Soy Protein Based Green Composite: A Review

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Review Article

ABSTRACT

Natural polymers can be obtained from natural resources such as plants, animals etc. Natural polymers are easily decomposable, ecofriendly, sustainable, low cost and help us to reduce the pollution. Soy protein is one of the most easily available biodegradable polymers. However there are some drawbacks such as low water resistance and mechanical properties that limits its application. Therefore soy protein resin was further modified and characterized to improve mechanical properties, water resistance, and productive life which could facilitate the application of soy protein. Recently, soy protein based bio-nanocomposites has proven to be a promising option in improving mechanical and moisture barrier properties. Soy protein based green composites show potential applications for housing, transportation and rigid packaging. The aim of this review is to discuss the current state of research in the field of soy protein based green composites

INTRODUCTION

Today there are increasing demands for the use of environmental friendly materials that are biodegradable and can replace petroleum based synthetic polymers. Non degradability and environmentally hazardous nature of plastics and some composites are the main problems as plastic waste disposal management become a great challenge due to the unavailability of free land for solid waste disposal in regions of high population density [1]. Therefore scientists have focused their research on using materials from nature because of its biodegradability. Green composites are specific class of biocomposites, where a bio-based polymer matrix is reinforced by natural fibers. Synthetic plastics can be replaced by green composite products which make the environment free of plastic wastes.

Soy protein has attracted great research interest for the development of environment friendly protein materials with potentially good properties, such as regeneration, biocompatibility, biodegradability, etc. [2-6]. In addition to its use as a food ingredient, non-food applications of soy protein as polymeric materials have attracted increasing attention in recent years. Soy protein based composites show potential applications for housing, transportation and rigid packaging. Many researches on forming plastic and composites from soy protein resin were carried out [7-9]. Soy protein resins have been used to fabricate green composites for many applications such as hydrogels, adhesives, plastics, films, coatings and emulsifiers, and it has also been reported as a promising material for biotechnological and biomedical utilization.

COMPOSITION OF SOY PROTEIN

Soy protein is made from soybean that has been dehulled and deffated. Soybean contains roughly 18-20% oil, 40-45% protein, 25-30% carbohydrate, and 3% ash [10]. Soy proteins are complex macromolecules composed of amino acids such as cystine, arginine, lysine, hystidine, etc. which can be used for inter or intra molecular interaction as amino acids have many active sites available for molecular interaction [11]. Soy proteins are mostly globulin, with the 7S and 11S fractions representing 37% and 31% respectively, of the total extractable protein [12].

Soybean protein is commercially available in form of defatted soy flour (DSF), soy protein concentrate (SPC) and soy protein isolate (SPI). After soybeans are dehulled and the oil is extracted, the remaining protein and carbohydrate meal is ground into soy flour (SF) containing roughly 56% protein and 34% carbohydrate and is the least expensive of the three products. Soy protein concentrate (SPC) is produced by leaching out the water/alcohol-soluble carbohydrates from soy flour to obtain a product with 65-

75% protein and 18% carbohydrate. The purest and most expensive type of commercially available soybean protein is soy protein isolate (SPI) and is composed of over 90% protein.

PROPERTIES OF SOY PROTEIN FILM

Soy proteins consist of both polar and non-polar side chains therefore there are strong intra- and inter-molecular interactions, such as hydrogen bonding, dipole–dipole, charge–charge, and hydrophobic interactions. The strong charge and polar interactions between side chains of soy protein molecules restricts segment rotation and molecular mobility, which increase the stiffness, yield point, and tensile strength of soy protein films [13].

The isoelectric point of soy protein is pH 4.5, at which point the positive and negative charges on the protein will be equal, causing the protein to precipitate out of aqueous solution [14]. It has been found that the soy protein could not form a film at or near its isoelectric point (pH 4.5) due to the coagulation. However, proteins can be denatured and unfolded at pH values away from their isoelectric point, thus exposing their functional groups and increasing the intermolecular interactions. Therefore the mechanical properties of soy protein can be affected by its pH. In alkaline conditions most of the protein-based films show better physical properties during processing [15].

SPC and SPI both show brittle nature when processed without any modification and plasticizer. Interactions between proteins and other small molecules including water, plasticizers, lipids and other additives dispersed in the matrix influence the mechanical strength of protein networks. Number of factors including hydrophobicity, polymer chain length and surface charges can considerably affect the structural stability and mechanical behavior of SPI films [16]. Due to their low mechanical strength and high moisture sensitivity compared to synthetic materials, application of soy protein films is limited. However, SPI films have been shown to possess strong oxygen barrier properties, having permeability values roughly 500 times lower than low-density polyethylene films under low relative humidity environments [17]. Functionality of soy protein films can be improved by several approaches, one of which is to reinforce soy protein films with natural fibres, forming a composite material. Natural fibre reinforced composites are an attractive option because fibres are eco-friendly, biodegradable, sustainable, low cost, low density, and can be derived from waste streams [11]. Another approach based on blending of soy protein with other natural polymers and use of additive such as cross-linking agents, plasticizers for improving mechanical properties and moisture sensitivity of soy protein film.

