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Biodegradable natural fiber composites

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9.1 Introduction

9.1.1 Composite materials

Fiber reinforced polymeric composites have been used in many structural applications because of their high strength and low density giving them significant advantages over conventional metals. Initially developed for the defense and aerospace industries, high performance or 'advanced' composites are now commonly used in many applications from circuit boards to sports gear and from automotive parts to building materials. The use of composite materials has expanded at more than 10% per year in developed countries. In developing countries such as India and China the use of composites is growing at even faster pace.

Fiber reinforced composites, depending on the properties needed, can be fabricated in three different ways. Very short fibers can be used as filler, short fibers can be organized with random orientation and long fibers can be laid in one direction to form unidirectional composites. Short staple fibers may also be twisted together to form continuous yarns to fabricate unidirectional composite laminates similar to those made using long fibers. Several unidirectional laminates may be combined by layering in different directions to form laminar composites. Yarns may also be woven or knitted into fabrics to form similar laminar composites.

Most of the fibers and resins currently available on the market are derived from petroleum. There are two major problems associated with using petroleum as the feedstock for polymers. First, it is a non-renewable (non-sustainable) resource and at the current rate of consumption, by some estimates, it is expected to last for only 50–60 years [1]. Also, the current petroleum consumption rate is estimated to be 100,000 times the rate of natural generation rate [1]. Second, most fibers and resins made using petroleum are non-degradable. Although this is desirable in many applications from the durability point of view, at the end of their life, they are not easy to dispose of. Discarded

in natural environment, these polymers and composite materials can last for several decades without decomposing. This has exacerbated the already existing ecological and environmental problems of waste building. Because composites are made using two dissimilar materials, they cannot be easily reused or recycled. Although some composites are incinerated, most composites end up in landfills. Both of these disposal alternatives are environmentally unsound, wasteful and expensive. In addition, landfills are decreasing in number, making less space available to discard waste. In the US alone, the number of landfills dropped from 8000 to 2314 between 1988 and 1998 [1]. As a result the tipping fees have been rising steadily.

In recent years, the ever-growing litter problem has raised environmental consciousness among many activists, consumers as well as manufacturers, forcing them to act. Many governments, in response, have established laws to encourage recycling and the use of bio-based 'green' products [2]. Some governments have enforced stricter 'take-back' rules requiring manufacturers to take back packaging and products at the end of their life. These environmental concerns and depletion of petroleum resources have given birth to the concepts of sustainability, eco-efficiency, industrial ecology and cradle-to-cradle design. These concepts form the principles that have triggered the search for new generation of 'green' materials, many of them plant-based. Most manufacturers are working hard to make their products eco-efficient and 'green' to the fullest extent possible. Composite materials are no exception to this new paradigm. Undoubtedly, environment-friendly, fully degradable 'green' composites will play a major role in greening the products of tomorrow [3].

Many applications, e.g. secondary and tertiary structures and those used in consumer products for casings and packaging, do not require the high strength and stiffness of advanced composites. In these products plant-based lignocellulosic fibers have been a natural choice. Worldwide availability of inexpensive plant-based fibers has fueled their use in the past few years for reinforcing or filling polymers/plastics to make them greener. Natural fibers have several advantages besides being biodegradable. They are nonabrasive to processing equipment, can be incinerated and are CO_2 neutral (when burned) [4]. In addition, because of their hollow tubular structure and cellular nature, most bast fibers, derived from plant stems, perform well as acoustic and thermal insulators [5]. Their hollow structure also reduces their bulk density, making them and their composites lightweight.

There are plenty of examples in the literature where plant-based fibers have been used for reinforcing or filling non-degradable resins such as polypropylene (PP), polyethylene (PE), nylons, polyvinyl chloride (PVC), epoxies and polyurethanes (PU), etc. [6–15]. The bulk of plant-based fiber composites, however, are made using wood flour, a byproduct from saw mills, or wood fiber obtained from waste or used wood products, e.g. packaging pallets, old furniture, and construction wood scraps. These inexpensive

composites, particularly the ones using recycled polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC), are used for applications ranging from decking (plastic lumber) to furniture and from rail road ties to window and door frames. Demand for such composites is predicted to double from 2001 to 2006 in North America [16].

Longer plant-based fibers, e.g. abaca, bamboo, flax, hemp, henequen, jute, kenaf, pineapple, ramie, sisal, etc., are being evaluated as a low cost replacement for glass fibers in composites. Most of these fibers are harvested annually as compared to wood which takes 20–25 years to grow before it may be cut and used. Some fibers, e.g. ramie, may be harvested a couple of times a year making their supply virtually inexhaustible [17]. Bamboo plants, belonging to the grass family, also grow very fast and may be harvested every 3–4 months [3].

Since these composites combine non-degradable resins with plant-based degradable fibers they can neither return to an industrial metabolism nor to a natural metabolism. Unfortunately, they cannot be food stock for either system. They can only be downcycled because of their property degradation during reprocessing or incinerated to recover the energy value.

9.1.2   Fully green composites

Significant research is currently being done to develop a new class of fully biodegradable and truly 'green' composites by combining plant-based cellulosic fibers with biodegradable resins, particularly those derived from plants [18–35]. A variety of natural and synthetic biodegradable resins are available for use in green composites [31, 36–42]. At the end of their life they can be easily disposed of or composted without harming the environment. Being in its infancy, most of the current green composites technology is still in the research and development stage although a few scattered and niche examples of commercial products can be found [31, 33]. For example, NEC Corp., Japan, has developed kenaf fiber reinforced polylactic acid (PLA) in place of epoxy resin for encapsulating silicon chips and Fujitsu, another Japanese technology company, is using PLA for laptop casings. All major automobile makers are also involved in developing green polymers and composites for interior applications. Green composites may be used in many applications such as mass produced non-durable consumer products with short life cycles or products intended for one-time or short-term use before being disposed. However, most green composites may be used in indoor applications extending their useful life to several years, just like wood. One of the major factors that limits the use of green composites today is their high cost compared to conventional materials. However, as their applications increase and they begin to be mass produced, the cost is expected to drop, as always is the case.

The following sections provide brief information regarding the plant-based fibers and describe some of the research efforts in developing green composites using plant-based fibers and soy protein-based resins.

9.2   Biodegradable fibers

Fibers used in most applications can be divided into two main categories; natural or synthetic. Much of the information about fibers regarding their chemistry, manufacture and properties can be found in general fiber handbooks [43]. Many fibers, natural, regenerated or synthetic, are biodegradable. Natural fibers can be subdivided into three main categories depending on the nature of their source: (1) vegetable, (2) animal or (3) mineral. While vegetable (plant-based) and animal fibers are fully biodegradable, mineral fibers are not.

9.2.1   Plant-based fibers

Many useful fibers have been obtained from various parts of the plants including the leaves, stems, (bast) and fruits/seeds. The lengths of these fibers depend mainly on their location within the plant, e.g., fibers from fruits/seeds are short (few centimeters) whereas fibers from the stem and leaves can be longer than one metre. Plants commonly produce cellulose, a linear polysaccharide, as the structural material. It is present in all parts of the plant, in different amounts, from roots to fruits. The other major constituents of fibers obtained from plants are hemicellulose and lignin. A small amount of pectin may also be present in many plant-based fibers. Cellulose is a condensation product consisting of a varying number of anhydroglucose monomeric units connected to each other by β-1,4-glycosidic linkages [44]. The degree of polymerization (DP) varies between 200 and 10,000, but 3000 is the acceptable average value for plant cellulose [45]. Three hydroxyl groups present in the glucose units form strong intramolecular as well as intermolecular hydrogen bonds between the adjacent cellulose molecules. Being linear, cellulose molecules can orient easily and form crystals that can organize into microfibrils, each of which orients at a specific angle in relation to the fiber axis. This microfibrillar angle has been found to vary with the fiber species [44]. Water molecules can penetrate through capillaries and spaces between fibrils and can chemically link to the groups present in cellulose molecule [46]. These water molecules can significantly reduce the rigidity of cellulose by forcing the cellulose molecules apart and acting as a plasticizer.

Hemicellulose comprises a group of polysaccharides and it differs from cellulose in terms of high degree of chain branching and low DP [45]. It also contains several different sugar units [42, 47, 48]. As a result of the branching

and presence of several different sugar units, it cannot crystallize. Lignin is a hydrocarbon polymer with a complex structure consisting of both aliphatic and aromatic constituents that forms the matrix sheath around fibrils and fibers [49]. It is responsible for binding cellulose microfibrils to form a composite structure. The exact chemistry of lignin is not well understood. Hemicellulose is thought to be responsible for the biodegradation, moisture absorption and thermal degradation of the fibers, whereas lignin is responsible for the UV degradation [50]. Cellulose with three hydroxyl groups on each glucose unit can also absorb moisture, but it is limited because of its high crystallinity. Pectins comprise a collection of heteropolysaccharides and are characterized by high uronic acid content [45, 51]. Pectin has higher DP than hemicellulose but much lower than cellulose itself [45].

