Biomacromolecules **2006,** *7,* 2783−2789

Characterization of Nano-Clay Reinforced Phytagel-Modified Soy Protein Concentrate Resin

Xiaosong Huang and Anil N. Netravali*

Fiber Science Program, Cornell University, Ithaca, New York 14853-4401

Received June 23, 2006

Phytagel and nano-clay particles were used to improve the mechanical and thermal properties and moisture resistance of soy protein concentrate (SPC) resin successfully. SPC and Phytagel were mixed together to form a cross-linked structure. The Phytagel-modified SPC resin (PH-SPC) showed improved tensile strength, modulus, moisture resistance, and thermal stability as compared to the unmodified SPC resin. The 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. Nano-clay was uniformly dispersed into PH-SPC resin to further improve the properties. The PH-SPC (40% Phytagel) resin modified with 7% clay nanoparticles (CPH-SPC) had a modulus of 2.1 GPa and a strength of 72.5 MPa. The dynamic mechanical properties such as storage modulus together with the glass transition temperature of the modified resins were also increased by the addition of clay nanoparticles. The moisture resistance of the CPH-SPC resin was higher as compared to both SPC and PH-SPC resins. The thermal stability of the CPH-SPC resin was seen to be higher as compared to the unmodified SPC.

Introduction

In the past few years, biodegradable polymers have attracted much attention due to the environmental problems caused by petroleum-based nondegradable materials.[1−6] In the future, polymers will not only have to be environmentally friendly and fully degradable, that is, "green", but also will have to offer superior mechanical properties and thermal stability, if they have to successfully replace conventional petroleum-derived plastics.

Soy protein has been considered to be one of the very promising raw materials for obtaining commercially useful plastics. Soy protein, which consists of 18 different polar and nonpolar amino acids, is globular, reactive, and often water soluble.[7,8] Soy proteins generally contain a wide range of molecular sizes. Based on the ultracentrifugal sedimentation fractions, soy protein can be classified as 2S (S stands for Svedberg units), 7S, 11S, and 15S fractions.[9,10] Out of these, 7S and 11S are the two major fractions.[10] The 7S globulin fraction is a trimer of glycoproteins, known as α (57 kDa), α' (58 kDa), and β (42 kDa).[11,12] The 11S fraction consists of glycinin with a molecular weight of 320−360 kDa.[10]

Two major drawbacks of soy protein, which have severely limited its commercial applications, are its high brittleness and moisture sensitivity.[2,3,13,14] Soy protein contains several amino acids containing hydrophilic groups, which make soy protein products very moisture sensitive. Without plasticizer, the brittleness of soy protein products makes it very difficult to process. Because of its brittleness, both fracture strain and strength of soy protein are low. Extensive research has been conducted to modify commercially available soy protein products, such as soy protein concentrate (SPC) and soy protein isolate (SPI).[2−4,13−16] SPC contains 68−72% proteins, 19−21% carbohydrates, 4−6% moisture, 0.5−1.0% crude free lipids, 3.4−4.8% crude fibers, and 3.8−6.2% ashes.[15] Glutaraldehyde has been used to cross-link soy protein molecules to increase mechanical properties and lower moisture resistance.[2−4,17] Polyphosphate has also been used to improve the stiffness and moisture resistance of soy protein.[18] Incorporating stearic acid into soy protein has also been shown to reduce the moisture sensitivity of SPI due to the inherent hydrophobic nature of the stearic acid.[14]

Gellan is an exocellular heteropolysaccharide produced by fermentation.[19] The native gellan is produced by the bacterium species known as *Pseudomonas*.[19,20] The native gellan produced from *Sphingomonas paucimobilis* is composed of a linear repeating tetrasaccharide sequence of D-glucose, D-glucuronic acid, and L-rhamnose in the ratio of 2:1:1.[20] Gellan forms weak gels in water in the absence of salts. However, in the presence of monovalent or divalent ions, a strong gel is formed through ionic and hydrogen bonds. Appropriate cations screen the electrostatic repulsion between the ionized carboxylate groups and serve as cross-linking points to cross-link the polysaccharide helix structure.[21,22]

Gellan is commercially sold by Sigma under the brand name of Phytagel, which is commonly used as a gelling agent substitute for agar.[19,20] It can form a colorless high-strength gel in water in the presence of cationic ions. In the presence of salts, carboxylate groups interact with the ions and act as cross-linking points. Intra- and intermolecular hydrogen bonding can also be formed through the hydroxyl and carboxyl groups. The carboxyl groups on glucuronic acid can also react with the amine, hydroxyl, and carboxyl groups present in soy protein under specific pH conditions.[23] The hydroxyl and carboxyl groups in Phytagel can also form hydrogen bonding with some hydrophilic groups on SPC.[23]

Nanocomposites, with nanoparticles dispersed, have been studied extensively due to their capability to improve mechanical, physical, thermal, and barrier properties with very low nanoparticle loading of 1−5 wt %.[24−28] For such composites, montmorillonite (MMT) and other clay nanoparticles have been used by many researchers.[29−33] With a structure of stacked platelets and one dimension of the platelet in the nanometer

---

* Corresponding author. E-mail: ann2@cornell.edu.