CHEMICAL MODIFICATION OF SOY PROTEIN

Effect of Plasticizers on Soy Protein Films

The combination of intermolecular hydrogen bonding, disulfide bonding, hydrophobic interactions and electrostatic forces between protein chains typically leads to brittle films therefore it is difficult to process [18]. Plasticizers is use to break intermolecular linkage and therefore stabilizes protein in their primitive structure and makes the protein chains mobile [19]. Hence, addition of a plasticizer is generally used to reduce protein chain-to-chain interaction and induce film flexibility [20]. Plasticizer that contains polar groups should be compatible with soybean proteins. The plasticization effect of a plasticizer could be influenced by its ease of insertion and position within a three-dimensional protein network [21]. Molecular weight, numbers, and positions of hydroxyl groups of a plasticizer are all variables affecting its ability to plasticize soybean protein-based polymer.

Various researchers have studied the effect of different plasticizers on the mechanical properties and moisture absorption of the SP resins. Park et al. [22] and Song et al. [17] concluded that plasticizer content increases the flexibility, extensibility and water sensitivity of the film. Lim et al. [23] reported that addition of hydrophilic plasticizers to protein films increased their water sensitivity and weaken their barrier behaviour towards other gases and vapours due to the enhanced segmental movement of the polymer chains.

Glycerol is one of the most widely used plasticizer for soy protein films because of its small size and hydrophilic nature, which make it compatible with soy protein films. Routray et al. [24] studied the effect of glycerol content on SPI plastic by analyzing tensile testing, Fourier transform infrared analysis (FTIR), Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) and found that films obtained with 25% and 35% by weight of glycerol are flexible and have good mechanical properties. On further increasing the amount of glycerol causes a decrease in tensile strength and an increase in elongation at break due to the fact that glycerol reduces the interactions between protein chains, thereby increasing the chain mobility [25]. Kumar et al. [26] examined the morphology, water resistance and biodegradation of banana fiber reinforced soy protein composites and concluded that the tensile strength and modulus was highest with SPI matrix having 25% (W/W) glycerol. On further increases the concentration of glycerol resulted in a decrease in the tensile strength and modulus of the composites. Su et al. [27] concluded that higher proportions of glycerol plasticizer, at a particular temperature and relative humidity result in more water absorption and retention in protein films.

Reddy and Yang [9] used water as an effective plasticizer for biopolymeric materials. Plasticizers such as stearic acid, ferulic acid, sodium dodecyl sulfate and waterborne polyurethane have also been considered to improve the water vapor barrier properties of SPI films by increasing the degree of crosslinking of the SPI structure [28-30]. This result is attributed to reaction between the carboxylic group of stearic acid and amine, imine and hydroxyl groups of SPI, depending on the pH and temperature,

and resulting in internal plasticization [31]. Lodha and Netravali [32] reported that stearic acid acts as an effective replacement for glycerol to modify tensile, thermal and the moisture resistance properties of the SPI resin. They also proposed that Stearic acid can improve the Young's modulus of the SPI resin by three mechanisms. Firstly, stearic acid is hydrophobic in nature therefore the moisture absorption of SPI decreased. Secondly, being hydrophobic, unreacted stearic acid can phase separate, at least partially, and crystallize into tiny crystals. And therefore crystal behaves similar to nanocomposites. Thirdly, the Stearic acid can react with the hydroxyl groups to form ester bonds and with the amino side and end groups to form amide linkages, resulting in internal plasticization of the SPI resin.

Kumar et al. [33] compared the plasticizing effect between Thiodiglycol (TDG) and glycerol and results from optical transmittance, Scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and Dynamic mechanical thermal analysis (DMTA) testing indicated that a good compatibility occurred between TDG and the soy protein which improve their mechanical properties, thermal stability and water resistance. **Figure 1** indicated improved tensile strength of the Soy protein-Thiodiglycol films as compared to Soy protein–Glycerol film.
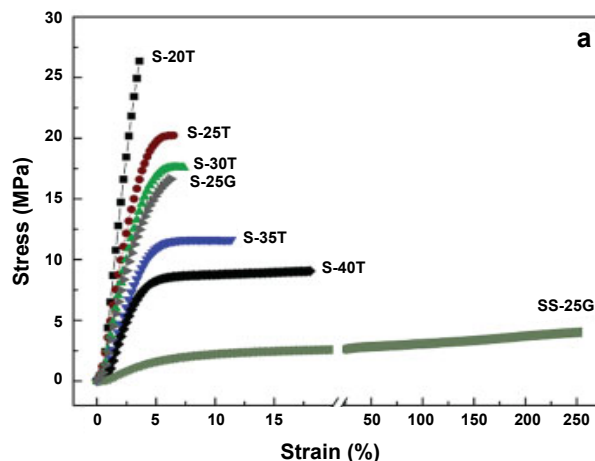

Figure 1. Stress–strain curves [33].

pH Treatment

It is required for modification of soy protein film Since soy proteins exposed to pH conditions far below or above their isoelectric point (pH 4.5) will experience intramolecular repulsion as increasing positive (acidic pH) or negative (alkaline pH) charge density causes the protein to unfold, exposing hydrophobic and disulfide groups which can participate in intermolecular bonding therefore SPI films can be prepared at both acidic and alkaline conditions, but films prepared at alkaline conditions (pH 8–11) were found to have superior mechanical properties and lower water vapour permeability (WVP) than SPI films prepared under acidic conditions (pH 1–3) [34].

