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Environmentally Friendly Green Materials from Plant-Based Resources: Modification of Soy Protein using Gellan and Micro/Nano-Fibrillated Cellulose

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Fully biodegradable micro/nano-composite resins were prepared by reinforcing soy protein concentrate (SPC) with micro/nano-fibrillated cellulose (MFC) and then blending with gellan. The composite resins showed excellent mechanical and physical properties under testing conditions. Due to the high aspect ratio of MFC, excellent mechanical properties of MFC and MFC/SPC interfacial properties, the SPC (100 parts) reinforced with glycerol (1.5 parts) and MFC (40 parts) showed fracture stress of 88.2 MPa and Young's modulus of about 4.1 GPa, which are higher than those of many conventional petroleum-based plastics. MFC reinforced SPC composite resins were then further modified by blending with gellan to obtain 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. Although the moisture sensitivity of the specimens was high, they have the potential to replace petroleum-based materials in many fields, particularly for indoor applications.

Keywords: Nano-composites, biodegradable, mechanical properties, plastics

1. Introduction

The world relies heavily on plastic materials due to their low cost, excellent durability and high mechanical and physical properties. However, the durability of these plastics is a result of their non-degradable nature. Currently there is no effective method to degrade these non-renewable petroleum-based materials in a reasonable period of time under normal environmental conditions. Their non-degradability has been of concern as these materials mostly end up in landfills or discarded in the environment polluting it, at the end of their life. Further, petroleum is a non-renewable resource. To improve the overall sustainability, researchers have been trying to develop environmentally friendly alternatives to conventional petroleum-derived plastics (1–10).

Many researchers have used soy protein as a fully sustainable and biodegradable resin (7–21). Soy protein has mainly four fractions, 2S, 7S, 11S and 15S, based on their sedimentation constants. The 7S fraction is also called conglycinin and comprises many important enzymes and storage proteins. The 7S fraction is about 30% of the total soy protein

by weight (7). The 11S fraction comprises about 35% of the total soy protein and is usually called glycinin (7). The polar groups in soy protein provide the convenience for chemical and physical modifications of soy protein molecules (7). Several methods have been developed to increase the mechanical properties and reduce the moisture sensitivity of the modified soy protein materials (9–21). Crosslinkers, such as glutaraldehyde, glyoxal and formaldehyde, have been useful in increasing the Young's modulus and fracture stress of soy protein moderately (9–14). Nano-clay has also been used to fabricate soy protein nano-composites with higher modulus (stiffness) (11, 15). However, most commonly, the toughness decreases with the addition of nano-clay (11, 15). Enzyme modifications (such as transglutaminase) have shown an increased moisture barrier and slightly increased mechanical properties (13, 14). Blending is also an efficient way to modify polymers for particular physical and mechanical properties. Blending of soy protein with other biodegradable polymers such as starch, PVA and gellan, has shown good increase in tensile properties (15–19).

Gellan is made through fermentation and has a linear structure with a high molecular weight (21–23). It can form a strong gel in water through hydrogen bonding and ionic interactions. The commonly accepted structure of gellan is a linear combination of 3 subunits in the form of →

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4)-L-rhamnopyranosyl-(1 → 3)- α -D-glucopyranosyl-(1 → 4)- β -D-glucuronopyranosyl-(1 → 4)- β -D-glucopyranosyl-(β 1 → (21–23)). Gellan has been used for blending with other biomaterials to achieve high mechanical properties (24–27). Among them, the blends of gellan and soy protein products have shown significantly improved fracture stress and Young's modulus due to the strong interactions formed between gellan and soy protein molecules (15, 21).

Fiber reinforced composites have been used for structural applications due to their excellent physical and mechanical properties. Short fiber composites can be made isotropic by randomly orienting fibers into the resin (28–30). Many plant-based fibers possess excellent mechanical properties and have been used for composite fabrication (31, 32). Plant-based cellulose fibers have a fibrillar structure and the cellulose nano-fibrils can have even higher mechanical properties due to their high cellulose orientation and crystallinity. Nano-fibrillated cellulose (NFC) has been estimated to have strength between 2 and 6 GPa and Young's modulus of about 140 GPa, which is higher than that of some high strength fibers, such as aramid and E-glass (33–37). Micro-fibrillated cellulose (MFC) which is made up of NFC also can have high strength and modulus.

In this research, fully biodegradable, green, soy protein composite resins with excellent mechanical properties were prepared by reinforcing SPC with MFC and then blending with gellan. All the components in the specimens were natural and are fully sustainable. Although the moisture resistance of the modified SPC was not as good as the petroleum-based plastics, the specimen provided excellent mechanical properties under ASTM testing conditions of 21°C and 65% R.H.