10.1021/bm060604g CCC: $33.50

scale, MMT has a high aspect ratio when exfoliated. If the platelets are dispersed properly, its nanosize can provide a significant amount of interface between the clay and the matrix resin with only a small weight percentage of MMT. This contributes to the excellent mechanical and physical properties of the nanocomposites.[29−33]

In the present research, SPC-based resin was modified in two steps. In the first step, Phytagel was used to form a cross-linked, interpenetrating network-like (IPN-like) structure with SPC. The effect of Phytagel on the mechanical and thermal properties of the SPC resin was studied. In the second step, the Phytagel-modified SPC was further modified using nano-clay to form nanocomposite and thus improve its properties. The nanocomposite material was characterized for its mechanical and thermal properties, and moisture resistance.

Experimental Section

Materials. SPC powder, ARCON S, was provided by Archer Daniels Midland Co., Decatur, IL. Analytical grade of Phytagel was acquired from Sigma-Aldrich Co., St. Louis, MO. Analytical grade glycerol was obtained from Fisher Scientific, Pittsburgh, PA. Both chemicals were used as received. Clay particles were obtained from Southern Clay Products, Inc., TX, under the brand name of Cloisite Na^+.

Preparation of Nano-Clay and Phytagel-Modified SPC Resin. Pure SPC resin was prepared by mixing SPC powder with distilled and deionized water in a ratio of 1:15 by weight. To make SPC processable and reduce its brittleness, a specified amount of glycerol was added as a plasticizer. SPC suspension was homogenized via a magnetic stirrer for 30 min. The suspension was then kept in a water bath at 75 °C for 30 min. This process is called the “procuring” of SPC resin. The “procured” SPC suspension (or slurry) was cast onto Teflon-coated glass plates and dried in an air-circulating oven at 35 °C for 16 h. The thickness of the sample sheets was controlled by spreading the SPC sample suspension with 7 g solid content onto the 18 cm × 18 cm bowl-like Teflon-coated glass plate mold. Because of the low viscosity of the SPC suspension, it can spread in the mold uniformly and the dried SPC sheets have very even thickness. The dried SPC sheets were finally hot pressed (cured) on a Carver hydraulic hot press (model 3891-4PROA00) for 25 min at 120 °C under a pressure of 7 MPa. Thicknesses of the cured SPC sheets varied between 0.12 and 0.13 mm.

The Phytagel-modified SPC resin (PH-SPC) was prepared in a similar way. Varying amounts of Phytagel (5%, 10%, 20%, 30%, 40%, and 50%, all of the percentages in this research refer to the weight percentage based on SPC) were dissolved in distilled water to form a solution or weak gel, which was then added to the initial SPC suspension (with glycerol) prepared by the steps described above. The precuring was achieved by reacting the mixture at 75 °C for 30 min. The precured PH-SPC sheets were dried and cured using the same procedures described as above for SPC. To study the plasticization effect and find out the optimum working percentage, glycerol was added in various proportions (5%, 10%, 12.5%, 15%, and 20%).

Before preparing the clay-modified PH-SPC nanocomposites (CPH-SPC), Cloisite Na^+ particles were purified. The particles were first dispersed into distilled and deionized water using a magnetic stirrer and ultrasonication. One gram of clay was dispersed into 200 mL of water by magnetic stirring for 10 h. The clay slurry was then further ultrasonicated for 30 min to improve dispersion and further exfoliation. The resulted clay suspension (slurry) was stabilized for 1 week before removing the nonexfoliated, larger aggregates that settled down. A freeze-drier was used to get the purified nano-clay powder from the stabilized slurry. The purified clay powder was redispersed into the distilled water in a weight ratio of 1:100 to form a yellowish clay slurry, which was stable due to the Brownian motion of the fully exfoliated dispersed nanosized particles and ready for dispersion in SPC resin. The SPC powder and Phytagel were first dispersed into distilled water separately and then mixed together using a magnetic stirrer. The uniform mixture was precured at 75 °C for 25 min. Various amounts of dispersed clay slurry were directly introduced into the precuring mixture. Another 5 min was needed to complete the precuring step and to obtain good nano-clay particle dispersion. The final solution with different clay loadings was dried into sheets and cured using the same procedure as described above for SPC sheets.

All cured SPC and modified SPC resin sheets were conditioned at 21 °C and 65% relative humidity (R.H.) for 72 h prior to characterizing their tensile properties and moisture content. All other characterization methods such as thermal properties and dynamic mechanical properties were conducted without conditioning the specimens.

Characterization of Resin Properties. An Instron tensile tester (model 1122) was used to characterize the tensile properties of SPC and modified SPC resins. The effect of Phytagel content, nanoparticle loading, and glycerol content on tensile properties was studied. Fracture stress, fracture strain, and Young’s modulus of the modified SPC resins were measured according to ASTM D 882-97. The test specimens (strips) were cut to dimensions of 10 mm × 80 mm. The thickness of the specimens varied between 0.12 and 0.13 mm. The gauge length for tensile tests was set at 50 mm, and the strain rate was 0.5/min. All specimens were conditioned according to ASTM 1776 at 21 °C and 65% R.H. for 3 days before testing.

Moisture content was recorded to understand the moisture sensitivity of the modified SPC resins. A Brabender moisture/volatiles tester (model 1153) was used according to ASTM D 2654-89a to obtain moisture content. A 10-g specimen was used for this test. After being dried in the oven chamber for 24 h at 105 °C, the specimen moisture content was read directly from the scale.

Thermal stability of the modified SPC resins was characterized using a thermogravimetric analyzer (TGA), TA Instruments (model 2050, New Castle, DE). A nitrogen environment was maintained during the TGA study. The scanning temperature range was set to be 25−450 °C, and the specimens were scanned at a ramp rate of 10 °C/min.