Kim and Netravali [15] fabricated composite based on soy protein –hemp yarn and investigated the effect of pH on mechanical and interfacial properties. **Figure 2** showed that on increasing pH, SPC resin/hemp yarn IFSS increased significantly from 17.7 MPa at pH 7 to 28.0 MPa at pH 10. Addition of NaOH causes unfolding of soy protein as reactive groups on the peptide chain of soy protein are expose which result in increased intermolecular interaction with hydroxyl groups of cellulosic hemp yarn. On further increasing alkaline condition beyond pH 10, it seemed to increase the electrostatic repulsive forces along soy protein molecules which result in reducing the interactions with cellulosic fibers.
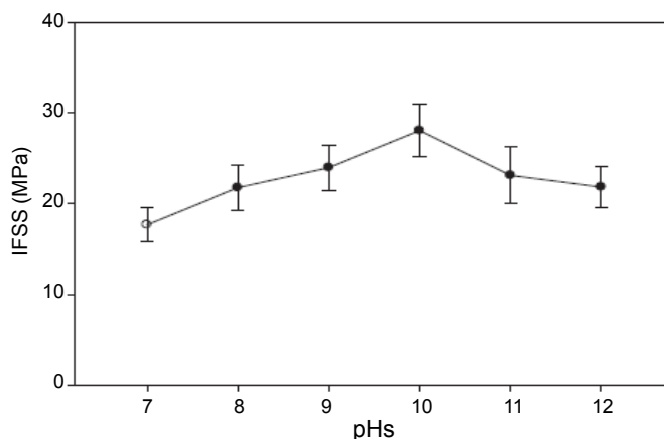

Figure 2. Effect of pH on IFSS of hemp yarn and SPC resin [15].

Effect of heating: Park et al. [14] investigated the heating effect of soy protein solution and found that mechanical properties of DSF, SPC and SPI film-forming solutions prepared at pH 9 and held at 95°C for 45 minutes had superior mechanical properties to solutions heat treated at 75°C for 45 minutes (pH 9). They also found that DSF, SPC and SPI solutions that were not heated were unable to formed films. Therefore heating and alkaline conditions are believed to promote soy protein interactions [35].

Cross-linking agent: It is another kind of additive which improve mechanical and water resistance properties of the soy protein plastics. Formaldehyde, acetic anhydride, glyoxal, Zinc sulfate, glutaric dialdehyde, epichlorohydrin are some cross-linking agents used in soy protein plastics [13]. Chabba and Netravali [36] studied the effect of cross-linking agent glutarldehyde (GA) on SPC resin system and reported that strength of the SPC resin increased significantly and moisture absorption decreased. Chabba et al. [37] modified soy flour (SF) by cross-linking it with glutaraldehyde (GA) and characterized for its tensile and thermal properties and reported that 40% GA solution and 0% glycerol (CSF) was selected as the optimum blend concentration for composites as shown in **Figure 3**.
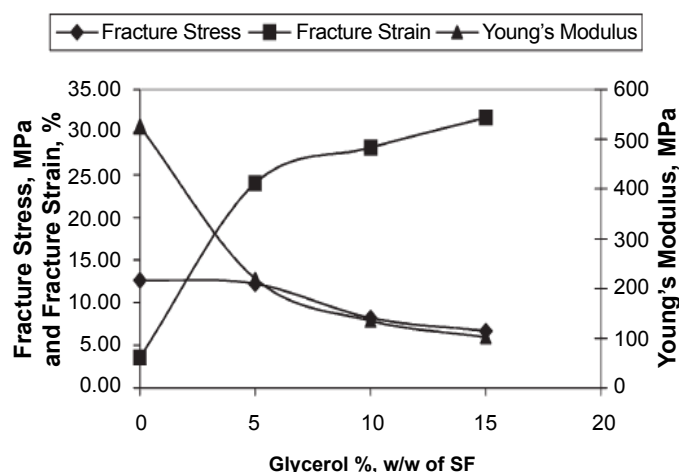

Figure 3. Effect of glycerol on the tensile properties of cross-linked SF resin containing 40% GA [37].

Huang and Netravali [38] examined the cross linked structure between SPC and Phytagel which showed improved tensile strength, modulus, thermal stability and moisture resistance as compared to the unmodified SPC resin and reported that incorporation of 40% Phytagel and 20% glycerol led to an overall 340% increase in the tensile strength (over 50 MPa) and approximately 360% increase in the Young's modulus (over 710 MPa) of the SPC resin.

Blending

Soy protein with other natural or synthetic polymers is another approach for enhancing the mechanical properties and moisture sensitivity of soy protein. Blending with biodegradable polymers such as gelatin, starch, cellulose and protein ensure that the final blend films can still be regarded as "green". Kim and Netravali [39] modified soy protein concentrate (SPC) by blending with gelling agents such as Agar, Agargel, and Phytagel and compared the effect of gelling agent concentration on the tensile and moisture resistance properties of modified SPC films. Phytagel modified SPC films (30% Phytagel) showed highest improvement about three times in both tensile stress and Young's modulus, Agar-modified SPC films (30% Agar) showed moderate improvement in the tensile stress and Young's modulus and improvement in tensile properties of Agargel-modified SPC films were in between Phytagel modified SPC films and Agar-modified SPC films as compared to control SPC films.