2. Experimental

2.1. Materials

Soy protein concentrate (SPC) powder was provided by Archer Daniels Midland Company, Decatur, IL, USA under the brand name of Arcon[®] S. Analytical grade NaOH and glycerol was obtained from Fisher Scientific, Pittsburgh, PA. NaOH and glycerol were used without any further purification. NaOH was dissolved into distilled and deionized (DD) water to obtain a 1 M solution. Gellan was acquired from Sigma-Aldrich Co., St Louis, MS, USA, under the commercial name of Phytigel[®]. A micro/nano-fibrillated cellulose (MFC) in the form of a paste containing 10% micro/nano-fibrils and 90% water was obtained from Daicel Chemical Industrial, Ltd., Japan. MFC was dispersed into DD water in a weight ratio of 1:100 while vigorous magnetic stirring to obtain a uniform suspension.

2.2. Specimen preparation

To prepare MFC reinforced SPC specimens, SPC was first dispersed into DD water in a weight ratio of 7:100. Magnetic stirring was used until a uniform suspension was obtained. Glycerol (15 parts based on the weight of SPC that is 100 parts) was added as a plasticizer to improve the processibility of the SPC specimens. Varying amounts of MFC suspension were then added into SPC while continually stirring to prepare the reinforced SPC composite resins. Once MFC was evenly dispersed in the SPC suspension, the mixture was brought to pH 8.0 using the NaOH solution and stirred in air at 75°C for 30 min. This process is called precuring. The precured resin was then poured on a poly(tetrafluoroethylene) coated mold and dried in an air-flowing oven at 35°C for 16 h to get specimens in the form of sheets. The specimens were then hot pressed using Carver hydraulic hot press (model 3891-4PROA00) at 120°C and 8 MPa for 25 min to obtain the cured specimen sheets. The composite resin sheets have thicknesses at around 0.15 mm.

Gellan modified SPC specimens were prepared to further improve the mechanical and physical properties of the MFC reinforced SPC resins. To prepare specimens, gellan was first dissolved into DD water at 85°C, and was then mixed with the SPC suspension in water at 85°C to obtain a blend. Premeasured amount of MFC was added once a uniform blend of SPC and gellan was obtained. Once a uniform mixture was obtained, the precuring was completed at 85°C for 30 min followed by the drying of the specimens at room temperature in an air-circulating oven. The same curing process was followed as described above.

2.3. Characterization

A Leica scanning electron microscope (SEM, model 440X) was used to observe the micro/nano-fibril size distribution. MFC first was dispersed in water to form a dilute suspension. The suspension was dried on freshly cleaved mica at room temperature by blowing air on the surface. The dried specimens were sputtered with gold-palladium for SEM scanning. The fracture surfaces of the SPC and modified SPC specimens were also observed using SEM.

An Instron universal tester (model 5566) was used to characterize the tensile properties of the specimens. All specimens were conditioned at standard ASTM conditions for three days before the test was conducted. Young's modulus, fracture stress, fracture strain and toughness were characterized according to ASTM D 882-97. The strain rate for the test was 0.5/min and the gauge length used was 50 mm. All specimens tested had a width of 10 mm.

Moisture content of the specimens was measured as per ASTM D 2654-89a using a Brabender moisture tester (model 1153). For this test, the oven chamber was maintained at 105°C and the change in the weight was measured

after 24 h drying. Specimens were conditioned for three days at standard ASTM conditions prior to measuring the moisture content.

Wide-angle X-ray diffraction (XRD) was used to evaluate the molecular morphology of SPC-gellan blends. The general area detection diffraction system (GADDS, Bruker-AXS, Inc., Madison, WI) was operated at 45 kV and 40 mA. The radiation used was the Cu-K α X-ray with a wavelength of 1.5405 Å. The specimens were scanned from 1° to 40° at the rate of 2°/min.

A thermogravimetric analyzer (TGA), TA Instruments (model 2050, New Castle, DE) was used to characterize the thermal stability of the SPC resin. The specimens were scanned from 25°C to 450°C at a ramp rate of 10°C/min in the protection of a nitrogen atmosphere.

A dynamic mechanical analyzer (DMA, model-2980, TA Instruments, Inc., New Castle, DE) was used to study the dynamic mechanical properties. Rectangular films were used to obtain the dynamic properties including storage modulus and tan δ . The tests were performed at 1 Hz frequency and 15 μ m amplitude. The specimens were scanned on the DMA from 35°C to 250°C at a ramp rate of 5°C/min.