Dynamic mechanical properties of all SPC resins were characterized using a dynamic mechanical analyzer (DMA, model-2980, TA Instruments, Inc., New Castle, DE) using tension film clamps. Cured resin sheets were cut into rectangular specimens of 25 mm × 5 mm dimensions. The test specimens were not conditioned to avoid the influence of the loss of moisture from the sample films at high temperature during testing. The tests were performed at 1 Hz frequency while maintaining an amplitude of 15 μm. The specimens were scanned from 35 to 250 °C at a ramp rate of 5 °C/min. The dynamic mechanical properties such as storage modulus, loss modulus, and tan δ were determined from the DMA plots as per the ASTM D4065-01. The glass transition temperature was determined according to ASTM E1640-99.

Wide-angle X-ray diffraction (WXRD) was used to evaluate the nanoparticle dispersion. The general area detection diffraction system (GADDS, Bruker-AXS, Inc., Madison, WI) was used at 45 kV and 40 mA. The X-ray diffraction patterns of the resin specimens were obtained using a Scintag $\theta-\theta$ powder diffractometer (PAD X, Scintag, Inc., Cupertino, CA) with a solid-state intrinsic germanium detector. The specimen films were scanned from 1° to 40° at 2°/min employing the Cu Kα X-ray radiation with a wavelength of 1.5405 Å. The d spacing information was recorded.

Nano-clay dispersion within the resin was also confirmed via a LEO 922 energy filtered transmission electron microscope (EFTEM). The CPH-SPC films were embedded in a potting epoxy resin and cut into thin specimens by using a microtome. A 300 mesh copper grid was used to hold the SPC specimens for TEM.

Results and Discussion

Effect of Phytagel on the Mechanical Properties and Moisture Absorption of PH-SPC Resin. PH-SPC resin was prepared with 20% glycerol (as a plasticizer) at a neutral pH.

Table 1. Effect of Phytagel Content on the Tensile Properties and Moisture Resistance of the Modified SPC Resins

phytagel content (%)	fracture stress (MPa)	fracture strain (%)	modulus (MPa)	toughness (MPa)	moisture content (%)
0	14.7 (6.6)[a]	25.7 (6.0)	201 (4.5)	2.8 (12.5)	16.7
5	21.1 (2.4)	22.7 (4.3)	314 (3.1)	3.1 (5.4)	16.3
10	26.1 (12.5)	18.8 (3.2)	406 (6.5)	3.5 (11.2)	16.2
20	34.9 (4.6)	17.1 (5.2)	538 (6.1)	3.9 (8.3)	16.0
30	43.7 (6.2)	15.9 (5.1)	651 (3.7)	4.5 (8.6)	15.8
40	50.1 (5.5)	14.8 (4.2)	717 (4.6)	4.8 (7.2)	15.5
50	52.4 (3.1)	14.2 (4.3)	742 (4.5)	4.9 (6.9)	15.5

[a] Values in parentheses are CV%.

Table 2. Effect of Glycerol Content on the Tensile Properties and Moisture Resistance of PH-SPC Resin

glycerol (%)	fracture stress (MPa)	fracture strain (%)	modulus (MPa)	moisture content (%)
20	50.1 (5.5)[a]	14.8 (4.2)	717 (4.6)	15.5
15	60.0 (3.9)	11.7 (6.3)	1154 (4.9)	14.7
12.5	66.2 (4.5)	10.0 (7.4)	1675 (2.4)	14.4
10	60.0 (5.2)	7.8 (7.6)	1975 (2.6)	13.4
5	61.1 (6.7)	6.1 (8.5)	2222 (6.9)	13.1

[a] Values in parentheses are CV%.

The tensile properties and moisture content of the resin are listed in Table 1. It can be seen from the data presented in Table 1 that, as the amount of Phytagel increased from 0% to 40%, Young's modulus and fracture stress increased from 201 to 717 MPa and 14.7 to 50.1 MPa, respectively. At the same time, the fracture strain decreased from 25.7% to 14.8%. It was realized that further increase in Phytagel content did not lead to significant increases in the Young's modulus or the fracture stress.

The gellan−agarose system has been found to form a molecularly interpenetrating network (IPN)-like structure.[34] In an IPN structure, polymer networks partially or completely interpenetrate each other on a molecular scale. Although there is no covalent bonding between different networks, it requires the breaking of polymer bonds to separate the cross-linked polymers. Both SPC (or SPI) and Phytagel, separately, form cross-linked systems.[19,23] When mixed together, an interpenetrating network-like (IPN-like) structure can be formed.[23] The blend was uniform, and there was no evidence of any kind of physical phase separation based on the visual observation or the stress−strain (tensile) curves. At high temperature, Phytagel, in solution, is in the coil form.[35] However, because of the polar amino acids in soy protein, Phytagel can also form strong interactions with SPC chains by hydrogen bonding and possibly through covalent bonding.[23] The hydroxyl groups on rhamnose and glucose provide the active sites for hydrogen bonding. The carboxyl groups present in the glucuronic acid unit are capable of reacting with hydroxyl and carboxyl groups in other Phytagel molecules as well as hydroxyl, carboxyl, and amine groups in SPC molecules to form covalent or hydrogen bonds during the curing process. In addition, the carboxylates in Phytagel molecules provide active sites for ionic linkages. As noted earlier, cationic ions are needed to form a gel structure for Phytagel.[19,20] The ashes and other impurities present in the SPC seem to be sufficient to provide cationic ions to promote cross-linking so as to allow the formation of a gel. No additional inorganic ions were employed in this research because a highly cross-linked structure would increase the brittleness of the modified SPC, resulting in lower stress. SPC molecules can penetrate into the gelled Phytagel structure and vice versa to form the IPN-like structure. Different SPC molecules are also capable of cross-linking with each other through hydrogen bonding, disulfide linkage, and other covalent bonding (e.g., ester) formed during the hot process. The stability of IPN structures depends on the relative cohesive energy densities of the two materials.[36] The formation of strong hydrogen bonding between two materials stabilizes the entanglements. Glass transition studies using dynamic mechanical analysis did not show phase separation. These results will be discussed later in this paper. The enhancement in mechanical properties is due to the increase in cross-link density due to the apparent extensive interpenetration. The strong interaction between the two networks also helps stress transfer from one network to the other increasing stiffness. Lodha and Netravali[23] showed that, due to the formation of the IPN-like structure, Phytagel-modified SPI resin was significantly stronger and stiffer than the pure SPI resin. A similar trend has been seen for SPC resin in this study. In addition, the toughness of the SPC increased with the addition of Phytagel as well. The toughness of a polymer was determined by the area under the stress−strain curve. This area measures the energy required to fracture the material in tensile mode. PH-SPC with 40% Phytagel showed a toughness of 4.2 MPa, which was about 71% higher than the SPC resin without Phytagel.