Since hydrophilicity is inherent in natural polymers, these blends cannot solve the moisture sensitivity problem of soy protein films to such extent therefore synthetic polymer which are biodegradable such as poly(vinylalcohol) (PVA), Poly (lactic acid) (PLA), poly (butylene adipate-co-terephthalate) (PBAT), can be used but blending of soy protein may result immiscible blend system as soy protein is hydrophilic in nature and PLA, PBAT are hydrophobic so they do not have good interfacial adhesion. This causes lots of defects in the surface, which will lead to low strain and strength under stretching therefore compatibilization is necessary for the immiscible blend system which can improve the properties of the blends greatly using compatibilizers such as maleic anhydride grafted PLA and maleic anhydride grafted PBAT. Compatibilizers are required to obtain high-performance polymer blends. Compatibilization of polymer blends mainly involves (1) reduction of the interfacial tension, (2) stabilization of phase morphology during subsequent processing, and (3) enhancement of interfacial adhesion [40]. Zhu et al. [41] produced soy protein concentrate (SPC) and Poly (lactic acid) (PLA) composites using a twin-screw extruder. By reactive extrusion, free radical grafting of maleic anhydride (MA) onto PLA was performed and PLA-g-MA was used as a compatibilizer in the composites and they examined the effects of compatibilizer concentration and degree of functionality on the tensile, morphological, and thermal properties of PLA/SPC composites and collectively concluded that the tensile strength of the composites containing 4 phr compatibilizer increased by 19% compared to that of the uncompatibilized one and also resulted in finer domain sizes of SPC.

Otaigbe and Jane [42] modified soy protein plastic composite by blending soy protein with bioabsorbable polyphosphate fillers to form composites with enhanced properties such as water resistance, stiffness, and strength for beneficial use in load-bearing applications and concluded that the polyphosphate fillers can change the failure micromechanism of the unreinforced soy plastic from a brittle to a pseudo-ductile mode therefore these materials are suitable for many load-bearing applications in both humid and dry environments. Cao et al. [43] prepared composite films (containing 0.1 g glycerin/g protein) made of SPI and gelatin and investigated the mechanical, swelling, and optic properties of composite films and concluded that as the proportion of gelatin increased, tensile Strength, Elastic Modulus and swelling capacity of the composite films increased and the films became much more transparent, easier to handle. So, gelatin could enhance film strength and flexibility. Guerrero et al. [44] added epoxidized soybean oil (ESO), virgin extra olive oil, variety picual (OO) or lactic acid (LA) on SPI based film and found the improved hydrophobic character of the films which is prepared by compression.

SOY PROTEIN FIBER – REINFORCED COMPOSITE

Dispersed fibers in fiber-reinforced composites have ability to absorb energy and arrest the propagation of structural failure therefore composites become tougher and mechanically stronger than the soy protein film Netravali [45]. Therefore many research efforts were made to improve the properties of the soy protein using natural fibers. Liu et al. [46] performed alkali treatment of Grass fibers which reduced the inter-fibrillar region of the fiber by removing hemicellulose and lignin led to a more homogenous dispersion of the biofiber in the matrix and increase in the aspect ratio of the fiber in the composite resulting in an improvement in mechanical properties therefore alkali treatment of the fibers is necessary to get composites with moderate mechanical properties as well as better adhesion between fibers and matrix.

Kim and Netravali [47] investigated Interfacial shear strength (IFSS) between ramie fiber and soy protein-based resins using the microbond technique and concluded that the IFSS increased with the protein content in the resins. The IFSS values ranged from 9.5 MPa for SF resin (53% protein), 20.7 MPa for SPC (72% protein) and 25.7 MPa for SPI resin (90% protein). Saenghirunwattana et al. [48] prepared soy protein/PLA biocomposite with silane 1.5% (w/v) treated cornhusk fiber and reported that on increasing% fiber loading from 3 to 5 wt%, strength and modulus of the composites improved due to better interfacial adhesion between the PLA–soy protein matrix and cornhusk fibers and also triethoxy vinylsilane, a functional groups in the silane coupling agent which improved the interfacial adhesion of soyprotein/PLA/cornhusk fiber biocomposites.