3. Results and discussion

3.1. SEM characterization of MFC

Figure 1 shows the SEM photomicrographs of the MFC. The diameters of the fibrils ranged from the nanometer (nm) level to several micrometers (μ m) as can be seen in Figure 1(a). The fibrils, especially the nm-sized fibrils, were

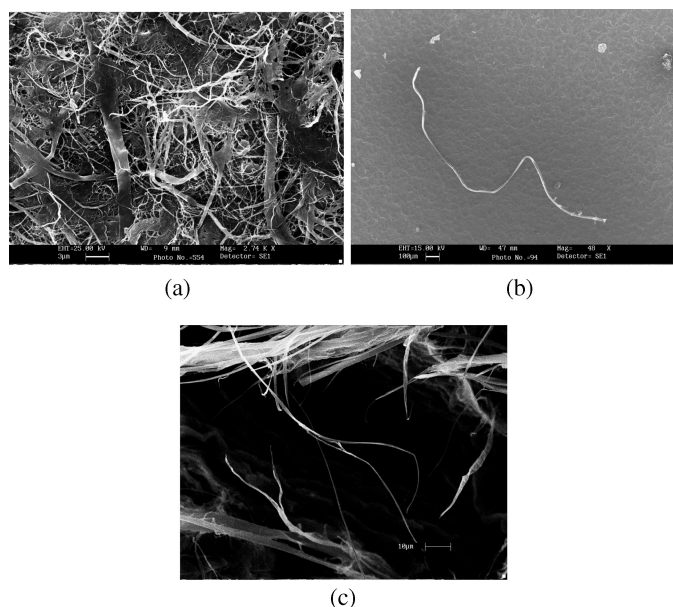


Fig. 1. SEM photomicrographs of the μ m/nm-sized cellulose fibrils

entangled with each other to form a network like structure. A single μ m-sized fibril is shown in Figure 1(b). As can be seen, the fibril has high aspect ratio. The μ m-sized fibrils can be expected to have rough surface since most of the plant-based fibers have a fibrillar structure (39). The more fibrillated (nm-sized) and less fibrillated (μ m-sized) fibrils are seen in Figure 1(c). It has been reported that single natural cellulose fibers can possess high mechanical properties with fracture stress of around 1 GPa (38, 39). Due to the higher orientation and crystallinity, the fibrils are much stronger than the fibers. For example, the nano-fibrillated cellulose has been estimated to have a fracture stress between 2 and 6 GPa (32–34).

3.2. Characterization of the MFC reinforced SPC composite resins

The mechanical properties and moisture content of the MFC reinforced SPC specimens containing 15 parts of glycerol and various amounts of MFC are shown in Table 1. With the increase in the MFC content, the Young's modulus of the specimen increased significantly from 589 MPa for SPC containing 15 parts of glycerol to 2346 MPa for SPC containing 15 parts of glycerol and 40 parts of MFC. This is almost a four-fold increase in the Young's modulus. The same trend was observed for the fracture stress, which increased from 21.7 MPa for SPC with 15 parts of glycerol alone to 71.2 MPa for SPC with 15 parts of glycerol and 40 parts of MFC, about 3.3 times the control value. However, for the same composite resins the fracture strain decreased from 14.4% to 11.1% as shown in Table 1.

Fukuda and Chou (40) proposed the following equation to predict the fracture stress of a random short fiber composite:

$$\sigma_c = \sigma_f V_f \left(1 - \frac{\bar{l}_c}{2\bar{l}}\right) C_0 + \sigma_r (1 - V_f) \quad (1)$$

Where σ_c , σ_f and σ_r are the fracture stresses of the composite, fiber and resin, respectively, V_f is the fiber volume fraction, \bar{l} and \bar{l}_c are the mean fiber length and mean critical fiber length, respectively and C_0 is the orientation factor for random fiber composites. It is clear from the formula that the fracture stress of a composite is closely related to the fiber strength, critical fiber length, fiber volume fraction and orientation as well as the resin properties. The critical fiber length, in theory, is the minimum length required to effectively transfer the load in the axial direction in a composite (21, 40). Fibers longer than the critical length contribute to the strength of the composite whereas those shorter than the critical length act mostly as fillers. Critical fiber length is significantly influenced by the interfacial adhesion and decreases with the increase of the interfacial shear strength (IFSS) and fiber diameter (41, 42). In other words, the higher the fiber/resin adhesion, the shorter the

Table 1. Mechanical properties and moisture content of the MFC modified SPC resin