The cellulose, hemicellulose and lignin contents in plant fibers vary depending on the plant species, origin, quality and conditioning [52]. A list of some plant-based fibers and their chemical compositions and microfibrillar angles are presented in Table 9.1. The mechanical properties of the fibers vary depending on their constitution and the amount of cellulose and the crystallinity. As mentioned earlier, they are also influenced by the DP of the cellulose and microfibrillar orientation. The part of the plant from which the fibers are derived is also a contributing factor in many cases. For example fruit/seed fibers, e.g., coir fibers obtained from coconut, are weaker than the fibers obtained from the stem of the plant, e.g., ramie, hemp or flax fibers. Table 9.2 gives the physical and mechanical properties and moisture content of some plant-based and viscose fibers. Microfibrillar angle, one of the internal structural parameters, and cellulose content determine the strength and stiffness of the fibers [53]. It is clear from Table 9.2 that hemp and ramie, both bast fibers, have high tensile strength and modulus, which are attributed to their low microfibrillar angle and high cellulose content, whereas coir fibers, obtained from coconut seed, have the least tensile strength resulting from their high microfibrillar angle and low cellulose content. It is, however, difficult to draw an exact relationship between the various factors. Yet, it is

Table 9.1 Chemical compositions and microfibrillar angles of some natural fibers

Fiber	Cellulose (wt %)	Hemicellulose (wt %)	Lignin (wt %)	Pectin (wt %)	Microfibrillar angle (°)
Bamboo	60.8	–	32.2	–	2.0–10.0
Coir	36.0–43.0	0.2–0.3	41.0–45.0	3.0–4.0	41.0–45.0
Flax	71.0	18.6–20.6	2.2	2.3	10.0
Hemp	70.2–74.4	17.9–22.4	3.7–5.7	0.9	6.2
Jute	61.0–71.5	13.6–20.4	12.0–13.0	0.2	8.0
Ramie	68.6–76.2	13.1–16.7	0.6–0.7	1.9	7.5
Sisal	67.0–78.0	10.0–14.2	8.0–11.0	10.0	20.0

Table 9.2 Comparative properties of some plant-based and viscose fibers

Fiber	Density (g cm^{-3})	Tensile stress (MPa)	Young's modulus (GPa)	Fracture strain (%)	Moisture content (wt. %)
Bamboo	0.8	221–661	22.8–49.0	1.3	–
Coir	1.2	131–175	4.0–6.0	15.0–40.0	8.0
Cotton	1.5	287–597	5.5–12.6	7.0–8.0	–
Flax	1.5	345–1100	27.6	2.7–3.2	10.0
Hemp	–	690	–	1.6	10.8
Jute	1.3–1.5	393–773	13.0–26.5	1.2–1.5	12.6
Pineapple	–	413–1627	34.5–82.5	1.6	11.8
Ramie	1.5	400–938	61.4–128	1.2–3.8	8.0
Sisal	1.5	511–635	9.4–22.0	3.9–7.0	11.0
Softwood kraft	1.5	1000	40.0	–	–
Viscose (cord)	–	593	11.0	11.4	–

well known that the strength of any fiber, including the ones obtained from plants, is more affected by defects than by structural elements per se.

Many of these fibers are strong, as seen in Table 9.2, and are increasingly being used as reinforcement in both biodegradable and non-biodegradable polymers [3, 4, 37, 52]. Because of the low specific gravity of these fibers, the specific mechanical strength and modulus of some fibers are excellent and comparable to glass fibers. As a result, they have been used to replace glass fibers in some applications.

9.2.2   Protein fibers

Protein fibers are made up of polypeptide chains composed of various amino acids as primary (monomeric) units. Protein fibers can be categorized into four distinct groups based on the source: hair fibers obtained from animals, fibers formed by their secretion, fibers obtained from avian feathers, and fibers that are regenerated from vegetable or animal proteins. The most common hair fiber used in the textile industry is wool obtained from sheep [43, 45]. Hair obtained from other animals such as goats, camels, llama, alpaca, guanaco, ox, rabbit, etc. have been also used as specialty fibers. The protein forming hair and feather fibers is known as keratin. Most hair fibers are made up of several different amino acids as basic monomeric units and cannot crystallize well. As a result, hair fibers tend to have low mechanical properties compared to plant fibers and hence are not generally used as reinforcements for composites. However, they tend to have excellent thermal properties and are commonly used as sweaters and winter jackets.

The most common fiber produced from animal (or insect) secretion is silk, which is secreted by the caterpillar (silkworm) of the moth *Bombyx Mori* [17, 43, 45]. Nearly the entire silk industry is based on the silkworm.

The cocoon formed by the caterpillar contains continuous length of 800–1200 m making silk the only continuous length natural fiber. Silk is also stronger than many of the animal hair fibers and has been used in reinforcing composites. However, silk production is expensive because of the labor-intensive and time-consuming nature of sericulture. Several wild varieties of silk are also commercially produced. One of the more common wild silks, known as tussah silk, is the secretion of the caterpillar of the moth *Antheraea Mylitta*. Tussah silk, in general, is coarser and stronger than silk but contains shorter fibers. It also tends to be less uniform compared to silk and contains defects such as varying thicknesses along the length [17].

There has been a significant interest, in recent years, in spider silk, particularly the dragline silk produced by the golden orb spider because of its excellent mechanical properties. Much effort has been spent understanding the chemistry and structure of these fibers and using biotechnology (biomimicry) to produce such fibers commercially. Nexia Biotechnologies Inc. has been successful in introducing the spider silk gene into goats to obtain the dragline silk protein in their milk [54]. This technology is still not mature and will take a few years before spider silk fibers will be commercially available.

Feathers of various bird species generate fibers with useful properties [55]. The annual US production of the most abundantly available feathers, a byproduct from poultry, is 2000 million kg [55]. Half of that weight is fibers, making this an abundant, readily harvestable agriculture resource. Use of feather fibers in thermal insulation in winter jackets and other applications is well known. Turkey feathers, with a length of approximately 3 cm, have also been spun into useful yarn. Other fibers have also been used to make functional, water repellent and filter paper, oil absorbing mats as well as composites. Some turkey fibers have also been processed into mats to be used for erosion control and other applications [56]. Since feather fibers generally don't have good mechanical properties, they cannot be used in load bearing composites.

9.2.3   Regenerated and modified fibers

Since cellulose from plants is a renewable resource, there have been several efforts in developing regenerated cellulose fibers. A secondary reason for these efforts is that no plant fibers come in continuous form for easy weaving or knitting into fabrics. One of the most common regenerated cellulose fibers is viscose rayon (viscose), derived from purified wood pulp. Many varieties of viscose fibers, e.g. viscose, high tenacity viscose, etc., are available commercially. The latest version of regenerated fiber, 'lyocell' fiber commercialized by Acordis in England, and Lenzing in Austria, employs an intrinsically cleaner process by dissolving cellulose in a non-toxic solvent N-methyl morpholine N-oxide (NMMO). NMMO is environmentally harmless

and biodegradable in waste water treatment. Also, most of the NMMO used in spinning the fibers is recovered and reused [57]. More information about this can be obtained elsewhere in this book.

Chitosan, a copolymer of 2-amino-2-deoxy-D-glucopyranose and 2-acetamido-2-deoxy-D-glucopyranose units, and alginate, a linear copolymer of b-(1,4)-linked D-mannuronic acid and a-(1,4)-linked L-guluronic acid units, have been spun into useful fibers. However, because of low mechanical properties they are mostly limited to medical and other non-load-bearing specialty applications [58]. Further information about chitosan fiber can be obtained elsewhere in this book.

9.2.4   Developments in fibers

There are several efforts in developing nano or submicron size fibers from cellulose and other polymers using electrospinning. eSpin Technologies, Inc., Chattanooga, TN, has been a leader in commercializing the electrospinning technology to spin fibers on a large scale. However, production on a large scale is still a thing of the future. Also, the current technology is still in its infancy and it is difficult to obtain molecular orientation and strong fibers. As a result, most of the current applications of electrospun fibers can only take advantage of their small diameters and large surface area per unit weight.

Another significant effort in developing high strength spider silk protein-based fibers under the trademark Biosteel[®] is by Nexia Biotechnologies Inc. [54].

Another development is to obtain microfibrillated cellulose (MFC) from inexpensive plant fibers. These microfibrillar structural units are comprised of oriented cellulose chains and exhibit excellent mechanical properties, almost comparable to high strength aramid fibers [30, 59–62]. MFC can be obtained through a process consisting of a mechanical treatment of pulp fibers, consisting of refining and high pressure homogenizing [59–62]. The refining process used is common in the paper industry and is accomplished using the refiner. In a disk refiner, the dilute fiber suspension is forced through a gap between rotor and stator disks. These disks have surfaces fitted with bars and grooves. During the process the pulp fibers get sheared into fibrils. In the homogenizing process, dilute slurries of fibrils obtained from refiner are pumped at high pressure and fed through a spring loaded valve assembly. As the valve opens and closes in rapid succession, the fibrils are subjected to large pressure drops with shearing impact forces. This combination forces the fibrils to further fibrillate into microfibrils. To obtain high degree of microfibrillation the homogenizing process may be repeated several times. The strength of MFC has been estimated at 2 GPa based on the experimental results of 1.7 GPa obtained for kraft pulp which mainly consists of cellulose microfibrils where 70 to 80% of the microfibrils are distributed

parallel to the fiber axis [63]. The nanofibrillar cellulose strength, which is made up of cellulose whiskers, has been estimated between 2 GPa and 12 GPa [59–62]. The modulus of the cellulose microfibrils can reach 134 GPa with a density of 1.5 g/cc [64].

Cellulose is also secreted by some bacterial species. Bacterial cellulose (BC) is produced by *Acetobactor* species cultivated in a culture medium containing carbon and nitrogen sources [65]. This extremely fine and pure fiber network structure has very high mechanical strength. The network structure in the form of pellicle made up of random assembly of ribbon-shaped fibrils, less than 100 nm wide, which are made up of a bundle of much finer nanofibrils, 2 to 4 nm in diameter. Unlike fibrillation of plant fibers, BC is produced by bacteria in a reverse way, synthesizing cellulose and building up bundles of nanofibrils. The BC fibrils are highly oriented and could be used in 'green' composites. In fact, Nishi *et al*. [66] have reported excellent dynamic modulus of about 30 GPa of sheets processed from BC pellicles. Nakagaito *et al*. [65] reported Young's modulus of 28 GPa of BC-based composites made using phenol-formaldehyde resin.

9.3   Biodegradable resins

As mentioned earlier, rising oil prices, widespread awareness of non-sustainability of petroleum oil, and the ever increasing tipping fees for landfills and incineration costs of commodity plastics and composites have contributed to renewed interest in fully biodegradable, renewable and environment-friendly, green plastics. Although the current market is very small compared to conventional resins, there are a variety of green resins available in the market today. As in the case of fibers, the resins can be classified into two broad categories based on their origin: natural and synthetic resins [1]. This chapter is mainly devoted to the natural soy protein-based resin and its modifications and use in composites.