Chabba and Netravali [49] modified SPI using glutarldehyde and poly (vinyl alcohol) followed by fabrication of composites with flax yarns and fabrics which resulted in improved properties. Lodha and Netravali [50] modified SPI resin with stearic acid as a plasticizer and fabricated composites with ramie fibers which showed improved tensile properties in both axial and transverse directions as compared to those made using SPI resin. Nam and Netravali [51] prepared composite of SPC resin and ramie fibers and reported that with 65% wt fiber loading, tensile strength and Young's modulus of composites were significantly higher compared to those of pure SPC resin. They also concluded that there was a good interfacial bonding between SPC resin and ramie fibers which was indicated by Scanning electron microscope (SEM) micrographs of the tensile fracture surfaces. Huang and Netravali [52] modified SPC resin with nano clay particles and cross-linking agent glutaraldehyde. Modified SPC resin showed significantly improved mechanical properties. They fabricated composite using modified SPC resin and flax yarns and fabrics. The flax yarn composites showed a longitudinal tensile failure stress of up to 298 MPa and Young's Modulus of up to 4.3 GPa. Both yarn and fabric reinforced composites have the potential to replace non-biodegradable materials in many fields due to their good mechanical properties. Huang and Netravali [53] investigated the micro/nano-sized bamboo fibril (MBF) reinforced SPC resin composites and **Figure 4** showed that fracture stress, Young's modulus and the toughness of the MBF reinforced SPC increased significantly while the fracture strain did not change significantly with the incorporation of MBF due to the flexibility and the entangled morphology of the MBF. They further modified MBF reinforced SPC using a silane, (3-isocyanatopropyl) triethoxysilane (ITES) as cross linking agent and finally reported that significant increase in the fracture toughness.
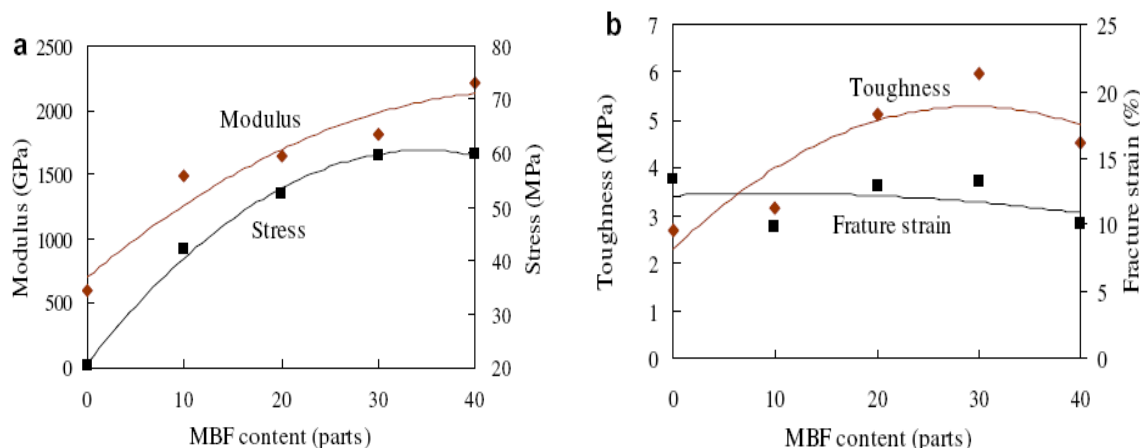

Figure 4. Mechanical properties of the MBF reinforced SPC composites (containing 15 parts of glycerol): (a) Young's modulus and fracture stress vs. MBF content, (b) toughness and fracture stain vs. MBF content [53].

Chabba et al. [37] examined glutaraldehyde cross-linked soy flour (CSF) resin and flax yarn composites and compared the fracture stress and Young's modulus of composite with CSF resin and found that with 60% fiber weight fraction, exhibited improvements of over 700% in fracture stress and over 2000% in Young's modulus in the longitudinal direction as compared to the CSF resin. Behera et al. [54] prepared jute reinforced soy milk based composites using non-woven and woven jute fabrics. Without any chemical treatment on jute surface and use of hazardous chemical solvent using compression molding process composite with 60 wt% jute felt showed highest tensile strength of 37.1 MPa and tensile modulus of 1040 MPa. Drzal et al. [55] reported increased in strength and higher heat deflection temperature on addition of hemp fibers and Soy Flour.

Mohanty et al. [56] fabricated soy flour based biocomposites using industrial hemp fiber as reinforcing material and found significant improved mechanical properties including tensile properties, flexural properties and impact strength, as well as the heat deflection temperature with the addition of hemp natural fiber to the soy flour bioplastics. Huang and Netravali [57] prepared micro/nano-composite of soy protein concentrate (SPC) reinforced with micro/nano fibrillated cellulose (MFC) which have potential to replace petroleum-based materials in many fields. **Figure 5a** showed the SEM photomicrographs of smooth fracture surfaces of the SPC resin while the surface roughness of MFC modified SPC resins increased as well as short fibrils protruding out of the resin can also be observed **Figures 5b and 5c**. Due to the high mechanical properties of MFC, fibril breaking can consume large energy and high aspect ratio of MFC and good interfacial properties SPC/MFC improved mechanical and physical properties of composite showed fracture stress of 88.2 MPa and Young's modulus of about 4.1 GPa. On further modification of SPC/MFC composite by blending with gellan showed further improvement in fracture stress and Young's modulus. SPC resin containing glycerol (1.5 parts), gellan (40 parts) and MFC (40 parts) had fracture stress of over 122 MPa and Young's modulus of about 5.8 GPa.
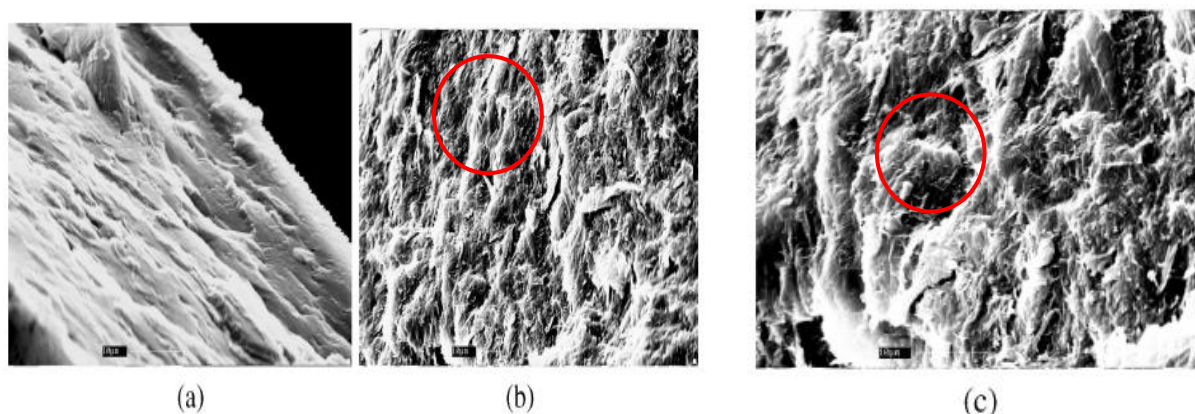