The moisture content of the modified SPC resin decreased from 16.7% to 15.5% (50% Phytagel). The moisture content of pure Phytagel resin was measured to be 10.2%. The interaction and cross-linking of polar groups, such as hydroxyl and carboxyl groups, on Phytagel with SPC is believed to have decreased the overall polarity and moisture sensitivity of the modified SPC resin. Water has been shown to be a good plasticizer for soy protein polymers.[37] As a result, the reduction in moisture content with the addition of Phytagel could be another factor to help increase the stiffness of the PH-SPC.

Because further increasing Phytagel content reduced specimen processibility, due to high viscosity, but did not increase the tensile properties of PH-SPC resin significantly, 40% Phytagel content was selected for further modification of PH-SPC with nano-clay.

Study of the Effect of Glycerol on the Mechanical Properties and Moisture Resistance of PH-SPC Resin. Glycerol has been shown to be effective in plasticizing soy protein resins.[2−4,38,39] Its high polarity due to the hydroxyl groups also increases the moisture absorption by the resin. Soy protein has both polar and nonpolar side chains. Polar groups are responsible for the moisture sensitivity of soy protein products. The polar attractions also increase the stiffness and brittleness of soy protein when no plasticizers are present. Glycerol penetrates into the polymer structure and improves the mobility of soy protein polypeptide chains, resulting in the plasticization effect.[39]

As mentioned earlier, for this study, Phytagel content was maintained at 40%. The effect of glycerol on the mechanical properties and moisture absorption by PH-SPC resins is presented in Table 2. As the amount of glycerol in the resin was reduced from 20% to 12.5%, the Young's modulus and fracture stress of the PH-SPC resin increased from 717 to 1675 MPa and from 50.1 to 66.2 MPa, respectively, while the fracture strain did not change significantly. The highest fracture stress was observed for the specimen containing 12.5% glycerol. Although further decreasing glycerol content from 12.5% to 5% increased the modulus, the fracture stress decreased due to the reduced fracture strain of the specimens. As mentioned earlier,

Table 3. Effect of Nano-Clay Loading on the Tensile Properties and Moisture Resistance of CPH-SPC Resin

clay (%)	fracture stress (MPa)	fracture strain (%)	modulus (MPa)	moisture content (%)
0	66.2 (4.5)[a]	10.0 (7.4)	1675 (2.4)	14.4
5	70.6 (3.2)	9.8 (3.8)	1983 (5.7)	14.4
7	74.5 (0.9)	9.5 (6.7)	2124 (2.1)	14.1
10	71.4 (5.7)	8.6 (8.1)	2302 (2.2)	13.9
15	70.6 (4.4)	8.6 (6.7)	2442 (7.8)	13.9
20	69.0 (5.5)	7.3 (7.5)	2608 (5.5)	13.7

[a] Values in parentheses are CV%.

glycerol is very moisture sensitive. It is clear from Table 2 that the reduction of glycerol content lowered the moisture content of the PH-SPC. Once glycerol was reduced from 20% to 5%, the moisture content of the specimen was reduced to 13.0% from about 15.5%. Lower moisture content is another factor for the higher strength and modulus of PH-SPC resin. Our preliminary study with other polysaccharides, for example, chitosan, showed some improvements. Chitosan can form hydrogen bonds, but it is not capable of forming IPN-like structure with SPC. Also, it cannot form ionic bonds.

Effect of Nano-Clay Loading on the Mechanical Properties and Moisture Resistance of CPH-SPC Nanocomposite Resin. The effect of nano-clay on the mechanical properties of the resin is primarily determined by its degree of dispersion in the matrix.[40,41] Exfoliated nano-clay platelets (particles) have a thickness of approximately 1 nm with the other two dimensions in the range of several hundred nanometers. This results in a large aspect ratio and high interfacial interaction between the polar polymeric matrix and polar clay particles. The dispersion of nano-clay in polymeric matrix also results in the high tortuosity for the polymeric molecules. These two factors contribute to the increased mechanical properties of the nanocomposites.[5,29−33] In addition, in the present case, sodium ions in clay can also enhance the gelation effect of Phytagel due to the screening of the electrostatic repulsion between carboxyl groups on Phytagel.

