in the MFC has been estimated to be between 2 and 6 GPa and tensile modulus to be around 140 GPa [17–19]. Another reason for the high tensile properties of resin #1 is its lower moisture content (11.8%) compared to other resins. Moisture acts as plasticizer reducing the resin stiffness. Since the MFC is highly crystalline, it cannot absorb more moisture. The resin #1 has the lowest density and the highest fracture toughness since it has fracture strain comparable to other

Table 1.
Tensile, physical and moisture properties of the SPC based resins

Resin	Fracture stress (MPa)	Fracture strain (%)	Young's modulus (GPa)	Moisture content (%)	Density (kg/m^3)
(#1) SPC + MFC	75.8	12.5	2.75	11.8	1340
(#2) SPC + PCA	50.6	12.4	1.99	13.6	1370
(#3) SPC + PCA + clay	51.1	14.0	1.48	14.3	1430
(#4) SPC + PCA + MFC	60.6	13.9	2.11	12.8	1420

resins and highest fracture stress. However, it should be noted that while resins #1 and #2 contain 10% and 8% glycerol, resins #3 and #4 contain 15% glycerol, respectively. With lower glycerol content the resins #3 and #4 would have had much higher strength as well. However, at the same time they would be much more brittle.

3.2. Properties of the fibers

The tensile properties and density of the three fibers used in this study are presented in Table 2. The data indicate that, while LC cellulose fibers have higher fracture stress than E-glass fibers, their fracture stress and modulus values are about 40% of those obtained for the Kevlar® fibers. The fracture strain of LC cellulose fibers was more than 3.5 times that of Kevlar® and E-glass fibers resulting in higher toughness than both Kevlar® and E-glass fibers.

3.3. Interfacial shear strength (IFSS) properties

The interfacial shear strength results for all fiber/resin combinations are presented in Table 3. The data suggest that the average IFSS over all four resins for Kevlar® was the highest followed by LC cellulose fibers and was the lowest for E-glass fibers. It was expected that the IFSS for LC cellulose fibers would be significantly higher than both Kevlar® and E-glass fibers. This was because of the hydroxyl groups on LC cellulose fibers which could strongly hydrogen bond with the hydroxyl, amine and carboxyl groups in soy protein as well as the PCA. However, their surface

Table 2.
Tensile properties and densities of the fibers used

| Fiber	Fracture stress (MPa)	Fracture strain (%)	Young's modulus (GPa)	Density (kg/m^3)
LC Cellulose	1680 (9.0)	11.46 (6.8)	39.9 (12.1)	1520
Kevlar® 49	4020 (10.0)	3.22 (8.3)	93.1 (7.1)	1440
E-glass	1402 (13.4)	3.04 (12.1)	52.6 (5.4)	2550

*Numbers in parentheses represent % coefficient of variation.

Table 3.
Interfacial shear strength values for all fiber/resin combinations

Resin	LC Cellulose	E-Glass	Kevlar®
(#1) SPC + MFC	15.3 (15.7)	10.5 (20.0)	13.6 (18.0)
(#2) SPC + PCA	12.0 (31.5)	9.9 (29.4)	12.5 (11.0)
(#3) SPC + PCA + clay	12.1 (23.5)	12.4 (19.9)	14.1 (13.2)
(#4) SPC + PCA + MFC	11.3 (27.7)	11.5 (28.5)	14.6 (15.2)
Average IFSS over 4 resins	12.68	11.08	13.70