Figure 5. SEM photomicrographs of the fracture surfaces of (a) SPC with SPC/glycerol of 100/15, (b) modified SPC with SPC/glycerol/MFC of 100/15/40 and (c) modified SPC with SPC/glycerol/MFC/gellan of 100/1.5/40/40 [57].

SOY PROTEIN BIO-NANOCOMPOSITE

Recently, bio-nanocomposites is a new class of material which has proven to be a promising route in improving mechanical and barrier properties of biopolymers. Bio-nanocomposites consist of a biopolymer matrix reinforced with particles with at least one dimension in the range of 1–100 nm and have improved properties due to high surface area and high aspect ratio of nanoparticles [58-60]. Nano-sized fillers act as a reinforcement which transferred matrix tension and improve mechanical and barrier properties [61-64]. Nanocomposites have been studied extensively because many new exciting materials with novel properties were generated as addition of nano-filler improved the mechanical, physical, thermal, barrier, water resistance, and other properties of soy protein materials. The nano sized fillers can be either organic or inorganic such as clay (e.g. Montmorillonite, (MMT), hectorite, sapnotite, and laponite), natural biopolymers (e.g. chitosan), natural antimicrobial agents (e.g. nisin), metal (e.g. silver), and metal oxides (e.g. TiO_2). The properties of nanocomposite materials depend not only on the properties of their individual parents, but also on their morphology and interfacial characteristics. Bio-nanocomposites can be obtained by several methods which include in situ polymerization, solution exfoliation, and melt intercalation [65,66].

Montmorillonite (MMT) is extensively used as a nanoparticle for soy protein plastic due to easy availability at a low cost, abundance in supply and physical characteristics including high elastic modulus (178 GPa), high surface area (750 m^2/g), and high specific aspect ratio (50-1000). Kumar et al. [67] prepared SPI/Montmorillonite (MMT) bio-nanocomposite films using melt extrusion and found significant improvement in tensile strength, storage modulus, water barrier property, glass transition temperature and thermal stability of the films with the addition of MMT. As MMT content increased from 0 to 15%, tensile strength increased due to high rigidity and aspect ratio of MMT and interaction of SPI with MMT. However Percentage of elongation decreased as the MMT content increased from 5% to 15% as MMT restricted the soy protein molecules motion in bio-nanocomposite films and interaction of SPI with MMT. They also concluded that properties of the SPI–MMT films were significantly affected by the pH of film forming solutions, MMT content, and extrusion processing parameters.

Nayak et al. [68] prepared polycaprolactone (PCL)/soy protein isolate (SPI) blend with organically modified montmorillonite

clay by melt compounding and reported a great improvement in tensile strength. Tensile strength of the nanocomposite containing 5 wt% clay is a little smaller than that of the nanocomposite containing 2.5 wt% clay. **Figure 6** showed the Transmission electron microscopic (TEM) photographs for 5 wt% of clay, agglomerated particles formed by filler-filler interaction and filler agglomerates reduce the interfacial area between filler and matrix polymer and act as a stress concentrator, with a detrimental effect on the tensile strength of a material [69,70].
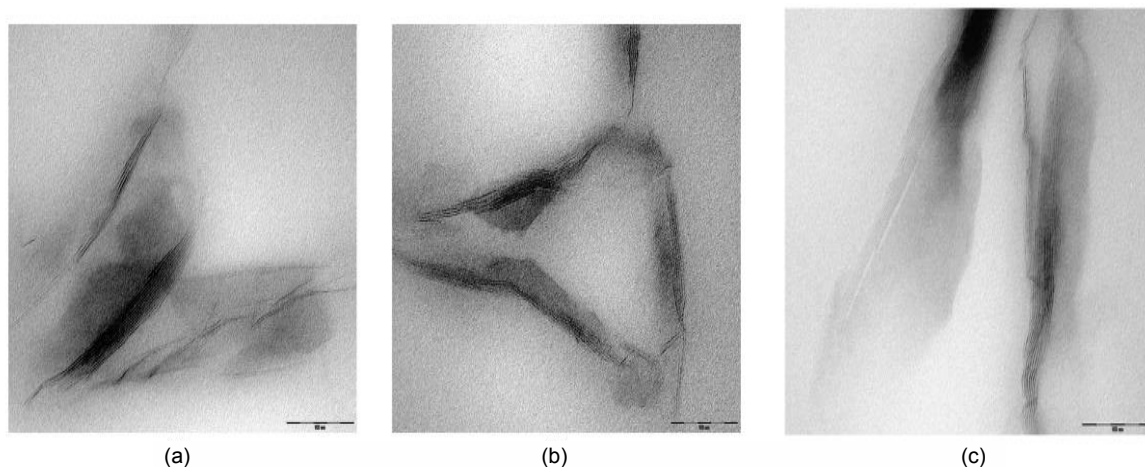

(a) (b) (c)

Figure 6. TEM photographs of PCL/SPI/organoclay hybrids containing (a) 1, (b) 2.5, and (c) 5 wt% organoclay [68].