<i>MFC/SPC/Glycerol (by weight)</i>	<i>Fracture Stress MPa</i>	<i>Fracture Strain %</i>	<i>Young's Modulus MPa</i>	<i>Toughness MPa</i>	<i>Moisture Content %</i>
0/100/15	21.7	14.4	589	2.7	15.2
10/100/15	45.8	12.2	1389	4.0	13.9
20/100/15	54.7	11.6	1727	4.1	14.0
30/100/15	65.2	12.0	1959	5.3	13.1
40/100/15	71.3	11.1	2347	5.3	13.3
50/100/15	74.9	10.2	2374	5.1	13.1

critical length. The hydroxyl groups on the MFC make the fibrils hydrophilic, but also provide the condition for good interfacial adhesion between MFC and soy protein molecules through hydrogen bonding. It has been reported that the interfacial shear strength between soy protein and ramie fiber (cellulose) can be as high as 29.8 MPa (21). In addition, the small diameter of the fibrils and the high surface roughness of the mm-sized fibrils, as shown in Figures 1, provided significantly large area for interfacial interaction with the resin. Therefore, the reduced critical length of the nm/mm-sized fibrils can effectively increase the load transfer efficiency in the MFC reinforced SPC specimens. As a result of high mechanical properties of MFC, good mechanical properties of the MFC reinforced SPC composite resins can be expected.

Toughness is an indication of the energy consumed during specimen fracture. In the present case, toughness as measured by the area under the stress-strain curve, increased with the addition of MFC as seen from Table 1. The toughness of specimens containing 15 parts of glycerol and 40 parts of MFC was found to be 5.3 MPa compared to the toughness of 2.7 MPa obtained for SPC resin containing 15 parts of glycerol. This is an increase of about 100%. Once the MFC content reached 40%, the toughness leveled off at around 5.3 MPa as a result of the decreased fracture strain. Compared to 15.2% moisture content obtained for SPC resin (15 parts of glycerol) and no MFC, the moisture content of the SPC resin (15 parts of glycerol) and 40 parts of MFC decreased to 13.1%. The decreased moisture content also contributed to the increased modulus and decreased fracture stain since water is an effective plasticizer for soy protein (7, 12–15). It should be noted that the highly crystalline nature of the MFC does not allow it to

absorb significant amount of moisture in spite of its highly hydrophilic nature.

As discussed earlier, the increased tensile strength and Young's modulus of the MFC reinforced SPC resin are also due to the excellent interfacial interaction between MFC and SPC resin as well as the network structure formed by the fibrils within the MFC. It has been shown earlier, through SEM (Figure 1), that fibrils can form intertwined network by entangling with each other. Most of the load applied on the specimens is shared by the fibril network. The excellent mechanical properties of fibrils ensure the high Young's modulus and fracture stress of the SPC resin, once blended together. This is also possible because of the excellent interfacial adhesion that allows the load to be transferred efficiently from broken fibrils to the intact neighboring fibrils. Since fibrils are linked to one another within the network, stress transfer is expected to be easier from one fibril to another.

Glycerol is known as a good plasticizer for soy protein resins (7–19, 43). Decreasing the glycerol content can increase the stiffness of the specimens. The mechanical properties and moisture content of the SPC resin containing 40 parts of MFC as a function of glycerol content are shown in Table 2. The fracture stress and Young's modulus of the SPC containing 40 parts of MFC and 15 parts of glycerol were 71.2 MPa and 2346 MPa, respectively. However, once the amount of glycerol was reduced to 1.5 parts, the fracture stress and Young's modulus increased to 88.2 MPa and 4065 MPa, respectively. The amount of glycerol was further reduced to 1 part to obtain even higher modulus. However, the specimens became brittle and the fracture strain reduced to 3.8%. The fracture stress of the SPC resin with 1 part glycerol was 85.4 MPa and the Young's

Table 2. Mechanical properties and moisture content of the modified SPC resin with varying amounts of glycerol

<i>Glycerol/SPC/MFC (by weight)</i>	<i>Fracture Stress MPa</i>	<i>Fracture Strain %</i>	<i>Young's Modulus MPa</i>	<i>Toughness MPa</i>	<i>Moisture Content %</i>
15/100/40	71.2	11.1	2346	5.3	13.1
9/100/40	78.9	9.0	2568	4.9	12.7
4/100/40	93.8	6.3	3146	3.2	11.9
1.5/100/40	88.2	4.9	4065	2.8	11.3
1/100/40	85.4	3.8	4483	2.1	11.3