*Numbers in parentheses represent % coefficient of variation.
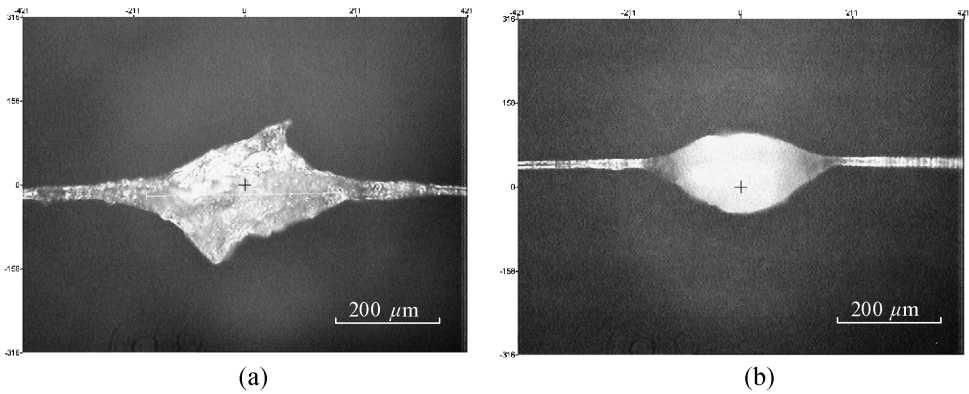
Figure 1. Microdrops on fibers (a) MFC containing resin, (b) nano-clay containing resin.
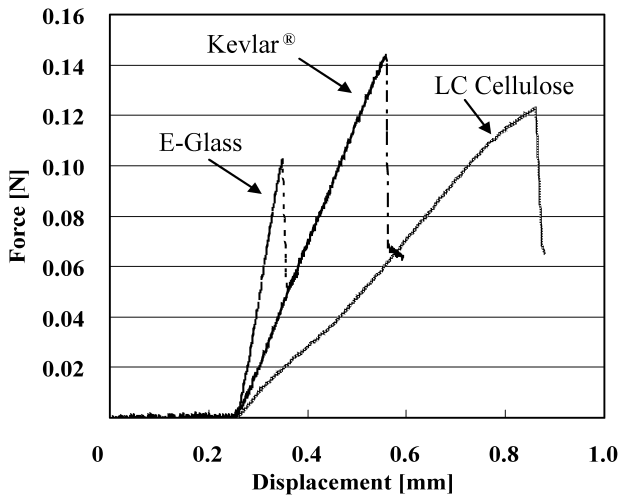
Figure 2. Typical Microdrop test plots for the three fibers used.

was very smooth and comparable to E-glass fibers allowing very little mechanical interlocking component in both cases. It is clear that among the three fibers, E-glass fibers with no size or coupling agent (water size) showed the lowest IFSS while Kevlar® fibers had the highest IFSS. It was also observed that Kevlar® fibers gave more successful IFSS tests. Since amide groups on Kevlar® can also form hydrogen bonding with soy protein resins, the difference in IFSS between Kevlar® and LC cellulose fiber composites was not statistically significant.

It was also noticed that the resins containing MFC showed irregular shapes of the microdrops because of their high aspect ratio whereas the resins containing nano-clay particles were much rounder. Typical examples of these are shown in Fig. 1. However, no effect of the microdrop shape was expected on the IFSS values obtained. Typical microdrop test plots for three fibers are shown in Fig. 2. It should be noted that for all resins the drying and curing processes result in significant

shrinkage of the microdrop as the moisture is lost. This creates significant stress, both compressive and shear, at the interface. While the compressive stress would give higher IFSS value, shear stresses would reduce the IFSS. Although the exact contribution of each factor is not known, the IFSS values are believed to be much smaller than they actually are. Since resin shrinkage is same in case of all fibers, the IFSS values are good for comparison.

3.4. Mechanical properties of the SPC resin based advanced composites

The flexural properties of the advanced composites fabricated using the three fibers and all 4 resins, obtained using three point bending tests, are presented in Table 4. The data clearly indicate that composites fabricated using Kevlar® fibers are superior to those made using either LC cellulose or E-glass fibers in terms of the flexural stress and flexural modulus. This is in line with the tensile properties of these fibers. It can also be seen that the flexural stress values of the LC cellulose reinforced composites are 50% higher than those obtained for the E-glass fiber reinforced composites whereas the flexural modulus values for these composites are comparable. The lower bond strength in the case of E-glass fiber reinforced composites was evident in the SEM photomicrographs which showed extremely long fiber pull-outs around the fractured region (in tensile mode) which are discussed later. One another reason for lower than expected flexural strength and modulus of E-glass fiber reinforced composites was that the fiber tows used in this study were larger and had small twist which made it harder to get proper resin penetration inside the tows in spite of the precautions taken. All these factors — poor bond strength, debonding and long fiber pull-outs, and insufficient penetration — resulted in lower flexural properties of the composites. Another