9.3.1   Natural resins

Most natural resins are derived from plants or animals. They may be modified chemically or blended with other materials to improve their mechanical, physical or thermal properties and to make them easier to process. There are two major categories of natural polymers: polysaccharide-based and protein-based. Many of these polymers can be used as resins; a partial list of natural and synthetic biodegradable resins is presented in Table 9.3. Most of these resins degrade through enzymatic reactions in environments such as natural composting while some may degrade by hydrolysis in the presence of moisture under acidic or alkaline conditions. However, it is important that all intermediate and final degradation reaction products be environmentally benign for the

Table 9.3 Natural and synthetic biodegradable polymer resins

Natural	Synthetic

1. Polysaccharides
   • Starch
   • Cellulose
   • Chitin
   • Pullulan
   • Levan
   • Konjac
2. Proteins
   • Protein from grains
   • Collagen/gelatin
   • Casein, albumin, fibrogen, silks, elastin
3. Polyesters
   • Polyhydroxyalkanoates, copolymers
4. Other polymers
   • Lignin
   • Shellac
   • Natural rubber
	1. Poly(amides)
	2. Poly(anhydrides)
	3. Poly(amide-enamines)
	4. Poly(vinyl alcohol)
	5. Poly(ethylene-co-vinyl alcohol)
	6. Poly(vinyl acetate)
	7. Polyesters
	   • Poly(glycolic acid)
	   • Poly(lactic acid)
	   • Poly(caprolactone)
	   • Poly(orho esters)
	8. Poly(ethylene oxide)
	9. Poly(urethanes)
	10. Poly(phosphazines)
	11. Poly(acrylates)

resins to be truly 'green'. The remainder of this chapter discusses soy protein resins and some of the modifications carried out to improve their mechanical, physical and thermal properties as well as the moisture resistance as well as green composites made using these resins.

Soy protein resins

Soy protein, with proper processing, enjoys several advantages such as the ability to form a network structure for use as resin [67]. It can be processed into films for use as garbage and grocery bags [68], edible films [69, 70] and adhesives in particle board and plywood [71, 72]. Soy protein resin has also been combined with natural fibers to produce reinforced composites [19–24, 35, 36]. Some of these efforts are described later in this chapter.

   The use of soy protein, however, is not new; as early as in 1910s Henry Ford experimented with using agricultural materials to make parts of cars [1]. He tried many crops including wheat gluten, soy meal and soy oil and was successful in making various automobile parts such as coil cases with wheat gluten reinforced with asbestos fibers and glove-box doors, gear-shift knobs, horn buttons, accelerator pedals, distributor heads, interior trim, dashboard panels, etc. with soy meal reinforced with fibers. In 1941, a prototype 'soybean' plastic car was developed by Ford Motor Co. The body of this prototype consisted of 14 compression molded panels fixed to a tubular frame. Unfortunately, his efforts were interrupted by the

Second World War. Later, with a variety of inexpensive polymers developed from petroleum, most efforts in the recent decades have been devoted to the use of non-degradable plastics and composites. However, renewed interest in environment and sustainability issues are bringing green materials to the forefront once again.

Commercially available soy proteins are classified into three major groups based on the protein content: soy flour (SF), soy protein concentrate (SPC) and soy protein isolate (SPI) [73]. Approximate compositions of these three varieties are presented in Table 9.4 [74]. SF containing about 55% protein and 35% starch (carbohydrates) is the least refined form of soy protein and is prepared by grinding defatted soy bean flakes. SPC is prepared by eluting soluble components from defatted soy flour and contains about 70% protein and 18% carbohydrates. SPI is the purest form of them all and contains about 95% protein.

Table 9.4 Typical compositions of commercially available soy protein varieties

Component	Protein	Carbohydrates	Ash	Fiber	Fat
Soy flours (%)	56.0	33.5	6.0	3.5	1.0
Soy protein concentrates (%)	72.0	17.5	5.0	4.5	1.0
Soy protein isolates (%)	96.0	0.3		3.5	0.1	0.1

Soy protein contains about 18 different amino acids. Some of them contain acidic groups, e.g., aspartic acid and glutamic acid, some of them contain basic groups, e.g., lysine and arginine, etc., and others contain non-polar groups, e.g., alanine, leucine, isoleucine, etc. [75, 76]. The polar groups, both acidic and basic, are responsible for high water absorption by soy protein. The amino acids combine through a condensation reaction to form amide linkages and long polypeptide chains. Most of the soy protein is globulin and is soluble in salt water. Soy protein has been fractionated into various molecular weight components by their sedimentation constants. Four major fractions known as 2S, 7S, 11S and 15S, where S stands for Swedberg units, have been studied extensively. The numbers are nominal and stand for various molecular weights as follows: 2S = 8–22 kDa, 7S = 180–210 kDa, 11S ≃ 350 kDa and 15S ≃ 600 kDa [77].

Soy proteins are least soluble in water in their isoelectric region of pH between 4.2 and 4.6 [73, 76]. However, solubility, measured by nitrogen solubility index (NSI, %), sharply increases above and below the isoelectric point as the soy protein denatures and unfolds. This exposes the sulfhydryl groups which associate to form covalent disulfide intermolecular bonding. Under acidic conditions of pH 1–3, significant repulsive forces develop among positively charged soy polypeptide chains, resulting in less

intermolecular cross-linking [78]. Because of the lower solubility in acidic conditions, various acids have been used to decrease the water absorption of soy proteins [79, 80]. Unfortunately, the acidic conditions do not tend to improve the mechanical properties of the resin. On the other hand, many alkalis, which have been utilized for the dissolution of soy protein, create bridges between the polypeptide chains to stabilize and strengthen the cross-linked network [81]. In such cases, smaller cations, e.g. Li^+ and Na^+, have been reported to perform better than larger cations, e.g. NH_4^+, because of the steric hindrance. Gennadios *et al.* [82] who studied the effect of pH on the physical and mechanical properties of SPI films, reported that soy protein films prepared at pH of 6–11 had higher fracture stress and strain and lower water permeability than those prepared at pH 1–3. Hettiarchchy *et al.* [83] were able to improve the adhesive strength of SPI at pH of 10–11. These observations suggested that the SPI molecules open up in more in alkaline conditions resulting in better intermolecular interactions.

Heat also has been shown to convert protein from its native state to an unfolded state allowing intermolecular interactions [84]. Mo and Sun [85] determined the denaturation temperatures of SPI through enthalpy changes using differential scanning calorimetry (DSC). They detected two peaks corresponding to the endothermic transitions of β-conglycinin and glycinin, at around 73 and 88°C, respectively. It is well known that β-conglycinin and glycinin have different structures and functional properties. β-conglycinin is a trimeric glycoprotein of various combinations of three subunits [86]. Glycinin, on the other hand, is a hexamer composed of various combinations of five subunits [87]. Each subunit is made up of an acidic and a basic polypeptide component, which is linked by a single disulfide bond [88]. Thermal treatments also promote intra- and intermolecular cross-links within soy proteins [84, 89]. Such cross-links obviously contribute to the higher tensile strength and modulus of SPI films. However, at the same time they reduce the fracture strain and toughness. Liang *et al.* [67] showed that both strength and modulus increased with an increase in processing temperature. However, above 160°C the soy protein starts to degrade and the properties begin to decrease. Thames and Zhou [35] showed using thermogravimetry that SPI starts to decompose above 190°C. Nam [90] confirmed degradation of SPC when processed above 140°C for longer exposures above 2 hr.

Cured pure soy proteins tend to be brittle. They are also weak as a result of their low fracture strains. To reduce their brittleness, plasticizers are commonly added. The most commonly used plasticizers include polyols, mono-, di- or oligo-sachcharides, lipids and their derivatives. However, glycerin (1,2,3-propanetriol) is by far the most used plasticizer with soy proteins. As in the case of other plasticizers, glycerol decreases the mechanical properties, e.g. strength and modulus, of soy proteins. Glycerin is a relatively small hydrophilic molecule and can easily be inserted between polypeptide chains

to establish hydrogen bonds with amide, hydroxyl and carboxyl groups. Because of its three hydroxyl groups, glycerin is also strongly linked to increased moisture absorption in the case of soy proteins [19–21, 32, 90, 91]. With further plasticization through the absorbed moisture, the mechanical properties decrease further. Mo *et al.* [72] showed that at moisture contents higher than 40%, cracks can be easily formed in straw-protein particle boards due to high water vapor pressure trapped in the composites. Jane *et al.* [79] also showed that the shape changed as water was lost through evaporation. Takagi *et al.* [92] found that the number of disulfide bonds formed in a protein is affected by the water absorption. The protein with higher number of disulfide bonds adsorbed less water than that with lower disulfide links. Kajiyama *et al.* [93] reported that the exposure of hydrophobic groups through the denaturation of soy protein molecules contributed to a reduction in water absorption. On this basis, various methods have been employed to improve the water vapor barrier properties of soy protein material, including changes in pH [82], heat treatment [80], enzymatic treatment with horseradish peroxidase [94] and treatment with formaldehyde and urea [95, 72].

Other attempts to increase moisture resistance and improve the mechanical and thermal properties of soy protein resins include cross-linking with maleinized tung oil (MTO) [35] and glutaraldehyde [32], internal plasticizing by stearic acid and forming a cross-linked complex with Phytagel® [19–21] and forming nano-composites with cloisite Na^+ clay nanoparticles [96]. Lower water absorption also translates to higher mechanical properties because of less plasticization. These modifications are briefly described below.

Soy protein modifications

Thames and Zhou [35] used several cross-linking agents to improve the properties of SPI and wood fiber-based composites. Soy protein and wood fiber (50/50 parts by wt) were mixed in a laboratory mixer and cross-linking agents (8%) were individually added by spraying. The composites were molded (hot pressed) using a laboratory press, at temperatures up to 185°C. Among the various cross-linking agents tried, MTO which was synthesized in their laboratory worked the best. The flexural strength of the composites molded at 165°C increased from 33 to 58 MPa while the water absorption decreased from 87% to 31%. This was attributed to the intermolecular cross-linking of the SPI introduced by the MTO. However, the long fatty acid chain of the MTO was perhaps a factor in reducing the moisture absorption by the SPI and thus a factor in increasing the flexural strength.