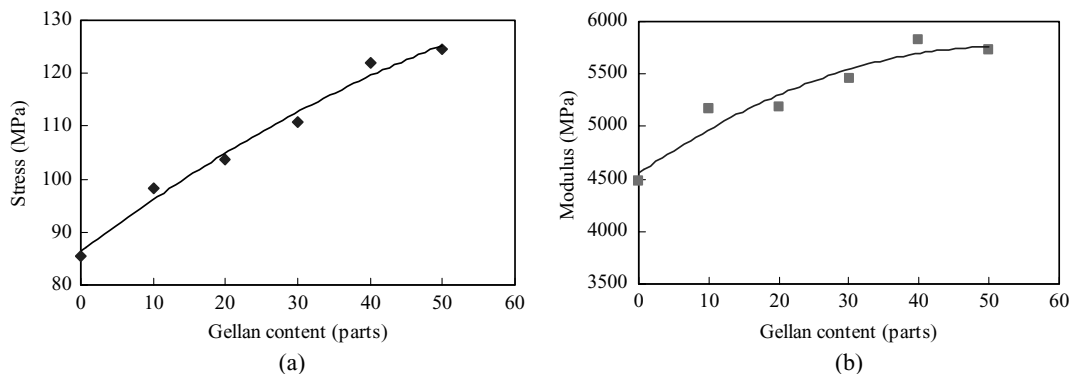


Fig. 2. (a) Fracture stress and (b) Young's modulus of the MFC (40 parts) reinforced SPC with glycerol (1.5 parts) and varying amounts of gellan.

modulus was 4483 MPa. As can be seen from Table 2 the moisture content reduced as the glycerol amount was reduced.

3.3. Characterization of the MFC reinforced SPC composite resins blended with gellan

Gellan was blended with the MFC reinforced SPC resins for improved mechanical and physical properties. Figure 2 shows the fracture stress and Young's modulus of the SPC resin containing 1.5 parts of glycerol, 40 parts of MFC and varying amounts of gellan. As seen in Figure 2, the SPC composite resin containing 1.5 parts of glycerol, 40 parts of MFC and 40 parts of gellan showed Young's modulus of 5.8 GPa and fracture stress of 122 MPa. These fracture stress and modulus values are higher than many of the traditional petroleum based plastics and comparable to many of the diglycidyl ether of bisphenol A (DGEBA) based epoxy resins.

Compatibility of the polymers in a blend is mainly determined by the chemistries and interactions between the components and can influence the properties of the modified polymers significantly. The interaction between gellan and SPC is expected to be strong due to the existence of strong hydrogen bonding between them (15, 18). In addition, SPC resin can form a cross-linked structure by itself. Thiols in soy protein are oxidized to disulfides by molecular oxygen in air during film preparing (44). The active amine, carboxyl and hydroxyl groups can also condense during the curing process. Gellan by itself can also form a strong gel (network) structure through hydrogen bonding and ionic interactions. Therefore, an interpenetrating network-like (IPN-like) structure is believed to have been formed by blending gellan and soy protein (15, 18). The increased cross-link density due to the formation of the IPN-like structure and the strong interaction between the two networks contributed to the increased mechanical properties of the gellan modified SPC specimens as shown in Figure 2.

Figure 3 shows the wide-angle X-ray diffraction (XRD) patterns of the gellan, MFC, SPC resin and the modified SPC resins individually. Gellan films showed two broad peaks at around 10° and 20° . Gellan molecules have been reported to form a double-helical structure in the crystal (45). Although the exact molecular structure of gellan films is not known, the two peaks correspond to some self-ordered structures of gellan molecules in the film state. MFC (cellulose) showed a distinct peak at around 23° and two small peaks at around 15° , which is a typical behavior of cellulose I structure (46, 47). Pure SPC film did not show any significant patterns (broad amorphous region) except the small peak at 24° . This peak most likely corresponded to a crystallized structure of cellulose I, as a small amount of cellulose remains in the SPC. The MFC reinforced SPC

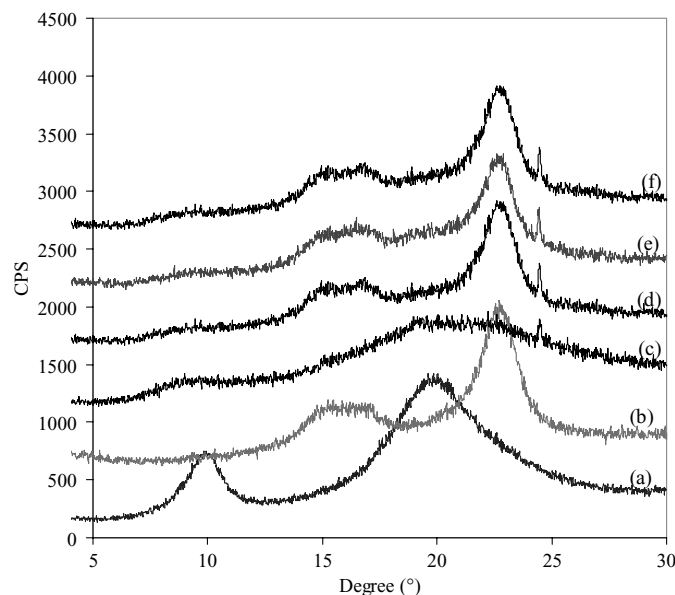


Fig. 3. XRD scans of (a) gellan, (b) MFC, (c) SPC, (d) modified SPC with SPC/glycerol/MFC of 100/1.5/40, (e) modified SPC with SPC/glycerol/MFC/gellan of 100/1.5/40/20 and (f) modified SPC with SPC/glycerol/MFC/gellan of 100/1.5/40/40.