Table 3 shows the mechanical properties of the clay and Phytagel-modified (CPH-SPC) nanocomposite resin with different nano-clay loadings. For these nanocomposite resins, 12.5% glycerol was used as a plasticizer. 40% Phytagel was used in a neutral pH to prepare the CPH-SPC resin. The results show that increasing the nano-clay loading primarily increases the modulus of the CPH-SPC resin. For 20% clay loading, the Young's modulus was 2.6 GPa as compared to 1.7 GPa for 0% clay loading. For 7% clay loading, the fracture stress was 74.5 MPa as compared to 66.2 MPa for 0% clay loading. Further increase in clay loading reduced the fracture stress due to the decreased fracture strain of the specimens. The data in Table 3 also show a steady increase in Young's modulus as well as a continuous decrease in fracture strain with increase in nano-clay loading as expected. Clay particle surface is negatively charged, and, at neutral pH, soy protein is also negatively charged. Although sodium ions in clay can screen the electrostatic repulsion, clay particles can also act as defects in the system so as to decrease the fracture strain. The reduction in fracture strain with nano-clay particle addition has been shown in many polymers.[24−28]

XRD and TEM Analysis of CPH-SPC Resin. Wide-angle XRD was used to evaluate the clay particle dispersion in CPH-SPC. Figure 1 shows the XRD patterns of pure Cloisite Na$^+$ particles as well as CPH-SPC resins with various amounts of nano-clay particles. As shown in Figure 1, the peak obtained for pure clay at around 9° disappeared in the CPH-SPC resins, indicating that the clay particles were exfoliated and dispersed into CPH-SPC almost completely. The peak at around 9° corresponds to a *d* spacing of about 1.2 nm in nonexfoliated (pure) clay. The breakdown of this layered structure of nano-clay resulted in the disappearance of this peak in CPH-SPC resin. Even at the high clay loading of 20%, no clustering can be seen as indicated by the XRD plots. The hydrophilic property of both the clay and the SPC provides the strong interaction between the two phases and prevents clustering of the nanoparticles, thus keeping the stable dispersion of clay nanoparticles in the CPH-SPC resin.

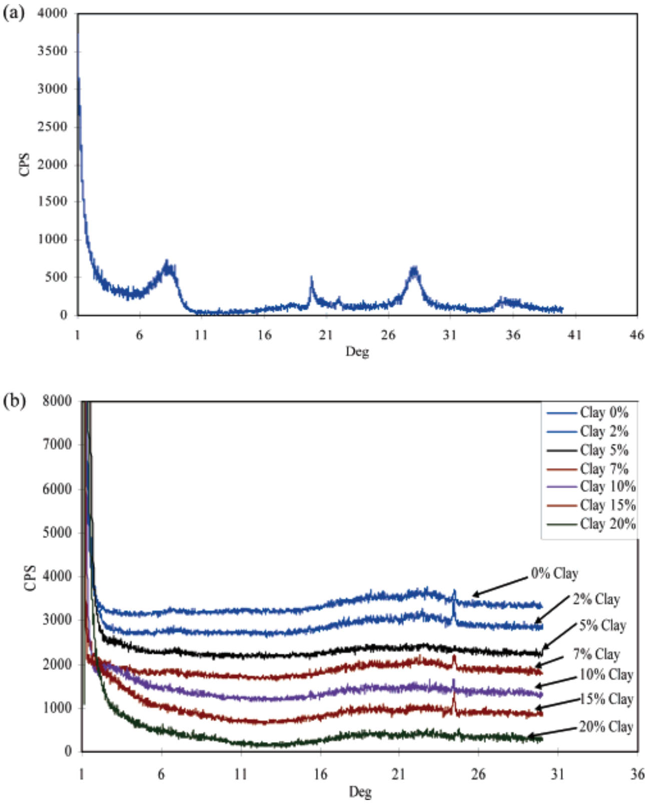

Figure 1. (a) XRD pattern of Cloisite Na$^+$ clay powder and (b) XRD pattern of CP-SPC resin with different clay loadings [*Y*-axis = % intensity, *X*-axis = goniometer angle].

TEM images are the most direct measurements of the dispersion of nanosized particles. Thin sections of CPH-SPC specimens with 7% clay were observed using EFTEM. Two TEM photomicrographs are shown in Figure 2 (with a scale bar of 50 nm). As indicated by the TEM images, most of the portion of the clay particles is exfoliated. This confirms the XRD results discussed earlier. The platelike nano-clay particles can take any position in CPH-SPC as a result of their random distribution in the three-dimensional SPC resin. For those clay particles perpendicular to the specimen surface, single clay platelets were clearly observed.

TGA Analysis of the Modified Resins. The TGA thermograms of pure Phytagel, pure SPC (without Phytagel), PH-SPC with 20% Phytagel, and 40% Phytagel are shown in Figure 3. The onset decomposition temperature (T_d) for pure SPC resin was 212 °C. The T_d was determined by extrapolating the tangents on two sides of the flexural point on the TGA thermogram. The incorporation of 20% Phytagel increased the T_d to 234 °C, and PH-SPC with 40% Phytagel showed a T_d of 242 °C. The incorporation of relatively thermally stable Phytagel