Several researchers have used glutaraldehyde (1,5 pentane-di-al) (GA), a colorless liquid with a boiling point of 101°C and a specific gravity of 1.062, as a cross-linking agent for proteins and soft tissues [97–102, 3]. Figure 9.1 shows the structure of GA. GA can react with the amine groups from various
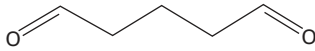
9.1 Structure of glutaraldehyde molecule.

amino acids present in the protein. Although there is no consensus, GA has been shown to react with α- and ε-amino groups in lysine, with α-group in glycine and only partially with α-amino groups of histidine and tyrosine [98]. Different mechanisms have been reported for explaining the reactions between GA and proteins [99, 103]. Matsuda *et al*. [99] showed a simple condensation cross-linking reaction scheme between GA and gelatin. GA has also been used as a cross-linking agent for SPI [101, 102], soy dreg [102], SPC [3, 32] and SPC nanocomposites [96].

Soy protein resin processing

Chabba and Netravali [32] used GA to cross-link SPC to improve its mechanical and thermal properties and increase its moisture resistance. The cross-linked (modified) SPC was used as a resin to fabricate green composites using flax yarns and fabrics. The processing of the unmodified SPC resin consisted of two steps: pre-curing and the final curing, simply referred to as curing. SPC powder was mixed with distilled deionized water in a ratio of 1:13 (by wt) in a beaker. In their studies glycerin was used as a plasticizer. The concentration of glycerin was varied from 5% to 20% (by wt of SPC) to study its plasticizing effect. This solution was homogenized using a magnetic stirrer for 15 minutes and then the pH of the mixture was adjusted to 11, using 1 N NaOH solution. SPC solution was again stirred for 15 minutes and then the beaker was transferred to a water bath maintained at 70°C. The solution was stirred in the water bath for 30 minutes at 70°C. This step was called pre-curing. To obtain cured SPC sheets, pre-cured SPC solution was cast on Teflon® coated glass plates and dried in an air circulating oven at 35°C for 20 hrs. Finally the dried SPC sheets were hot pressed (cured) in a Carver hot press at 120°C for 25 min under a pressure of 7 MPa. Similar processing steps were also utilized for processing SPI and SF by others.

Glutaraldehyde modification of SPC

The curing process for GA modified SPC (GA–SPC) was similar to that described above for SPC with a few modifications [3, 32]. In this case, distilled and deionized water was added in a ratio of 1:15 (by wt) and a required amount of glycerin was added as plasticizer. The concentration of glycerin was varied between 10% and 20% (by wt of SPC) to study its effect. The solution was homogenized for 15 minutes and the pH of the solution was adjusted to 11 ± 0.1 using 1 N NaOH solution. SPC solution was stirred

for 15 minutes and then the beaker containing the mixture was transferred to a water bath maintained at 70°C. The solution was pre-cured for 27 minutes and then the desired amount of GA solution (25% concentration in water) was added. The solution was further stirred for 3 minutes in a water bath to uniformly disperse the GA. GA is very reactive and starts to react immediately increasing the viscosity of the resin. The GA solution content was varied between 5% and 50% (by wt of SPC), to study the effect of GA cross-linking on cured SPC polymer properties. After pre-curing, the resin solution was cast on Teflon® coated glass sheets, dried at room temperature for 36 hrs and cured in a hot press at 120°C for 25 minutes under a pressure of 7 MPa.

Table 9.5 presents the effect of GA % on the tensile properties of the SPC resin. This resin contained 15% glycerin. It is clear that both fracture stress and modulus increased with the GA content up to 10%. Beyond 10%, however, both stress and modulus dropped. This was because the $-NH_2$ sites were available for the GA to react up to content of 10% GA. Any additional GA, that remained unreacted, resulted in plasticizing the SPC resin. Table 9.6 shows the effect of glycerin content on the moisture absorption of GA–SPC resin containing 10% GA. These data clearly show the positive correlation between the glycerin and moisture content. As stated earlier, this is very much expected because of the three –OH groups present in glycerin. It is also one of the main reasons to eliminate the use of glycerin as plasticizer.

*Table 9.5* Effect of GA% on the tensile properties of SPC resin containing 15% glycerin

GA (%)	Fracture stress (MPa)	Young's modulus (MPa)	Fracture strain (%)
0	16.9 (3.8)*	367.6 (3.3)	21.9 (10.2)
5	17.7 (5.8)	374.2 (9.3)	25.6 (11.8)
10	18.4 (5.4)	402.1 (7.9)	25.4 (12.6)
30	19.6 (4.2)	447.5 (5.9)	21.5 (13.0)
40	19.9 (6.4)	484.2 (6.7)	20.9 (14.9)
50	19.5 (4.5)	480.9 (4.7)	21.9 (15.3)

*Figures in parentheses are CV%

Table 9.6 Effect of glycerin content on the moisture absorption of GA–SPC resin containing 40% GA

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

Figure 9.2 shows the thermograms for the SPC and GA–SPC resins obtained using a thermogravimetric analyzer (TGA). It is clear from Fig. 9.2 that within the entire temperature range, the weight loss for the GA–SPC resin is lower compared to SPC. Also, the GA–SPC resin starts final degradation around 270°C compared to 235°C for the SPC resin. Both of these observations indicate improved thermal stability for the GA–SPC resin compared to SPC. Dynamic mechanical analysis and differential scanning calorimetric (DSC) studies have further confirmed that the GA–SPC was more stable compared to SPC resin with higher glass transition temperature (Tg) than SPC [104]. Properties of composites made using SPC and GA–SPC resins and flax fabrics are discussed later in Section 9.4.
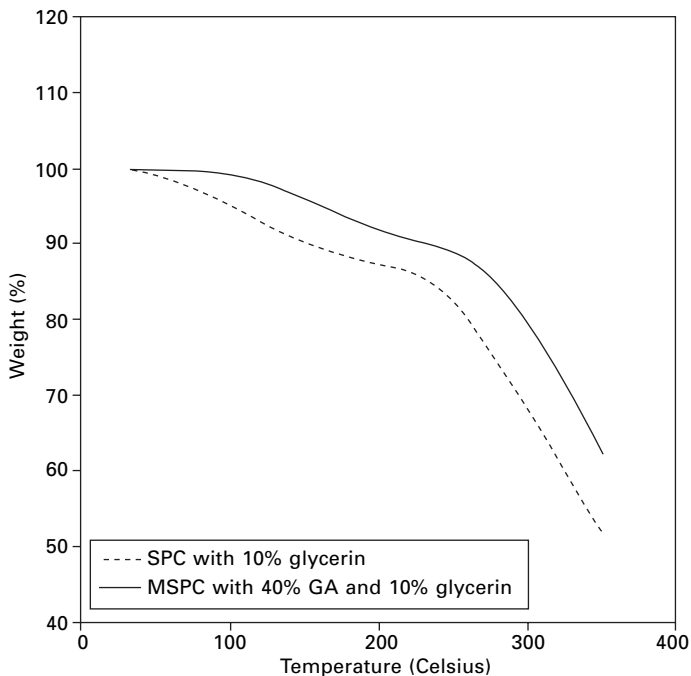
9.2 TGA thermograms of SPC and MSPC resin containing 40% GA and 10% glycerin.

Stearic acid modification

The use of glycerin as an external plasticizer in soy protein has some disadvantages in addition to increased moisture absorption and a lowering of mechanical properties. As a small molecule, it can leach out easily over time making the resin brittle again. Since the glycerin containing soy protein absorbs more moisture, the leaching of glycerin is further facilitated. This

has prompted the use of internal plasticizers that will covalently bond to the polypeptide chains and thus will not leach out during use. Also, the use of a higher molecular weight plasticizer, compared to glycerin, could reduce the leaching rate. One such modification of SPI using stearic acid (n-octadecanoic acid) (SA) was carried out successfully by Lodha and Netravali [20, 105, 106]. The carboxylic group in SA can react with amine, imine and/or hydroxyl groups on the soy protein chain depending on the pH conditions to form amide and ester groups. Once reacted, SA acts as an internal plasticizer that is covalently bonded to the polypeptide molecule and cannot leach out. Its 18-carbon long non-polar hydrocarbon chain can also be helpful in reducing the moisture absorption and resulting in higher mechanical properties. The SA modifications were carried out under alkaline (pH 10) as well as near neutral pH conditions. Better improvements in mechanical properties were obtained with the modifications at near neutral pH conditions. Lodha and Netravali [20, 105, 106] studied the effects of both stearic acid and glycerol on the mechanical, thermal and moisture absorption properties of the resin. Best mechanical properties were obtained with 20% stearic acid. At that concentration no glycerin was needed as a plasticizer and the resin processing and handling was as easy as SPC or GA–SPC resins. This stearic acid modified SPI (SA–SPI) resin was then used to fabricate flax yarn reinforced composites. The pre-curing and curing process was similar to the one described earlier for the SPC resin except that the pre-curing was done at 90°C and the final curing process was done at 110–120°C and 11 MPa pressure.

The effect of stearic acid content on tensile properties and moisture absorption of the SPI resin containing 30% glycerin is presented in Table 9.7. It is clear that with an increase in SA content up to 50% (on SPI wt basis) both fracture stress and modulus increased significantly whereas the fracture strain decreased. Further increase in SA content did not continue to increase fracture stress. It is also clear from the data in Table 9.7 that the moisture content decreased with an increase in SA, as was expected. The decreased moisture absorption was perhaps the main reason for improved mechanical properties. Some of the hydrophobic SA was observed to phase

Table 9.7 Effect of stearic acid content on the tensile properties and moisture absorption of SPI resin containing 30% glycerol

Stearic acid (%)	Fracture stress (MPa)	Young's modulus (MPa)	Fracture strain (%)	Moisture content (%)
0	6.1[a]	124.7[a]	154.1[a]	16.3[a]
20	6.1[a]	181.3[b]	64.5[b]	14.0[b]
30	6.8[b]	212.2[c]	31.4[c]	13.9[b]
50	6.6[b]	278.2[d]	10.6[d]	12.6[c]
75	6.2[a]	307.2[e]	3.4[e]	12.8[c]

Means within a column with the same superscript did not show a statistically significant difference at $a = 0.05$.

separate from SPI, particularly at higher concentrations, and form crystals of small dimensions. This was confirmed by both X-ray diffraction (XRD) and DSC. The SA-SPI resin, containing well dispersed SA crystals, behaved somewhat like a nanocomposite, increasing the tortuosity of the polypeptide molecules and restricting their mobility when loaded, thus increasing its modulus. They concluded that the carboxyl group on the SA also reacted with some of the amine, imine and hydroxyl groups on polypeptide chains forming amide, and ester groups. Once grafted, the SA acts as an internal plasticizer, eliminating the need for the external plasticizer, glycerin. In addition, as the SA reacted along the polypeptide chain, it increased the molecular weight and increased the viscosity and the Tg of the resin. All these mechanisms together were responsible in making the SA–SPI resin stronger and stiffer.