Table 4.
Flexural properties of SPC resin based 'advanced' composites

Composite	Flexural stress (MPa)	Flexural strain (%)	Flexural modulus (GPa)
Kevlar — (#1)	319 (6.3)[*]	0.78 (10.2)	79.1 (8.9)
Kevlar — (#2)	379 (5.2)	0.74 (8.4)	88.5 (7.0)
Kevlar — (#3)	387 (8.4)	0.74 (7.5)	89.6 (3.8)
Kevlar — (#4)	357 (6.8)	0.77 (11.3)	83.5 (9.2)
Glass — (#1)	126 (11.9)	1.34 (13.7)	20.4 (10.2)
Glass — (#2)	148 (9.6)	1.45 (11.5)	23.7 (8.1)
Glass — (#3)	155 (8.6)	1.37 (12.1)	24.2 (7.9)
Glass — (#4)	151 (10.2)	1.52 (9.8)	22.4 (7.5)
LC Cellulose — (#1)	202 (8.2)	2.51 (7.8)	17.6 (3.8)
LC Cellulose — (#2)	228 (5.1)	2.08 (7.1)	24.3 (5.7)
LC Cellulose — (#3)	248 (8.7)	2.03 (9.2)	27.8 (5.9)
LC Cellulose — (#4)	240 (9.4)	2.02 (12.7)	26.9 (6.8)

#1–4 represent the resins used.
[*] Numbers in parentheses represent % coefficient of variation.

reason for lower flexural stress is the interlaminar debonding observed in many cases. The composites were made by hot pressing four laminates that were air dried. It seems that, by comparison, the Kevlar® and LC cellulose fiber reinforced composites showed much lower amounts of fiber pull-outs in the fracture region. The hydroxyl groups on the LC cellulose and amide groups on Kevlar® fibers seem to provide good sites for the soy resin to have hydrogen bonding. Based on the flexural stress and strain values, the LC cellulose based composites can be expected to absorb maximum energy during fracture. This results from their high fracture strains.

In all cases, the resin #3, containing clay, gave the best flexural performance, in spite of its lower strength and modulus compared to other resins. This is perhaps because of the lower viscosity of this resin compared to other resins which allowed better penetration. However, the effect was not statistically significant at 5% level of significance. Also, the resin #1 which had the highest fracture stress and Young's modulus did not result in higher flexural stress or modulus values. This suggests that these values are controlled mostly by the fiber properties.

Table 5 presents the tensile properties of the advanced composites. The results again show superior performance of the Kevlar® fiber reinforced composites, as could be expected, with fracture stresses in the range of 1 GPa and modulus of about 30 GPa. This is in comparison to the fracture stresses of about 380 MPa obtained for E-glass fiber reinforced composites and about 620 MPa for LC cellulose fiber reinforced composites. This is, again, expected because of the fiber properties. However, both modulus and strength values are somewhat lower than those predicted by the rule of mixture. This is because of the hand layup technique used and the defects (air bubbles, misalignment, etc.) introduced during their

Table 5.
Tensile properties of SPC resin based advanced composites

Composite type	Fracture stress (MPa)	Fracture strain (%)	Young's modulus (GPa)
Kevlar — (#1)	921 (4.3)[*]	3.71 (5.6)	30.4 (3.9)
Kevlar — (#2)	1002 (5.4)	3.97 (6.2)	31.7 (3.2)
Kevlar — (#3)	1086 (4.1)	4.02 (6.8)	34.0 (4.3)
Kevlar — (#4)	984 (5.6)	4.02 (5.7)	27.9 (4.7)
Glass — (#1)	332 (6.6)	4.29 (7.9)	14.5 (5.8)
Glass — (#2)	385 (7.1)	4.03 (7.5)	14.9 (6.4)
Glass — (#3)	379 (8.0)	4.32 (8.2)	16.4 (6.1)
Glass — (#4)	383 (5.3)	4.58 (6.9)	15.8(5.9)
LC Cellulose — (#1)	588 (6.3)	9.98 (7.4)	12.2 (7.7)
LC Cellulose — (#2)	565 (4.8)	9.59 (6.5)	13.1 (5.2)
LC Cellulose — (#3)	638 (5.5)	10.07 (5.9)	12.5 (6.1)
LC Cellulose — (#4)	583 (6.4)	9.99 (7.1)	11.9 (5.8)