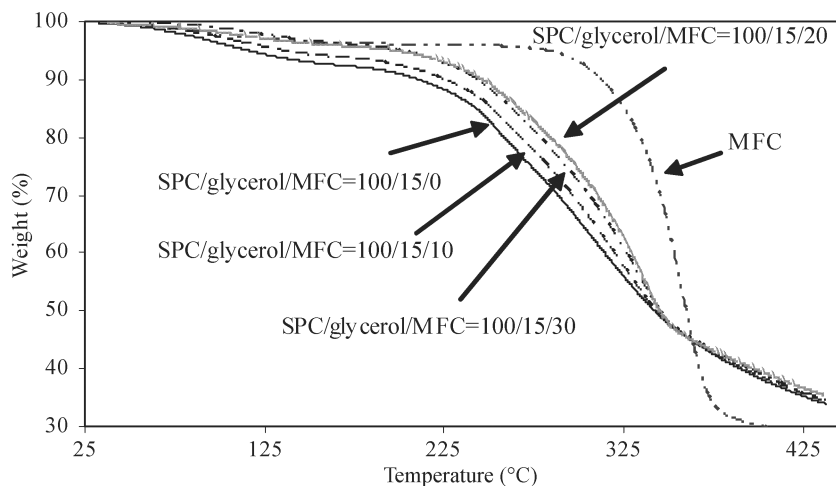


Fig. 4. TGA thermograms of the SPC, MFC and MFC reinforced SPC.

specimens were simply the overlap of the XRD patterns of MFC and SPC. It is from Figure 4 that the pure MFC and MFC reinforced SPC did not differ in the peak positions in the X-ray pattern. However, the peaks observed in gellan films were not seen in the XRD patterns of the SPC resins containing both gellan and MFC. Gellan, in SPC resin, was organized differently and lost its structure such as the unit cell parameters and chain conformation. It is possible that rigorous blending was responsible for this. Or, in the presence of SPC molecules, gellan was not allowed to form structures as in the case of pure gellan. This is most likely due to its strong hydrogen bonding interactions with SPC molecules in the blend. In the pre-curing step to prepare the uniform blend, a temperature of 85°C was used. This high temperature is known to open the protein aggregates and probably disturbs the protein folding behavior. Therefore, soy protein molecules trap gellan molecules preventing them from organizing due to the relatively fast cooling and drying rates in the fabrication of the specimen sheets. This suggests strong interactions and the possible formation of a single phase system.

3.4. Thermal and dynamic mechanical properties of the modified SPC composite resins

Figure 4 shows the TGA thermograms of SPC, MFC and MFC reinforced SPC composite resins. It is clear that cellulose fiber is thermally more stable than the SPC resin. The mixture of the two materials showed an improved thermal property compared with the unmodified SPC resin. SPC with 15 parts of glycerol has a decomposition onset temperature at about 236°C which increased to about 257°C after the addition of 40 parts of MFC. This is probably due to the insulating effect of cellulose fibers. The weight loss below 120°C can be attributed to the evaporation of moisture in the specimens. It is clear from Figure 4 that once the MFC was added, the moisture content of the SPC

resin decreased. The thermograms of the MFC reinforced SPC with different amounts of gellan were not included here since the addition of gellan did not show any evident change on the onset decomposition temperatures of the modified SPC resins.

Storage moduli and $\tan \delta$ of the SPC containing varying amounts of MFC and SPC containing both gellan and MFC as a function of temperature are shown in Figure 5. As seen in Figure 5 (a), the incorporation of MFC increased the storage modulus significantly. The SPC resin containing 15 parts of glycerol showed storage modulus of about 3 GPa at room temperature. This value increased to 7.5 GPa when 50 parts of MFC was added. For all specimens, the storage modulus decreased significantly at around 160°C. Once the temperature reached above 200°C, the specimens lost most of their properties. According to the TGA results, SPC specimens start to degrade in the range of 210°C to 250°C. Therefore, the decrease in the storage modulus in this temperature range is due to the decomposition of the specimens. The $\tan \delta$ behaviors of SPC containing varying amounts of MFC and SPC containing both gellan and MFC as a function of temperature are shown in Figure 5(b). The peak temperature corresponds to the glass transition temperature (T_g). T_g of the SPC resin was reported to be influenced by the moisture content and the amount of glycerol added (48, 49). It can be seen from Figure 5(b), T_g increased from about 165°C for SPC containing 1.5 parts of glycerol to 180°C for SPC containing 1.5 parts of glycerol and 40 parts of MFC.