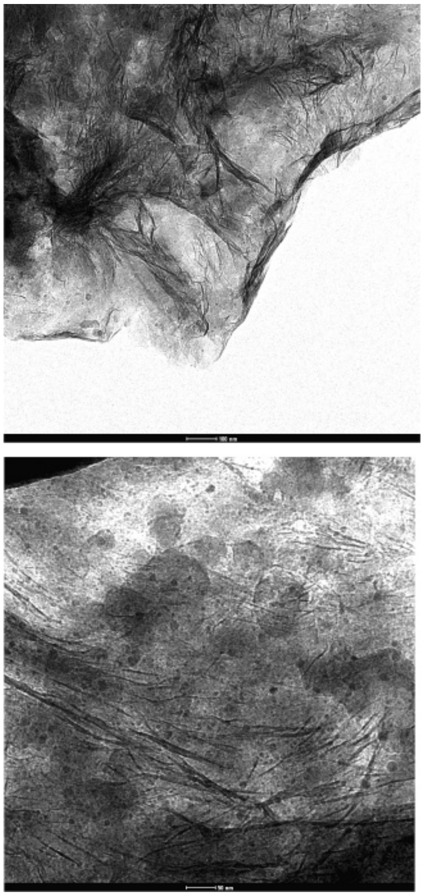

Figure 2. TEM photomicrographs of CPH-SPC nanocomposites with 7% clay (both scale bars are 50 nm).

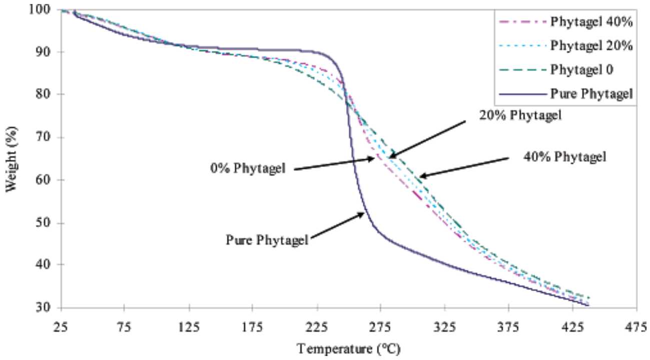

Figure 3. TGA thermograms of pure SPC and PH-SPC resins.

in SPC resin leads to an improvement in the thermal stability of the IPN-like PH-SPC resin. The improvement in thermal stability was directly related to the Phytagel content.

The weight loss of the specimen at 120 °C can be attributed mainly to the loss of moisture from the specimen. As seen from Figure 3, Phytagel does not change the moisture sensitivity of the PH-SPC significantly, which is consistent with the moisture absorption results.

TGA thermograms of the CPH-SPC containing 40% Phytagel and varying clay loadings are shown in Figure 4. Several researchers have reported that clay has the ability to increase the thermal properties of the modified polymer due to the thermal insulation.[42] Our results indicate that nano-clay particles do not have a significant effect on increasing the onset decomposition temperature of CPH-SPC. The weight fraction remaining (char) at temperatures above 250 °C, however, increased with clay loading as would be expected due to the insulating effect of clay particles. This is due to the fact that the clay particles are not affected by temperatures up to 450 °C.

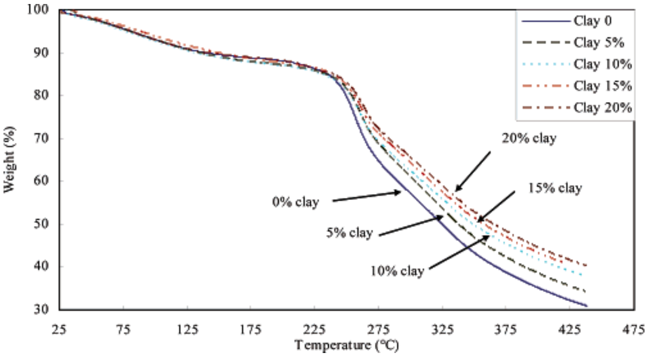

Figure 4. TGA thermograms of CPH-SPC resins with nano-clay loadings of 0−20%.

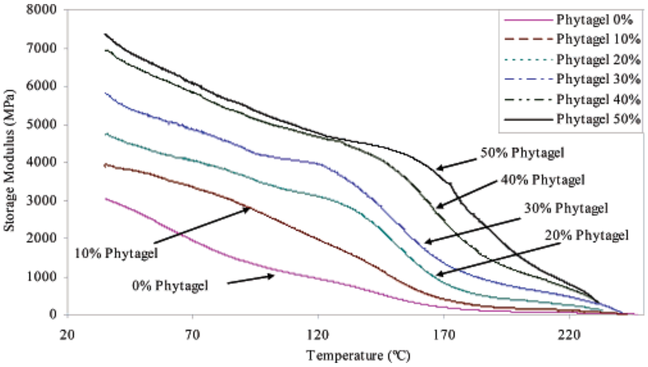

Figure 5. Plots of storage moduli for PH-SPC resins with different amounts of Phytagel as a function of temperature.

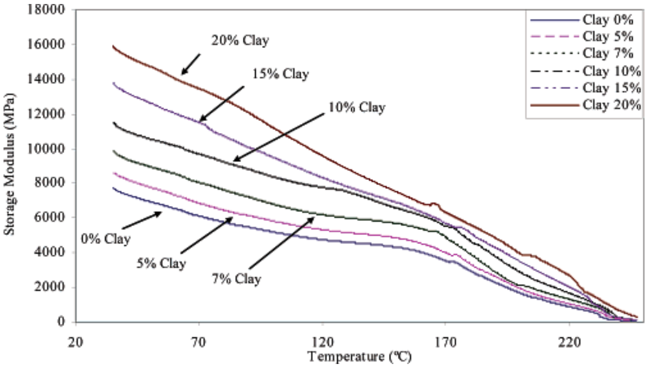

Figure 6. Plots of storage moduli for CPH-SPC resins with different clay loadings as a function of temperature.