Huang and Netravali [38] modified Phytagel (PH)-Soy Protein Concentrate (SPC) resin (40% Phytagel) by incorporated 7% clay nanoparticles resulted in increased young's modulus, tensile strength and thermal stability. **Figure 7** showed the XRD patterns of pure Cloisite Na+ particles and CPH-SPC resins with various amounts of nano-clay particles which indicated the completed exfoliation and dispersion of clay particles into CPH-SPC as the peak obtained for pure clay at around 9° disappeared in the CPH-SPC resins. Strong interaction between clay and SPC due to hydrophilic nature prevents clustering of the nanoparticles.
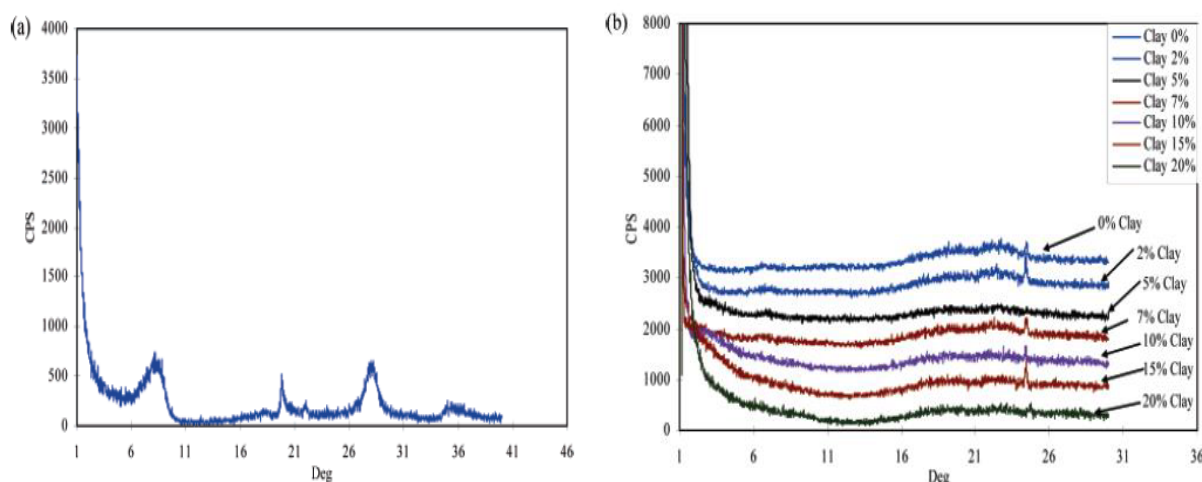

Figure 7. (a) XRD pattern of Cloisite Na+ clay powder and (b) XRD pattern of CP-SPC resin with different clay loadings [Y-axis)% intensity, X-axis) goniometer angle [38].

Wang et al. [71] suggested that addition of 0 to 30 wt% of cellulose whiskers to reinforced soy protein isolate (SPI) plastic improved tensile strength and Young's modulus of the SPI/cellulose whisker composite. As the content of cellulose whiskers increased it resulted in greater thermal stability and water-resistance of SPI matrix due to cross-linking networks caused by intermolecular hydrogen bonds between the cellulose whiskers and the SPI matrix. Lu et al. [72] incorporated chitin nano-whiskers (0 to 30 wt%) into SPI matrix and concluded that as chitin content increases from 0 to 20 wt%, Young's modulus and tensile strength increases as compared with a glycerol plasticized SPI sheet. Increased content of chitin whiskers in the SPI matrix improved water-resistance property of SPI matrix. They also suggested that there is a improvement in properties due to three-dimensional networks of intermolecular hydrogen bonding interactions between filler and filler and between filler and SPI matrix Iman et al. [73] examined nanocomposites based on glutaraldehyde (GA) cross-linked soy flour (SF), jute fabric and cellulose whiskers (CWs) in combination with nanoclay which is used as reinforcing agents and reported a strong interfacial interaction between the filler and the matrix also composite with 5% CWs was found to show better physical properties than those of either unfilled composites or containing lower percentages of CWs. Rahman et al. [74] reported the significant improvements in Young's modulus, tensile strength and thermal stability nanocomposite when dispersed eggshell nanopowder (ESNP) were incorporated

in SPI using solution casting process. Above studies have shown that mechanical, thermal and water resistive properties of the bio-nanocomposites are significantly improved and dependent on the amount of nanofillers.