The dynamic behaviors of the SPC resin with 1.5 parts of glycerol and 40 parts of MFC and the SPC resin with 1.5 parts of glycerol, 40 parts of MFC and 40 parts of gellan are shown in Figures 5(c) and (d), respectively. The SPC specimen containing 1.5 parts of glycerol and 40 parts of MFC showed storage modulus of 10.6 GPa at room temperature. This value was further increased to 13.9 GPa once 40 parts of gellan was added. With the addition of

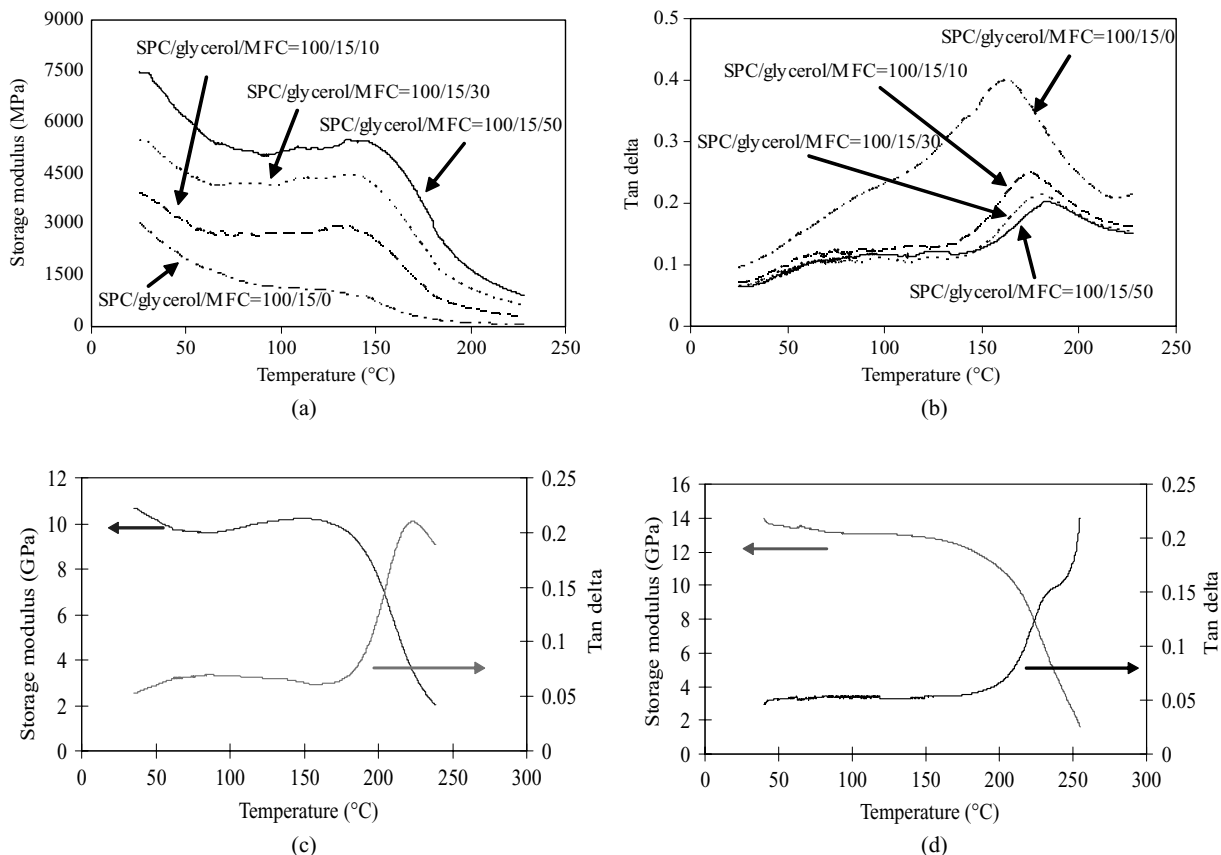


Fig. 5. (a) Storage moduli of SPC and MFC reinforced SPC resins; (b) $\tan \delta$ of the SPC and MFC reinforced SPC resins; (c) storage modulus and $\tan \delta$ of modified SPC with SPC/glycerol/MFC/gellan of 100/1.5/40/0; and (d) storage modulus and $\tan \delta$ of modified SPC with SPC/glycerol/MFC/gellan of 100/1.5/40/40.

gellan an IPN-like structure formed, which contributed to the increased storage modulus. No clear T_g was observed from Figure 5(d). This confirms that an IPN-like (or intercrosslinked) structure was formed with the addition of gellan since cross-linking reduced the freedom of motion of soy protein molecules.