#1–4 represent the resins used.
[*] Numbers in parentheses represent % coefficient of variation.

fabrication. What is interesting is that the fracture stress of the LC cellulose fiber reinforced composites is about 60% of the Kevlar® fiber reinforced composites in spite of their strength being only 40% of Kevlar® fiber strength. In addition, the fracture strain of the LC cellulose fiber based composites, about 10%, is about 2.5 times that of Kevlar® reinforced composites, giving the LC cellulose fiber reinforced composites significantly higher energy absorbing performance during fracture. This is because of the high fracture strain of LC cellulose fibers as discussed earlier. E-glass fiber reinforced composites showed lower fracture stress and slightly higher modulus than LC cellulose fiber reinforced composites. As discussed earlier, poor bonding with the resins and poor resin penetration into the fiber tows are the main reasons for their lower strength. In the case of E-glass fibers, as mentioned earlier, the bundles had slight twist. As a result, the resin penetration was poor. This significantly affected the tensile properties. It seems that these factors affect the flexural properties more than the tensile properties. In addition, since the composites were made by hot pressing four laminates, some interlaminar debonding was also observed. It is obvious that the interlaminar debonding would affect the flexural properties more than the tensile properties. It is possible to improve upon these properties by using suitable coupling agents and processing smaller tows without twist. Interlaminar interaction can be strengthened by adding some resin prior to hot pressing or by using higher pressure.

The results in Tables 4 and 5 also suggest that fiber properties control the ultimate properties of the composites. It should be mentioned that all composites had 40% fibers by volume. If the volume could be increased to 60% the LC cellulose reinforced 'green' composites could have strengths of up to 950 MPa and modulus of more than 19 GPa making them truly 'advanced green composites'.

Figure 3 shows typical SEM photomicrographs of the fracture surfaces of composites fractured in tension for all three fibers. It is clear from these SEM photomicrographs that the E-glass fibers show significant pull-out compared to LC cellulose and Kevlar® fibers. Also, a significant amount of resin was seen sticking to the fibers in the case of LC cellulose and Kevlar® fibers compared to E-glass fibers. This was expected from their lower IFSS values. This also confirms why the performance of

100µm	120µm	200µm
(a)	(b)	(c)
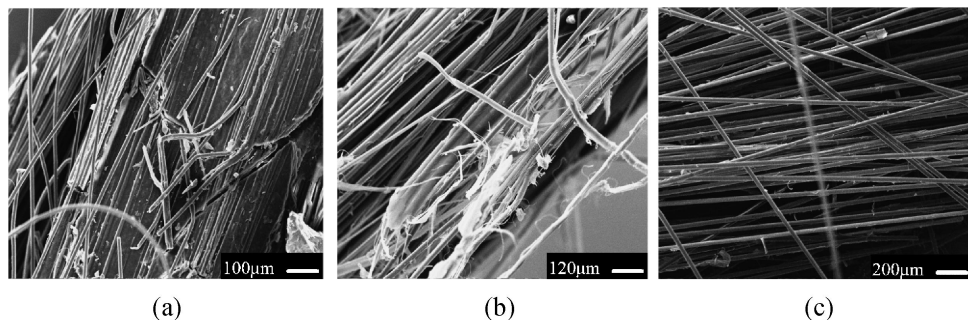
Figure 3. SEM photomicrographs of the composite fracture surfaces, (a) LC cellulose, (b) Kevlar® and (c) E-glass.

E-glass fibers was lower compared to the other two fibers. However, as mentioned earlier, this could be corrected by using appropriate coupling agent.