Lodha and Netravali [20, 105] also studied the effect of glycerin on the moisture content. Again, a similar positive relationship was found. As the glycerin content of the SA–SPI resin (with 20% SA) was lowered from 30% to 0%, the Young's modulus and the fracture stress increased from 181 MPa to 1096 MPa and from 6.1 MPa to over 20 MPa, respectively. At the same time the fracture strain decreased from 64.5% to 2.8%. The SA–SPI resin containing 20% stearic acid and 0% glycerin was used for fabricating flax yarn reinforced unidirectional composites. The TGA and DSC studies of the SA–SPI resin further confirmed that the SA–SPI resin was thermally more stable than the SPI resin.
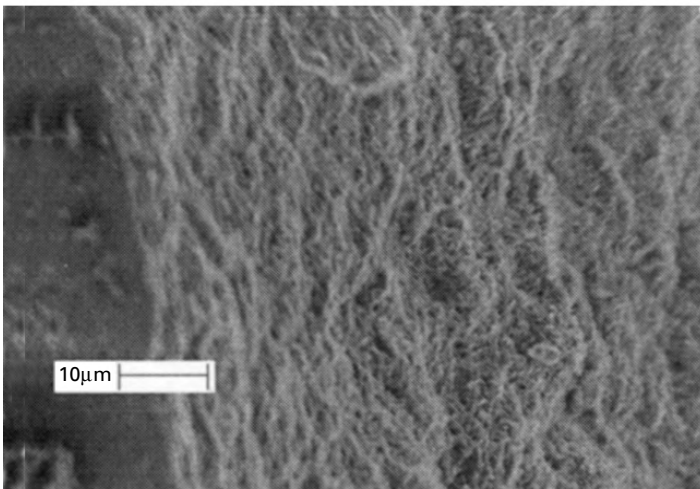
The SEM photomicrographs of the SA–SPI resin, presented in Fig. 9.3, showed a significantly rougher and layered surface compared to SPI resin. A similar layered surface was also observed by Lodha and Netravali [105] for SA–SPI resin prepared under alkaline conditions. The formation of layered structure was also observed in the case of stearic acid modified zein protein by Lai *et al.* [107].

Phytagel® modification of SPI

In another modification, Lodha and Netravali [106, 108] blended Phytagel®, a polycarboxylic compound, to improve the mechanical properties of SPI resin by forming a cross-linked complex structure. Phytagel® is produced by bacterial fermentation and is composed of glucuronic acid, rhamnose and glucose. It is commonly used as a gelling agent for electrophoresis to determine the molecular weights of DNA molecules as well as in detection of microbial contamination (MSDS by Sigma-Aldrich Co.). Phytagel® is known to form a strong gel via ionic cross-links at its glucuronic acid sites, using divalent cations naturally present in most plant tissue culture media. The carboxyl group in glucuronic acid is the main reactive group in Phytagel® which can react with amine and hydroxyl groups in SPI to form amide and ester groups,
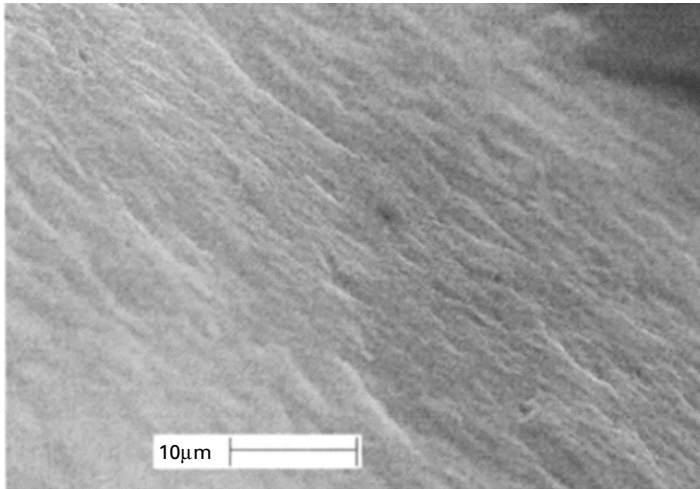
(a) SPI resin

(b) SAM–SPI resin

9.3 SEM photomicrographs of the fracture surfaces of (a) SPI and (b) SA-SPI resins.

respectively. The hydroxyl groups on rhamnose and glucose molecules may also react with carboxyl groups present on aspartic and glutamic acids in SPI, under suitable conditions, to form ester bonds. The carboxyl and hydroxyl groups can also interact with SPI via hydrogen bonds. All these possible reactions and interactions formed a complex, cross-linked and hydrogen bonded structure that was much stiffer than the SPI alone. Lodha and Netravali [106, 108] did the sol–gel analysis of these resins and found out that the

Phytagel® modified resins had a significantly higher gel fraction confirming the possibility of cross–linking between Phytagel® and SPI or formation of interpenetrating network (IPN) type structures.

The resin pre-curing and curing processes for the Phytagel® modified SPI (PH–SPI) resin were essentially similar as used for SPI and required only minor modifications. To study the effect of Phytagel® content, Lodha and Netravali [106, 108] varied the amount of Phytagel® between 5 to 50% (by wt of SPI) prior to pre-curing. Water (15 times wt of SPI) and glycerin, in varying amount, were added to the mixture and pre-curing was done at 70°C for 30 minutes. The final curing included 120°C for 5 minutes at 2.8 MPa and 120°C for 25 minutes at 11 MPa pressure. Table 9.8 presents the effect of Phytagel® content on the mechanical properties and moisture absorption of the PH–SPI resin. The tensile properties and moisture absorption of two formulations containing 20% Phytagel® (PH2–SPI) and 40% Phytagel® (PH4–SPI), both with 12.5% glycerin, are compared with those of SPI resin in Table 9.9. These resins were later used to fabricate flax yarn reinforced composites. Dynamic mechanical analyzer was used to characterize tan δ, loss and storage moduli of the three resins. The data indicated a Tg of 115°C for SPI whereas the Tgs for PH2–SPI and PH4–SPI resins were 171°C and 177°C, respectively, indicating much higher thermal stability. It should be noted that the pure Phytagel® material processed similarly did not show any

Table 9.8 Effect of Phytagel® on the tensile properties and moisture absorption of SPI resin, containing 30% glycerol

| Phytagel®	Fracture stress (MPa)	Young's modulus (MPa)	Fracture strain (%)	Moisture content (%)
0	6.0	98.7	206.4	19.2
5	10.5	123.6	53.4	19.0
7	12.7	136.3	51.7	18.5
10	14.9	146.3	42.4	18.2
20	22.4	225.8	35.5	17.2
30	29.7	277.0	33.9	16.2
40	31.8	388.7	20.4	17.2
50	28.9	337.2	20.0	17.2

Table 9.9 Tensile properties and moisture absorption of SPI, PH2–SPI and PH4–SPI resins

Resin	Fracture stress (MPa)	Young's modulus (MPa)	Fracture strain (%)	Moisture content (%)
SPI	6.0	98.7	206.4	19.15
PH2–SPI	42.6	657.6	28.9	12.7
PH4–SPI	60.0	896.5	19.5	12.4

glass transition of its own within the temperature range studied. Thermal degradation temperatures from TGA measurements also showed significant increases for PH2–SPI (247°C), PH4–SPI (249°C) compared to 208°C for SPI resin. This again indicated that the Phytagel® modified SPI resins have higher cross-linking and hydrogen bonding compared to SPI resin which results in better thermal stability. The SEM photomicrographs of the fractured surfaces presented in Fig. 9.4 also showed a rougher and layered surface similar to those seen earlier for the SA–SPI resin.


10μm

(a)

10μm
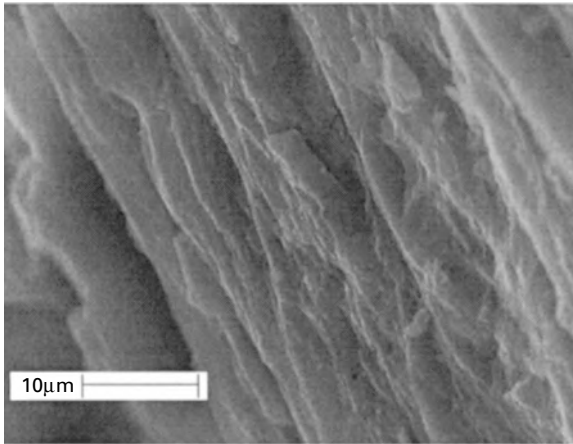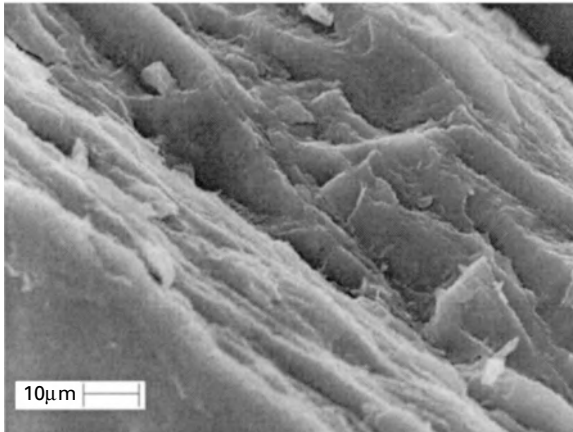
(b)

9.4 SEM micrographs of fractured surfaces of (a) PH2-SPI and (b) PH4-SPI resins.

Soy protein nanocomposite

Blending nanoparticles with various types of polymers, particularly to form nanocomposites, have been shown to offer several advantages including higher mechanical properties [109]. As mentioned earlier, the nanoparticles increase the tortuosity of the polymer molecules and restrict their mobility under loading, thus increasing its modulus. This effect is significant when the particles are uniformly dispersed in the polymer [109]. Inclusion of nanoparticles, e.g. clay, have also been shown to improve the gas and liquid barrier properties of the polymers [109]. Simultaneous increases in glass transition temperatures (Tg) can also be seen due to the organosilicate–polymer interactions that restrict molecular motion. Thermo-mechanical properties such as yield strength, tensile modulus and heat distortion temperature (HDT) also show significant improvements with the introduction of nanoparticles [110]. However, toughness, elongation at break and impact strength, in general, may be lowered. Nanocomposites experiencing thermal degradation also show significant delay in weight loss indicating enhanced thermal stability. This arises due to the barrier effect of the silicates that prevents the escape of the volatile thermo-oxidation products and simultaneously reduces the rate of oxygen diffusion into the nanocomposite. Reduction in flammability of nanocomposites has also been reported in many cases [110]. The general nanocomposite flame retardant mechanism involves the build-up of a layer of carbonaceous silicate char on the surface during burning. This layer insulates the underlying material and slows the rate of mass loss of the byproducts formed during thermal degradation.