Behera et al. [75] found improved mechanical properties of jute reinforced soy composite by utilizing Cloisite 30B nanoclay as an additive. For 5 wt% clay loaded composite the Tensile Strength, Flexural Strength and storage modulus were 1.55, 1.51, and 2.62 times greater than that of nanoclay free jute-soy composite respectively. Swain et al. [76] investigated the packing application of soy protein and Cloisite130B nanocomposites by solution intercalation process and found that for 8% clay concentration the oxygen permeability was reduced by 6 times as compared to the 0% clay loading as clay nanoparticles act as physical obstacle retarding the movement of the gas which can be shown in **Figure 8**.
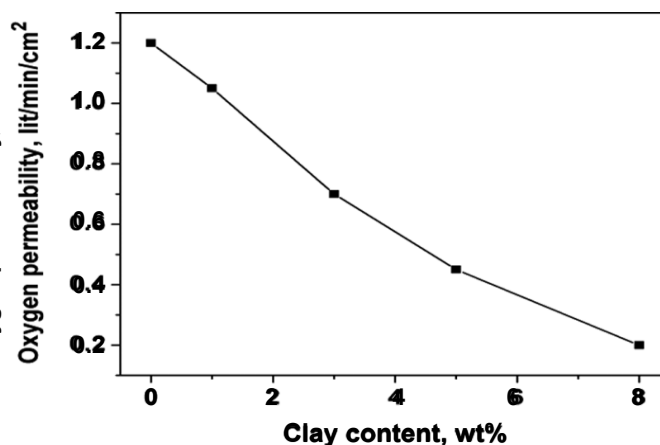

Figure 8. Oxygen permeability values of the bio-nanocomposites as a function of clay wt% at a pressure of 5 psi [76].

SOY PROTEIN COMPOSITE IN BIOMEDICAL FIELD

Soy protein has advantages over the various types of natural proteins employed for biomedical applications due to its low price, non-animal origin thus carrying no risk of transmissible diseases which pose a danger in human, relatively long storage time and stability and degradation into natural components.

Various researchers in the biomedical field have investigated the soy protein, as a natural biomaterial for various applications such as tissue regeneration, bioactive bone fillers and wound dressings. It was also reported that soybean-based products promote tissue regeneration, such as new bone growth. Furthermore, these materials integrate into the blood clot and stimulate collagen deposition and therefore have high potential for wound-healing applications [77]. Peles et al. [78] incorporated antibiotic drug gentamicin into the SPI matrix and investigated the effects of gentamicin release on bacterial inhibition and wound-dressing applications. They reported SPI films exhibit a high potential for use as wound dressings. Soy protein-based thermoplastic reinforced with tricalcium phosphate was investigated for orthopaedic biomedical applications [79]. Merolli et al. [80] used soy bean based bone filler and demonstrated that it has the ability to promote bone formation in a rabbit model. It was highlighted that the material is cost effective and it can be prepared readily, which are two important advantages for its application as bone filler. Lin et al. [80] produced soy and zein fibers for tissue scaffolds for skin regeneration by applying electrospinning.

Soy hydrogels made by different fabrication processes have been used for molecular delivery and other biomedical applications. Snyders et al. [81] also used soy protein and poly ethylene glycol hydrogels to prepare moist wound dressings and a transdermal drug delivery system. Chien et al. [82] fabricated non-modified soy protein hydrogels for biomedical application. Properties of soy hydrogels was changed with increased wt% of soy protein. Drug release properties and the biocompatibility of the hydrogels in vitro and in vivo were tested for applicability of soy protein as a hydrogel. As gelled soy hydrogels were able to be injected in vivo showed biocompatibility and degraded over approximately three weeks, indicating its potential use for wound healing applications and other minimally invasive procedures [83].

In the particular case of SPI the moderate concentration of polar, non-polar and charged amino acids, enables incorporation of a variety of drugs [84]. Additionally, because of this balanced composition of different types of amino acids, SPI has a higher capability to be incorporated with a variety of drugs in comparison to zein, human or bovine serum albumin [85]. Thus soy proteins, because of their inherent properties represent an attractive system for controlled drug delivery. Nayak et al. [85] prepared nanocomposite films containing SPI and montmorillonite (MMT) by the extrusion technique for the control release of ofloxacin as drug model. It was observed that >80 wt.% of the drug was released at pH 7.4 in the medium within 8 hours; while for pH 3.2 < 44 wt.% ofloxacin was released within 4 hours indicating that this nanocomposite is appropriate for drug release vehicles in basic environments [86].

CONCLUSION

Soy protein based films and composites show poor mechanical and moisture resistance properties which can be improved by chemical modification methods. The resulting film properties depend on the methods of modification and conditions. The type of plasticizers and the ratio of the plasticizers in the mixtures had a significant effect on the water barrier and mechanical properties of SP films. Other factors such as pH, heating and blending also played important roles in the formation and properties of soy protein films. Soy protein films prepared at alkaline conditions as compared to acidic medium were found to have more superior mechanical properties. Fiber reinforced soy protein composites were mechanically stronger and tougher than the protein film due to better interfacial adhesion between the soy protein matrix and fibers also soy protein based nanocomposite have improved thermo-mechanical and water resistive properties which depend on the amount of nanofillers.

The emerging fields of applications of soy protein in biomedical and material industry in the last few years indicate that research efforts in this area will increase in the near future application of soy-protein based products.

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