4. CONCLUSIONS

To build advanced green composites, three things are essential: high strength fibers, resins with improved properties and good fiber/resin interfacial bonding. This paper discusses the properties of advanced composites fabricated using three high strength fibers, namely, Kevlar®, E-glass and LC cellulose fibers. Four different resins, based on modified soy protein concentrate (SPC), were used. Although the mechanical properties of the resins differed, the composite properties showed no significant difference in the case of Kevlar® or LC cellulose fibers. The LC cellulose fiber reinforced 'advanced green composites' consistently showed 60% of the fracture stress and 40% of the Young's modulus of the Kevlar® fiber reinforced composites. These numbers are better than the ratio of the fiber properties, in favor of LC cellulose fibers. This is because of the excellent bonding between the LC cellulose fibers and the SPC resins. Also, the LC cellulose fiber reinforced composites showed higher energy absorbing performance during fracture than the Kevlar® fiber reinforced composites. The flexural properties of the Kevlar® fiber reinforced composites were about 50% better than the LC cellulose based composites. The glass reinforced composites showed poorest properties. However, this was a result of the water sized (no coupling agent) fibers used in this study. By using appropriate coupling agent or fiber surface treatment it should be possible to improve their properties.

Unlike the current advanced composites which end up mostly in landfills at the end of their life and make that land unusable for several decades, the SPC based 'advanced green composites', reinforced with LC cellulose fibers, are fully biodegradable, sustainable and can be composted after their useful life. They should find applications from sports gear to auto parts and from electronics to primary structural parts for housing. Although significant additional research is needed in this area, it is clear that advanced green composites will some day replace today's advanced composites made using petroleum based fibers and resins in many applications.

REFERENCES

1. E. S. Stevens, *Green Plastics*. Princeton University Press, Princeton, USA (2002).
2. A. N. Netravali and S. Chabba, Composites get greener, *Materials Today* **6**, 22–29 (2003).
3. S. Chabba and A. N. Netravali, 'Green' composites using modified soy protein concentrate resin and flax fabrics and yarns, *Japan Soc. Mech. Engng. (JSME) Int. J.* **47**, 556–560 (2004).
4. P. Lodha and A. N. Netravali, Characterization of stearic acid modified soy protein isolate resin and ramie fiber reinforced 'green' composites, *Compos. Sci. Technol.* **65**, 647–659 (2005).
5. S. Chabba, Characterization of environment friendly 'green' composites with modified soy protein concentrate and flax yarn and fabric, *MS Thesis*, Cornell University, USA (2003).

6. P. Lodha, Fundamental approaches to improving performance of soy protein isolate based 'green' plastics and composites, *PhD Thesis*, Cornell University, USA (2004).

7. A. K. Mohanty, M. Misra and G. Hinrichsen, Biofibers, biodegradable polymers and biocomposites: an overview, *Macromol. Mater. Engng.* **276**, 1–24 (2000).

8. A. Gomes, K. Goda and J. Ohgi, Effects of alkali treatment to reinforcement on tensile properties of curaua fiber green composites, *JSME Int. J.* **47**, 541–546 (2004).

9. S. Ochi, H. Takagi and H. Tanaka, Mechanical properties of cross-ply 'green' composites reinforced by malina hemp fibers, in: *Proc. Int. Workshop 'Green' Compos.*, Tokushima, Japan, November 19–20 (2002).

10. A. N. Netravali, Biodegradable 'green' composites using ramie fibers and soy protein polymer, in: *Natural Fibers, Plastics and Composites*, F. T. Wallenberger and N. E. Weston (Eds), pp. 321–343. Kluwer Academic Publishers, Boston, USA (2004).

11. S. C. Chabba, G. T. Matthews and A. N. Netravali, 'Green' composites using modified soy flour and flax yarns, *Green Chemistry* **7**, 576–581 (2004).

12. S. Nam, Environment-friendly 'green' biodegradable composites using ramie fibers and soy protein concentrate (SPC) polymer, *MS Thesis*, Cornell University, USA (2002).