Huang and Netravali [96] formed nanocomposites using SPC and GA-SPC resins by dispersing exfoliated Cloisite® Na+ clay (Southern Clay Products, Inc., TX) nanoparticles. Clay nanoparticles were first dispersed into distilled water using magnetic stirring and ultrasonication. Dispersed clay particle solution was then introduced into SPC and GA–SPC resins during the pre-curing process. This process has been described earlier for various resin modifications. The nanoclay particle dispersion in SPC and GA–SPC resins was evaluated using both XRD and transmission electron microscopy (TEM) using thin microtomed sections of the resins. Figure 9.5 shows the X-ray diffraction patterns of Cloisite™ NA+ clay powder (a) and SPC resin with different clay loadings (b). For all specimens the disappearance of the peak at 9° indicates that the particles were exfoliated and almost fully dispersed into SPC. Both XRD and TEM techniques indicated good dispersion, although some sections indicated agglomeration of nanoclay particle, particularly at higher clay loadings. Effects of nanoparticle loading on the mechanical properties and moisture absorption of the SPC resin are presented in Table 9.10. The SPC resin in this case contained 30% glycerin. From the data, it is clear that the nanoclay loading has a significant effect on the fracture stress and modulus of the SPC resin. For 30% nanoclay loading the modulus of the
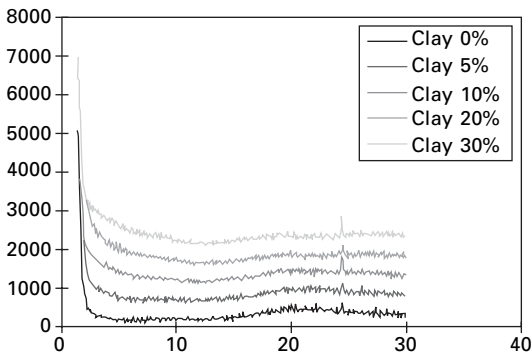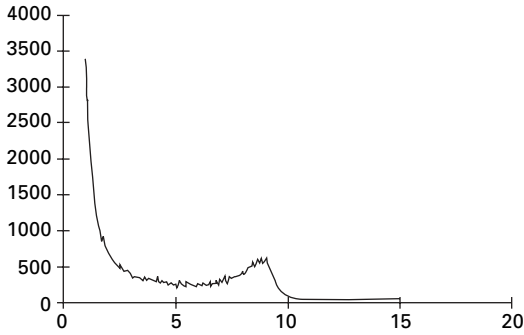
9.5 XRD of Cloisite® Na+ clay powder (a) and XRD of SPC composites with different clay loadings (b) [Y-axis = % intensity, X-axis = goniometer].

Table 9.10 Effect of clay nanoparticle loading on the tensile properties and moisture absorption of the SPC resin

| Clay (%)	Stress at max. load (MPa)	Strain at max. load (%)	Modulus (MPa)	Moisture content (%)
0	8.0	28.6	84.3	22.0
0.5	8.0	30.3	84.8	21.4
1	8.6	30.0	91.8	20.6
3	10.0	27.2	131.6	20.4
5	12.3	23.5	179.5	20.0
7	12.5	20.3	238.9	19.6
10	14.2	16.4	327.9	19.5
15	16.7	11.0	589.1	18.0
20	17.2	9.4	725.4	18.0
30	20.2	6.0	1023.9	17.1

resin was over 1 GPa compared to 84 MPa for resin without clay, a 1100% increase, and the fracture stress increased to 20 MPa from 8 MPa, a 150% increase. At the same time the resin became brittle as the fracture strain decreased from over 28% for resin without any nanoclay to 6% at 30% loading. Similar changes in mechanical properties have been observed for various polymer nanocomposite systems as well [109]. Of particular importance was the reduction in moisture absorption from 22% to 17.1%. This suggested that the nanoclay particles were also effective in blocking moisture from entering into the resin. The increases in the modulus and fracture stress are also a result of lower moisture absorption by the resin.

The effect of GA content on the GA–SPC nanocomposite resin mechanical properties and moisture absorption are presented in Table 9.11. The SPC nanocomposite resin in this case contained 15% glycerin and 5% nanoclay. It is clear from these data that as the GA content increased from 0% to 10% the modulus increased from 778 MPa to over 1 GPa. However, any increase in GA content above 10% resulted in a drop in modulus. This is because of the unreacted GA acting as a plasticizer. Similar trends were also obtained for GA–SPC resins discussed earlier. The effect of clay loading on the thermal properties of the clay/SPC nanocomposites, containing 15% glycerin, is shown in Fig. 9.6. With an increase in nanoclay loading, the GA modified resin became increasingly stable at higher temperatures and their degradation temperatures increased significantly and the weight loss decreased along the entire temperature range. Part of this is due to the lower moisture absorption of the nanocomposite resins. It is interesting to note that the moisture content for all resins remained in a very narrow range in spite of increased cross-linking with increased GA content. This suggests that the nanoclay particles may be more effective for the moisture control than cross-linking with GA.

Table 9.11 Effect of glutaraldehyde content on the tensile properties and moisture absorption of GA–SPC resin

GA (%)	Stress at max. load (MPa)	Strain at max. load (MPa)	Modulus (MPa)	Moisture content (%)
0	24.9	11.6	778.0	14.7
1.3	27.4	9.9	901.3	14.6
3.8	26.2	8.9	973.4	14.4
5.0	28.5	9.6	969.3	14.3
7.5	29.5	8.7	993.1	14.1
10.0	28.9	7.8	1043.0	14.0
14.4	25.7	8.3	838.8	14.5

Several of these modified SPI and SPC resins were used to fabricate fiber, yarn and fabric reinforced green composites. The fabrication process and properties of these composites are discussed in the next section. Data for green composites using nanoclay were, however, not available at this time.
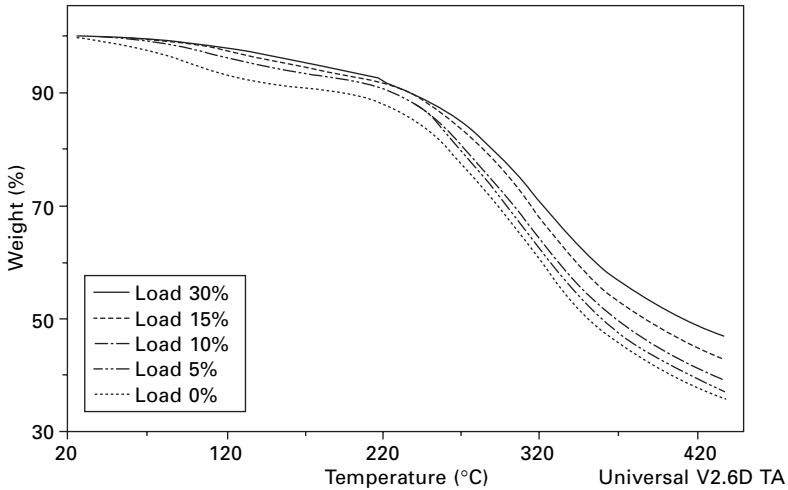
_9.6_ Effect of nanoclay loading on thermal stability by TGA.

9.4   Soy protein-based green composites

As stated earlier, most plant fibers are termed 'staple', i.e. short length fibers. Fibers derived from the stem of the plant, e.g. ramie and flax, and those derived from some plant leaves, e.g. sisal and henequen, could be longer than 1 meter. Although it is easier to fabricate random, short fiber composites, with some manipulation, unidirectional composites of small dimensions can also be made using these fibers. Lodha and Netravali [19] used chopped ramie fibers and SPI resin to make random fiber green composites. Nam and Netravali [23, 90] fabricated unidirectional composites using SPC resin with ramie fibers. Flax yarn and fabric reinforced SPC and modified SPC resin composites have also been made and have shown to have excellent properties [20, 22, 32, 105, 106]. Fabrication of these composites and their properties are briefly discussed in the next subsections.

9.4.1   Fiber-reinforced composites

Short fiber composites

Lodha and Netravali [19] studied the effect of fiber length and content on the short ramie fibers/SPI resin composite properties. The average diameter of the fibers was about 50 μm. The average fiber fracture stress and modulus were measured to be 620 MPa and 48 GPa, respectively. A wide variability in mechanical properties was found for these fibers as is the case for all natural plant-based fibers. To prepare random, short fiber composites, ramie fibers were chopped to 5, 10 and 15 mm lengths. These fiber lengths were based on the interfacial shear strength (IFSS) measured using the microbead

test [24, 40, 41]. For the ramie fiber/SPI resin system the IFSS was found to be in the range of 30 MPa. Based on this IFSS value the critical length of the fiber was calculated to be just over 2.5 mm. Based on theory of reinforcement, below this critical length, there should be no effect of fiber inclusion on the mechanical properties of the resin. Above this length, however, the fibers are expected to reinforce the resin and thus improve the strength and modulus. However, this theory applies mostly to fibers that are laid in the direction of the stress. To prepare short fiber composites, the SPI powder was mixed with 30% glycerin and 300% water (by wt of SPI) and stirred to make uniform dough. Predetermined amounts of chopped fibers were added to the dough in small increments and the mixture was stirred with compressed air to obtain uniform fiber distribution. However, they noted that the composites showed resin-rich and fiber-rich areas indicating uneven fiber distribution due to the high viscosity of the resin. Once all the fibers were added, the dough was made into small balls and subjected to hot pressing at 70°C for 30 minutes, dried in air for 24 hr and cured by hot pressing at 110°C for 2 hr under 5.5 to 7 MPa pressure to form composite sheets. These composites were then conditioned at ASTM conditions of 21°C and 65% relative humidity (RH) prior to characterizing their properties.