Dynamic Mechanical Properties of the Modified Resins. The dynamic mechanical properties of the modified resins were characterized to study their storage modulus and changes in glass transition behavior.

The storage modulus of the SPC resins modified with different amounts of Phytagel and clay loadings, as a function of temperature, is presented in Figures 5 and 6, respectively. The storage modulus of the PH-SPC resin increased with Phytagel content, indicating a more solidlike behavior. This confirms the tensile test results that showed the stiffness of the SPC resin increased with the addition of Phytagel. At room temperature, the pure SPC specimen had a storage modulus of about 3 GPa. With the addition of 40% Phytagel, the storage modulus of PH-SPC increased to more than 7 GPa. As can be seen from Figure 6, clay loading also increases the storage modulus significantly. With the addition of 7% clay, the sample

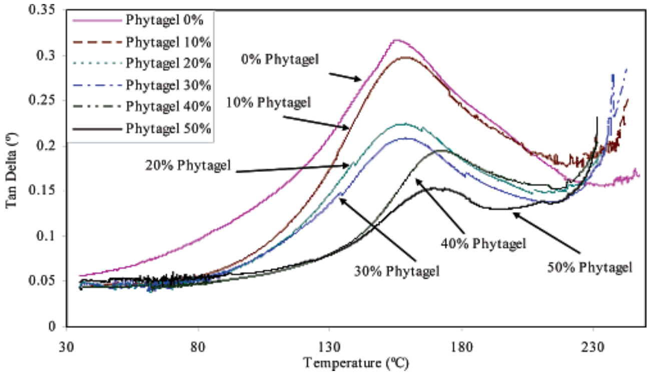

Figure 7. Plots of tan δ for PH-SPC with different amounts of Phytagel as a function of temperature.

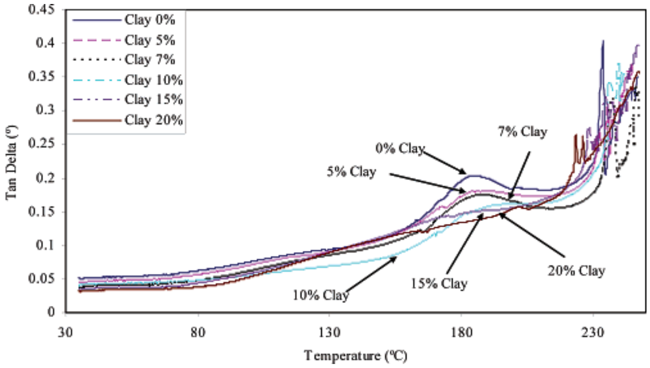

Figure 8. Plots of tan δ for CPH-SPC resins with different clay loadings as a function of temperature.

showed a storage modulus of around 10 Gpa, and it was further increased to more than 16 GPa once the clay loading reached 20%. As seen in Figures 5 and 6, both PH-SPC and CPH-SPC resin can withstand higher temperatures than the pure SPC resin. The storage modulus value is obtained for PH-SPC and CPH-SPC resins at significantly higher temperatures as compared to pure SPC resin. The storage modulus decreased with temperature in all of the resins. Once the temperature reached above 170 °C, the resins lost most of their mechanical properties. This can be due to the specimens being just above their glass transition or thermal decomposition temperature. The color of the specimens changed from light beige to dark brown, indicating some degradation.

Tan δ is given by the ratio of loss modulus to storage modulus. The plots of tan δ for different PH-SPC and CPH-SPC resins as a function of temperature are presented in Figures 7 and 8, respectively. As the plots in Figure 7 indicate, a single glass transition temperature (T_g) was observed for all modified resins and T_g increased from 156 to 174 °C as the Phytagel content increased from 0% to 40%. This indicates that the incorporation of Phytagel led to an intermolecular IPN-like structure, limiting the mobility of the SPC molecules. The reduced molecular mobility results in the increase in the glass transition temperature of PH-SPC.

However, as shown in Figure 8, nano-clay was not as effective in increasing the glass transition temperature of CPH-SPC as expected. The peak temperature of tan δ increased by about 5.7 °C (from 186.7 to 193.4 °C) as clay loading increased from 0% to 10%.

Conclusions

The tensile properties, moisture resistance, and thermal stability of the modified SPC increased significantly with the addition of MMT nano-clay particles and Phytagel. Phytagel increased the modulus and fracture stress of PH-SPC resin by forming an IPN-like structure. PH-SPC resin with 40% Phytagel content showed a tensile strength of 50.1 MPa and a modulus of 717 MPa. The thermal stability as well as moisture resistance was also improved with the addition of Phytagel as compared to the unmodified SPC resin. The SPC resin modified with 40% Phytagel and 7% clay had a modulus of over 2.1 GPa and a strength of 74.5 MPa. The storage modulus improved with MMT nano-clay particles and Phytagel. The glass transition temperature of the modified resins also increased with Phytagel.

Acknowledgment. We would like to acknowledge the National Textile Center (NTC) for financial support and the College of Human Ecology at Cornell University and Cornell Center for Materials Research (CCMR) for providing the testing equipment. We would also like to thank Professor Dotsevi Sogah and Dr. Xiaoping Chen in the Department of Chemistry at Cornell University for providing nano-clay particles.