13. T. Fujii, K. Okubo and N. Yamashita, Development of high performance bamboo composites using micro fibrillated cellulose, in: *Proc. 2nd Intern. Conf. High Performance Structural Materials*. Ancona, Italy, May 31–June 2 (2004).

14. A. N. Netravali, Green composites: current trends and developments, in: *Proc. MACRO-04*, Thiruvananthapuram, India, December 14–17 (2004).

15. A. N. Netravali, Towards advanced 'green' composites, in: *Proc. Int. Workshop 'Green' Compos. -3*, Kyoto, Japan, March 16–17 (2005).

16. W. Helbert, J. Y. Cavaille and A. Dufresne, Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. 1. Processing and mechanical behavior, *Polym. Compos.* **17**, 604–611 (1996).

17. T. Nishino, K. Takano and K. Nakamae, Elastic-modulus of the crystalline regions of cellulose polymorphs, *J. Polym. Sci. Part B-Polym. Phys.* **33**, 1647–1651 (1995).

18. A. N. Nakagaito and H. Yano, Novel high-strength biocomposites based on microfibrillated cellulose having nano-order-unit web-like network structure, *Appl. Phys. A* **80**, 155–159 (2003).

19. A. N. Nakagaito, S. Iwamoto and H. Yano, Bacterial cellulose: the ultimate nano-scalar cellulose morphology for the production of high-strength composites, *Appl. Phys. A* **80**, 93–97 (2004).

20. J. Turner and C. Karatzas, in: *Natural Fibers, Plastics and Composites*, F. T. Wallenberger and N. Weston (Eds). Kluwer Academic Publishers, Boston, USA (2004).

21. D. T. Grubb and L. Jelinski, Fiber morphology of spider silk: the effects of tensile deformation, *Macromolecules* **30**, 2860–2867 (1997).

22. H. Borstoel, Liquid crystalline solutions of celulose in phosphoric acid, *PhD Thesis*, Rijksuniversiteit, Groningen, The Netherlands (1998).

23. S. Salmon and S. M. Hudson, Crystal morphology, biosynthesis, and physical assembly of cellulose, chitin, and chitosan, *J. Macromol. Sci. Rev.* **37**, 199–276 (1997).

24. X. Huang and A. N. Netravali, Characterization of nano-clay reinforced phytagel-modified soy protein concentrate resin, *Biomacromolecules* **7**, 2783–2789 (2006).

25. P. Lodha and A. N. Netravali, Characterization of Phytagel® modified soy protein isolate resin and unidirectional flax yarn reinforced 'green' composites, *Polym. Compos.* **26**, 647–659 (2005).

26. G. O. Shonaike and G. P. Simon (Eds), *Polymer Blends and Alloys*. Marcel Dekker, Inc, New York, USA (1999).

27. D. Klempner, L. H. Sperling and L. A. Utracki, *Interpenetrating Polymer Network*. American Chemical Society, Washington DC, USA (1994).

28. A. C. Finnefrock, R. Ulrich, G. E. S. Toombes, S. M. Gruner and U. Wiesner, The plumber's nightmare: a new morphology in block copolymer-ceramic nanocomposites and mesoporous aluminosilicates, *J. Amer. Chem. Soc.* **125**, 13084–13093 (2003).

29. D. Shah, Polymer nanocomposites: structure and dynamics at the interface and their effect on nanohybrid properties, *PhD Thesis*, Cornell University, USA (2004).
30. P. Lodha and A. N. Netravali, Characterization of interfacial and mechanical properties of 'green' composites with soy protein isolate and ramie fiber, *J. Mater. Sci.* **37**, 3657–3665 (2002).
31. S. Luo and A. N. Netravali, Interfacial and mechanical properties of environment-friendly 'green' composites made from pineapple fibers and poly(hydroxybutyrate-co-valerate) resin, *J. Mater. Sci.* **34**, 3709–3719 (1999).
32. B. Miller, P. Muri and L. Rebenfeld, A microbond method for determination of the shear-strength of a fiber–resin interface, *Compos. Sci. Technol.* **28**, 17–32 (1987).