Table 9.12 presents ramie fiber/SPC short fiber composite fracture stress as a function of fiber content and length. Table 9.13 presents the modulus of

Table 9.12 Fracture stress of ramie/SPC short fiber composites for various fiber lengths and contents

| Fiber content (% w/w)	Fracture stress (MPa)		
	5 mm	10 mm	15 mm
0	5.9	5.9	5.9
10	3.2	9.3	15.7
20	9.8	17.1	25.5
30	12.5	24.5	33.4*

*A large amount of delamination was observed for these specimens

Table 9.13 Young's modulus of ramie/SPC short fiber composites for various fiber lengths and contents

Fiber content (% w/w)	Young's modulus (MPa)		
	5 mm	10 mm	15 mm
0	18.0	18.0	18.0
10	68.0	235.6	521.2
20	238.4	613.1	1082.3
30	431.0	1173.1	1654.3*

*A large amount of delamination was observed for these specimens

the composites as a function of fiber content and length. Typical load-displacement curves for various composites with 5 mm long ramie fibers and various fiber contents are shown in Fig. 9.7. These data confirm that both fracture strength and modulus are a strong function of the fiber content and fiber length and increase with both fiber length and content, as would be expected. However, at small length, 5 mm in this case, and at low fiber content, the fibers seemed to act as defects. As a result, instead of contributing to the strength, the fibers reduced the strength of the composites to lower than that of the resin. As mentioned earlier the critical length of 2.5 mm applies when the fibers are in the direction of the stress. Any fibers at an angle to this direction cannot contribute fully. Theoretical values of modulus were higher than the experimental values for all specimens. The differences between the theoretical and experimental values were much higher at smaller fiber lengths and volume content and narrowed down as the fiber length and volume increased. Several factors including defects such as the uneven distribution of the resin and fibers, lack of perfect randomness, voids, shrinkage during processing etc. were responsible for this behavior [19].
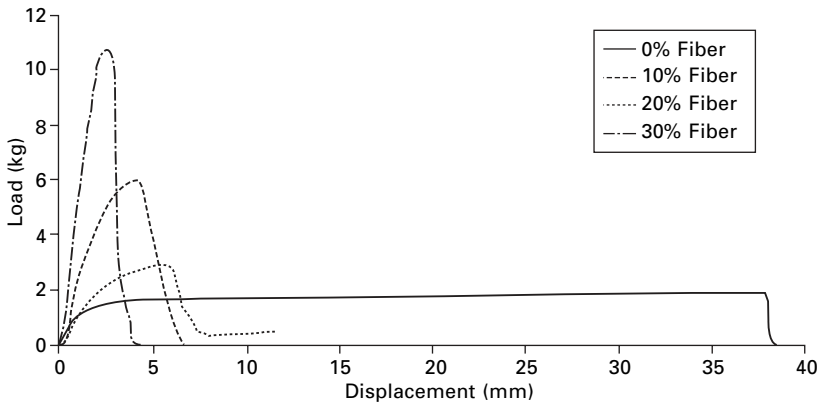
9.7 Typical load-displacement plots of tensile test of various composite specimens with 5 mm long ramie fibers and various fiber contents.

Unidirectional composites

Unidirectional composites using ramie fibers and SPC resin were prepared by Nam and Netravali [23, 90]. Composites with unidirectional lay up of fibers was possible because of the small dimensions of the specimens prepared. The fibers used in this case were between 600 and 1700 mm long. The average diameter of the ramie fibers was measured to be 123 μm. The average tensile stress and modulus were found to be 627 MPa and 31.8 GPa, respectively.

The fabrication of unidirectional composites was accomplished in two steps. During the first step, fibers, in a parallel bundle form, were soaked in the pre-cured SPC resin (30% glycerin) and the excess resin was squeezed out. This process was repeated a few times to ensure the full penetration of the resin in between fibers. The wet fibers were aligned on Teflon® coated glass plates layer by layer, in a parallel array, to make a 100 mm × 100 mm sheet and dried for 48 hr at room temperature to form pre-impregnated sheet (prepreg). In the second step the prepreg was placed between two stainless steel plates and hot pressed at 120°C for 2 hr at a pressure of 5 MPa. The cured ramie fiber/SPC 'green' composite was then allowed to cool and thereafter conditioned at ASTM conditions of 21°C and 65% RH for 2 days prior to characterizing the mechanical properties. The total fiber content of these green composites, calculated from the fiber weight and the final composite weight, was 65%. Because of the higher density of the fibers compared to the resin, the volume content was slightly less.

Table 9.14 compares the tensile properties of the ramie fiber/SPC unidirectional composites, in both longitudinal and transverse directions, with those of the SPC resin. Properties of SPC polymer are also included for comparison. Being unidirectional, the composites have significantly higher tensile modulus (4.9 GPa) and fracture stress (271 MPa) in the longitudinal direction compared to the modulus of 0.9 GPa and fracture strength of 7.4 MPa in the transverse direction. In unidirectional composites, the tensile properties in the longitudinal direction are controlled by the fiber properties whereas the transverse direction properties are controlled by the resin and/or the fiber/resin interface properties. In this case, the fracture strength in the transverse direction was controlled by the SPC resin strength. However, slightly higher values for both fracture stress and modulus in the transverse direction were because of not having a perfect alignment of the fibers as a result of being hand laid and having no control over them while hot pressing. In addition, ramie fibers, like any other plant-based fibers are fibrillar and fibrillate during processing. The protruding fibrils generally tend to go tangentially to the fiber axis, improving the interface strength. Any fiber

Table 9.14 Tensile properties of ramie fiber/SPC unidirectional composites in longitudinal and transverse directions compared with SPC resin

Material	Test direction	Tensile stress (MPa)	Young's modulus (GPa)	Fracture strain (%)
Composite*	Longitudinal	271.4	4.9	9.2
	Transverse	7.4	0.9	5.3
SPC resin		6.9	0.1	30.2

*65% fiber volume fraction

misalignment reduces strength and modulus in the longitudinal direction and increases them in the transverse direction. Fiber fibrillation, a common property of plant-based fibers, is also believed to be partially contributing to this.

The theoretical calculations of the tensile fracture stress and modulus in the longitudinal direction were calculated using the simple rule of mixtures as shown in equations 9.1 and 9.2 [111]

$$\sigma_c = \sigma_f V_f + \sigma_m V_m \qquad\qquad\qquad 9.1$$

$$E_c = E_f V_f + E_m V_m \qquad\qquad\qquad 9.2$$

where σ_c, σ_f and σ_m represent the tensile stress values for composite, fiber and matrix, respectively. E_c, E_f and E_m represent the Young's modulus values of the composite, fiber and matrix, respectively, and V_f and V_m are volume fractions of fiber and matrix, respectively. The calculated values of tensile stress and modulus of composite were 407 MPa and 24.3 GPa, respectively. The experimental values of 271 MPa and 4.9 GPa for fracture stress and modulus are significantly smaller than the theoretical values. This discrepancy was attributed to several reasons including resin shrinkage during curing, fibers no having perfect alignment, presence of voids and thermal degradation of the ramie fibers. As mentioned earlier, a significant amount of water is used in processing of the composites. As the water is dried during the curing process, the resin shrinks significantly. As a result, the fibers undergo longitudinal compression and lose their alignment resulting in lower modulus. In addition, the hand lay-up process is not so accurate and results in misalignment of the fibers as well. The voids, especially around the fibers, also contribute to the lower composite properties. The voids are commonly generated because of the water present in the resin as well as the ramie fibers which evaporates during curing at 120°C. Garcia-Zetina *et al*. [112] used a correction factor to account for the void content to predict the strength of short fiber composites. However, in the case of ramie fibers/SPC composites it was difficult to estimate the void content and hence the correction factor could not be estimated.

Although lower than the predicted, the ramie fiber/SPC green composite strength of 271 MPa is close to the strength of soft steel. The density of steel is about 7.75 g cm^{-3} which is over 5.5 times higher than the 1.35 g cm^{-3} estimated for the green composites. As a result, on strength per weight basis, the ramie fiber/SPC green composites are superior to steel by 5.5 times. Nam and Netravali [23, 90] also compared the mechanical properties of ramie fiber/SPC green composites to three varieties of wood [40, 41]. The fracture strength of the green composites in the longitudinal direction was almost twice and the modulus was between 5 to 10 times that of commonly used bass, cherry and walnut wood varieties. The properties in the transverse direction were comparable. The flexural strength and modulus of these unidirectional composites, in the longitudinal direction, were about 230 MPa

and 12.5 GPa, respectively, which are significantly better than the wood varieties. With their excellent mechanical properties, these composites may be used in many indoor structural applications as well. As mentioned earlier, trees take 20–25 years for their full growth before they can be harvested and used as wood. On the other hand, ramie and other fibers such as flax and hemp, etc., as well as soybeans, are yearly renewable.

Yarn-reinforced composites

Lodha and Netravali [20, 21, 106] fabricated unidirectional composites using flax yarns and SPI, PH2–SPI (containing 20% Phytagel®) and PH4–SPI (containing 40% Phytagel®) resins. As mentioned earlier, plant-based fibers are not continuous. However, they can be spun into continuous yarns for making unidirectional composites. To fabricate composites, flax yarns were aligned parallel by manually winding them on a metal frame and wetting by immersing the frame in the pre-cured resin solution. Winding gave two layers of parallel aligned layers of yarns to obtain the desired thickness of the composite specimens. Additional amount of pre-cured resin was also poured in between the layers to ensure good resin impregnation if needed. The resin impregnated flax yarn sheets were oven dried at 35°C for 24 hr. The dried sheets were hot pressed at 120°C for 5 minutes at a pressure of 2.8 MPa and for additional 25 minutes at a pressure of 11 MPa to form composites. All composites had 45% yarn content by wt. Tensile and flexural properties of the composites were measured after conditioning them for 72 hr.