References and Notes

(1) Kylma, J.; Seppala, J. V. *Macromolecules* **1997**, *30*, 2876−2882.
(2) Chabba, S.; Netravali, A. N. *J. Mater. Sci.* **2005**.
(3) Chabba, S.; Netravali, A. N. *J. Mater. Sci.* **2005**.
(4) Chabba, S.; Netravali, A. N. *Green Chem.* **2005**, *7*, 576−581.
(5) Huang, X.; Netravali, A. N. *Polymer*, submitted.
(6) Nishino, T.; Matsuda, I.; Hirao, K. *Macromolecules* **2004**, *37*, 7683−7687.
(7) Dickerson, R. E.; Geis, I. *The Structure and Action of Proteins*; Harper and Row Publishers: New York, 1969; p 5.
(8) Creighton, T. E. *Proteins: Structure and Molecular Properties*, 2nd ed.; Freeman: New York, 1993; pp 1−20.
(9) Ly, Y. T. P.; Johnson, L. A.; Jane, J. Soy Protein as Biopolymer. In *Biopolymers from Renewable Resources*; Kaplan, D. L., Ed.; Springer: New York, 1998; pp 144−176.
(10) Kumar, R.; Choudhary, V.; Mishra, S.; Varma, I. K.; Mattiason, B. *Ind. Crop. Prod.* **2002**, *16*, 155−172.
(11) Morales, A.; Kokini, J. L. *Biotechnol. Prog.* **1997**, *13*, 624−629.
(12) Thanh, V. H.; Shibasaki, K. *J. Agric. Food Chem.* **1976**, *24*, 1117−1121.
(13) Lodha, P.; Netravali, A. N. *Compos. Sci. Technol.* **2005**, *65*, 1211−1225.
(14) Lodha, P.; Netravali, A. N. *J. Mater. Sci.* **2002**, *37*, 3657−3665.
(15) Vaz, C. A.; Mano, J. F.; Fossen, M.; van Tuil, R. F.; de Graaf, L. A.; Reis, R. L.; Cunha, A. A. *J. Macromol. Sci. Phys.* **2002**, *B41*, 33−46.
(16) Endres, J. G. *Soy Protein Products: Characteristics, Nutritional Aspects and Utilization*; AOCS Press: Champaign, IL, 2001.
(17) Park, S. K.; Bae, D. H.; Rhee, K. C. *J. Am. Oil Chem. Soc.* **2000**, *77*, 879−883.
(18) Otaigbe, J. U.; Adams, D. O. *J. Environ. Polym. Degrad.* **1997**, *5*, 199−208.
(19) Doner, L. W.; Douds, D. D. *Carbohydr. Res.* **1995**, *273*, 225−233.
(20) Banik, R. M.; Kanari, B.; Upadhyay, S. N. *World J. Microbiol. Biotechnol.* **2000**, *16*, 407−414.
(21) Chandrasekaran, R.; Thailambal, V. G. *Carbohydr. Polym.* **1990**, *12*, 431−442.
(22) Nakajima, K.; Ikehara, T.; Nishi, T. *Carbohydr. Polym.* **1996**, *30*, 77−81.
(23) Lodha, P.; Netravali, A. N. *Polym. Compos.* **2005**, *26*, 647−659.
(24) Park, J. H.; Jana, S. C. *Polymer* **2003**, *44*, 2091−2100.
(25) Lu, H. B.; Nutt, S. *Macromolecules* **2003**, *36*, 4010−4016.
(26) Ji, X. L.; Hampsey, J. E.; Hu, Q. Y.; He, J. B.; Yang, Z. Z.; Lu, Y. F. *Chem. Mater.* **2003**, *15*, 3656−3662.
(27) Zhang, Q.; Archer, L. A. *Macromolecules* **2004**, *37*, 1928−1936.
(28) Ash, B. J.; Siegel, R. W.; Schadler, L. S. *Macromolecules* **2004**, *37*, 1358−1369.
(29) Pegoretti, A.; Kolarik, J.; Peroni, C.; Migliaresi, C. *Polymer* **2004**, *45*, 2751−2759.
(30) Lee, K. M.; Han, C. D. *Macromolecules* **2003**, *36*, 804−815.
(31) Chang, J. H.; Seo, B. S.; Hwang, D. H. *Polymer* **2002**, *43*, 2969−2974.
(32) Ma, J.; Xiang, P.; Mai, Y. W.; Zhang, L. Q. *Macromol. Rapid Commun.* **2004**, *25*, 1692−1696.

(33) Fornes, T. D.; Paul, D. R. *Macromolecules* **2004**, *37*, 7698−7709.
(34) Amici, E.; Clark, A. H.; Normand, V.; Johnson, N. B. *Biomacromolecules* **2002**, *3*, 466−474.
(35) Tanaka, F. *Macromolecules* **2003**, *36*, 5392−5405.
(36) Sperling, L. H. *Macromol. Rev.* **1977**, *12*, 141−180.
(37) Zhang, J.; Mungara, P.; Jane, J. *Polymer* **2001**, *42*, 2569−2578.
(38) Mo, X. Q.; Sun, X. S.; Wang, Y. Q. *J. Appl. Polym. Sci.* **1999**, *73*, 2595−2602.
(39) Liang, F.; Wang, Y. Q.; Sun, X. S. *J. Polym. Eng.* **1999**, *19*, 383−393.
(40) Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J. Mater. Res.* **1993**, *8*, 1185−1189.
(41) Hasegawa, N.; Okamoto, H.; Kato, M.; Usuki, A.; Sato, N. *Polymer* **2003**, *44*, 2933−2937.
(42) Ray, S. S.; Okamoto, M. *Prog. Polym. Sci.* **2003**, *28*, 1539−1641.

BM060604G