Table 9.15 summarizes the tensile properties of flax yarn reinforced SPI, PH2–SPI and PH4–SPI composites in the longitudinal direction. Both PH2–SPI and PH4–SPI resin composites showed higher modulus and lower fracture strain compared to composites prepared with SPI resin. However, within the Phytagel® modified resins, both fracture strength and modulus were higher for PH2–SPI composites when compared to PH4–SPI composites. It was reported that the yarn pull out lengths were higher in the cases of SPI and PH4–SPI resins. While the theoretical predictions for modulus values, based on the simple rule of mixture, were significantly higher than the experimentally obtained values, the fracture stress values were very close. As explained in

Table 9.15 Tensile properties of flax yarn reinforced SPI, PH2–SPI and PH4–SPI composites in the longitudinal direction

	Fracture stress (MPa)	Young's modulus (GPa)	Fracture strain (%)
Flax yarn/SPI composites	197.2	2.41	11.2
Flax yarn/PH2–SPI composites	220.2	4.11	7.5
Flax yarn/PH4–SPI composites	174.0	3.10	8.8

the case of ramie fiber/SPC composites, these resins were also prepared using significant amounts of water which is driven out during the drying and curing processes. As the resin dries, it shrinks pulling with it the yarns. The longitudinal shrinkage of the yarns significantly affects the modulus but not as much the fracture stress if the yarn does not kink. No kinking was observed in these composites. In the case of PH4–SPI composites, it was observed that the addition of 40% Phytagel® raised the resin viscosity significantly as it gelled quickly. The higher viscosity of the resin resulted in poor penetration and longer pull-out lengths and, consequently, lower modulus and strength values compared to PH2–SPI composites. Poor penetration of the resin was also a result of the high twist yarns used in the study. It was observed that the high twist in the yarn packs the fibers together leaving no space in between for the resin to penetrate. As a result, though bonded, the resin remained only on the yarn surface. Highly twisted yarns also increase obliquity factor (a function of the angle made by the fibers with the yarn axis) and making the yarn brittle and reducing the yarn strength, thus, resulting in lower composite strength. Lower twist yarns should perform much better in such cases.

The flexural properties in terms of flexural stress, strain and chord modulus (between 0.25% and 0.75% of the yield point) of the flax yarn reinforced composites with SPI, PH2–SPI and PH4–SPI composites are presented in Fig. 9.8. As in the case of tensile properties, flax yarn reinforced PH2-SPI composites showed significantly higher chord modulus and flexural stress, 7.8 GPa and 105 MPa, respectively, than the SPI (2.8 GPa and 48.9 MPa)
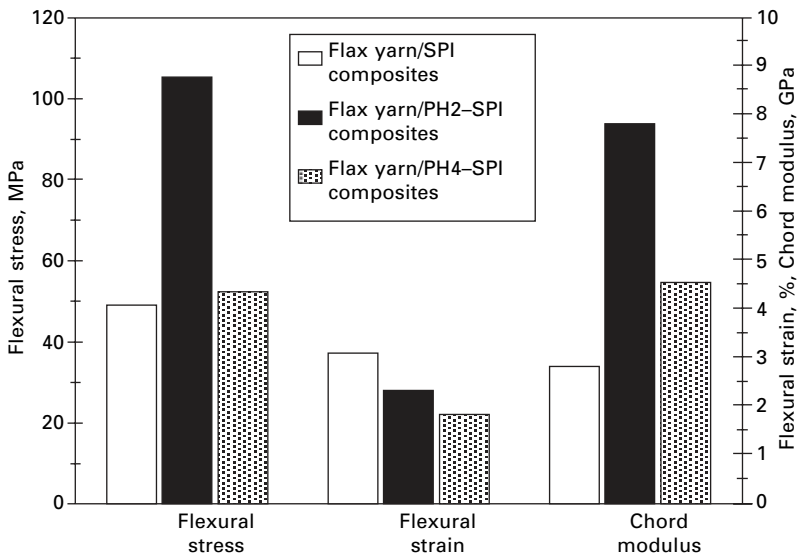
9.8 Flexural properties of flax yarn/SPI, flax yarn/PH2–SPI and flax yarn/PH4–SPI composites tested in lengthwise direction.

and PH4–SPI (4.5 GPa and 52.3 MPa) composites. The flexural strains for all three composites were within a narrow range. These results were consistent with the expectations.

In another study Chabba et al. [113] modified soy flour (SF) with GA (GA–SF) and reinforced it with flax yarns. During the impregnation and fabrication of composites, the flax yarns were held under high stress to achieve good orientation and to counter the effects of resin shrinkage. The cured composites had 60% yarn content (by wt). These composites exhibited fracture stress and Young's modulus of 260 MPa and 3.71 GPa, respectively. The flexural strength was about 174 MPa in the longitudinal direction.

As in the case of ramie fibers/SPC composites, these flax yarn reinforced composites have excellent mechanical properties comparable to steel. These green composites could also be used for indoor structural applications.

Fabric-reinforced composites

Chabba and Netravali [22, 32, 104] fabricated two dimensional composite sheets using flax fabrics and GA–SPC resin. They prepared composites with either all layers oriented at 0° (warp direction, longitudinal) or 90° (weft direction, transverse). Strips of flax fabrics, 2.5 cm wide and 13 cm long, were cut in the desired directions (warp and weft). Four strips were layered to fabricate each composite specimen and the weight of the fabric strips was recorded. Fabric strips were held under tension in a glass container. Pre-cured GA–SPC resin was poured over the strips and allowed to stand for 15 minutes at room temperature. The fabric strips were transferred to Teflon® coated glass plates. Further resin was added between the layers to assure good penetration and the specimens were allowed to dry in an oven at 35°C for about 24 hr. The dried specimens were cured in a mold by hot pressing at 125°C for 25 minutes at a pressure of 8 MPa. The fabric weight content was calculated to be 45% on the basis of final composite weight and initial weight of the fabric strips. The cured specimens were conditioned as per ASTM, prior to characterizing their properties.

Table 9.16 summarizes the tensile properties of fabric reinforced GA–SPC composites as well as the flax fabric, in both longitudinal and transverse directions. As can be seen from the data in Table 9.16, both fracture stress and modulus of the composites were higher in the transverse directions, merely reflecting fabric properties in the two directions. However, it is clear that the composite fracture stress and modulus values are significantly higher than the fabric values, as expected. It was noticed that during the tensile testing of the composites, the resin at the surface begins to crack at different locations as the composite is strained. This was because of the higher crimp in the fabric that allowed it to be strained while the cross-linked GA–SPC resin was comparatively more brittle. As the resin cracked the load was

Table 9.16 Tensile properties of flax fabric reinforced GA–SPC composites and flax fabric

Material	Test direction	Fracture stress (MPa)	Young's modulus (GPa)	Fracture strain (%)
Flax fabric	Longitudinal (warp)	50.3	1.01	21.0
Reinforced GA–SPC composite	Transverse (weft)	55.7	1.26	7.8
Flax fabric	Longitudinal (warp)	33.3	512.9	17.7
	Transverse (weft)	41.2	1017.9	7.1

transferred to the fabric layers and at some strain the composite fractured at one of these cracks. The fracture sequence in the longitudinal direction also showed similar resin cracking behavior, but at higher strains. The photographs also show some resin adhering to the yarns in the fabric indicating good adhesion. However, being brittle, most of the resin that cracked, seemed to separate from the fabric. Another reason for the resin separation from yarns was the highly twisted yarn used in the fabric which, as discussed earlier, limited the resin penetration.

Theoretical analysis of flax fabric reinforced GA–SPC composites in both directions was carried out using pcGINA© (PC based Graphical Integrated Numerical Analysis) software. This software was created by Dr Y. Gowayed and his group at Auburn University, Auburn, USA, for Pratt & Whitney, NASA Lewis and GE and was obtained from Dr P.L.N. Murthy, NASA Glen [104, 114–116]. Table 9.17 shows the comparison of the experimental and theoretical values of fracture stress and modulus of the flax fabric reinforced GA–SPC composites. The fracture stress values predicted by pcGINA in both longitudinal and transverse directions were 48.4 MPa. The modulus values predicted in the longitudinal and transverse directions were 1.09 GPa and 1.11 GPa, respectively. It is clear that the theoretical and experimental

Table 9.17 Comparison of experimental tensile properties of flax fabric reinforced GA–SPC composite with the theoretical predictions (by pcGINA©)

Source	Fracture stress (MPa)	Young's modulus (GPa)
Experimental (L)*	50.3	1.01
pcGINA© (L)	48.35	1.09
Experimental (T)*	55.7	1.26
pcGINA© (T)	48.35	1.11

L: Longitudinal, T: Transverse

values are not significantly different. This indicates that green composites using fabric- and soy-based resins could be designed to have required properties depending on the applications.

9.5   Conclusions and future trends

This chapter presents some of the recent research on environmentally friendly, fully biodegradable green composites made using various soy protein (SPI, SPC, SF) resins and their modified versions reinforced with random short ramie fibers, unidirectional ramie fibers and flax yarns as well as flax fabrics. The properties obtained, both tensile and flexural, are sufficient for many applications in packaging and as casings and other applications in consumer goods as well as in the automotive and housing industry. Some unidirectional composites using ramie fibers and flax yarns have sufficient strength for use as primary structural components in some applications. All the fibers and resins used in these composites are plant based and yearly renewable. At the end of their life these composites can be disposed of safely and easily or composted without harming the environment. Some of the modified SPC and SPI resins and the soy protein nanocomposite may be used as a replacement for petroleum-based non-degradable plastics. The green nanocomposite can be further reinforced with fibers, yarns or fabrics for use in many of the applications mentioned above. The SPC nanocomposites may be used in applications where higher thermal stability is desired.

Most of the current research in green composites is based on plant-based fibers because of their ready availability. There are several other resins and fibers, not based on plants, which can be used to make useful green composites. Synthetic biodegradable fibers and resins are also being developed or existing ones modified for use in green composites with improved properties. Biotechnology will also play a key role in this development [3, 54]. Thus research is already in progress to develop 'Advanced Green Composites' with superior mechanical properties, thermal stability and better moisture resistance using fully sustainable materials. As the petroleum becomes more expensive and scarcer in the not so distant future, there will be no alternative but to accelerate these efforts.

9.6   Acknowledgements

9.7   References

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