3.5. Fracture surfaces of the M SPC composite resins by SEM

Figure 6 shows the photomicrographs of the fracture surfaces of the SPC and SPC with different modifications. Unmodified SPC resin showed a smooth fracture surface as in Figure 6(a). The surface roughness of the MFC modified SPC resins increased evidently as shown in Figure 6(b) and (c) compared to the fracture surface of the SPC resin. Short fibrils protruding out of the resin can be observed in both Figures 6(b) and (c). Fibril breaking can consume large energy due to the high mechanical properties of MFC. In addition, as explained earlier, the interfacial adhesion between MFC and SPC is expected to be high. Therefore, fibril pull-out in this case can also consume certain amount of energy. The extra energy consumed by fibril pulling-out

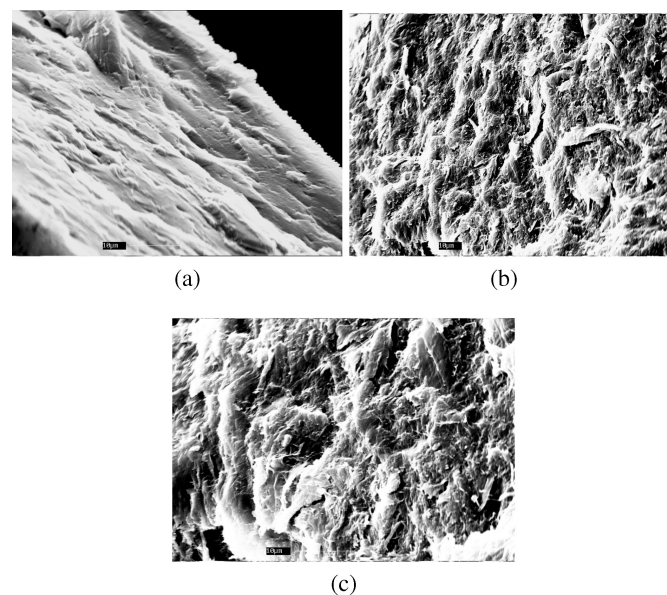


Fig. 6. SEM photomicrographs of the fracture surfaces of (a) SPC with SPC/glycerol of 100/15, (b) modified SPC with SPC/glycerol/MFC of 100/15/40 and (c) modified SPC with SPC/glycerol/MFC/gellan of 100/1.5/40/40.

and breaking contributes to the increased toughness of the MFC reinforced SPC resins.

4. Conclusions

Soy protein was reinforced with a micro/nano-fibrillated cellulose and further blended with gellan to prepare the biodegradable composite resins. The addition of the micro/nano-sized fibrils showed significant increase in the mechanical properties such as Young's modulus, fracture stress and toughness. With the incorporation of 40 parts of MFC, Young's modulus, fracture stress and toughness were increased to 2346 MPa, 71.2 MPa and 5.3 MPa, respectively compared to the Young's modulus of 589 MPa, fracture stress of 21.7 MPa and toughness of 2.7 MPa obtained for SPC without MFC. Gellan was then added to further modify MFC reinforced soy protein resin to improve its mechanical and physical properties. Addition of gellan to SPC forms an IPN-like structure. The SPC containing 1.5 parts of glycerol, 40 parts of MFC and 40 parts of gellan showed excellent mechanical properties with a fracture stress of 122 MPa and modulus of 5.8 GPa. These resins could be used with high strength cellulose fibers to form composites with excellent mechanical properties.

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References

- Koenig, M.F. and Huang, S.J. (1995) *Polymer*, 36, 1877–1882.
- Athanasiou, K.A., Niederauer, G.G. and Agrawal, C.M. (1996) *Biomaterials*, 17, 93–102.
- Lee, S.Y. (1996) *Biotechnol. Bioeng.*, 49, 1–14.
- Chandra, R. and Rustgi, R. (1998) *Prog. Polym. Sci.*, 23, 1273–1335.
- Abdelmoez, W. and Yoshida, H. (2006) *AIChE J.*, 52, 2607–2617.
- Blaker, J.J., Maquet, V., Jerome, R., Boccaccini, A.R. and Nazhat, S.N. (2005) *ACTA Biomater.*, 1, 643–652
- Ly, Y.T.P., Johnson, L.A. and Jane, J. In: *Biopolymers from Renewable Resources*, Kaplan, D.L. (ed.); Springer: New York, 144–176, 1998.
- Paetau, I., Chen, C.Z. and Jane, J.L. (1994) *Ind. Eng. Chem. Res.*, 33, 1821–1827.
- Chabba, S., Matthews, G.F. and Netravali, A.N. (2005) *Green Chem.*, 7, 576–581.
- Ghorpade, V.M., Li, H., Gennadios, A. and Hanna, M.A. (1995) *T ASAE*, 38, 1805–1808.
- Rhim, J.W., Gennadios, A., Handa, A., Weller, C.L. and Hanna, M.A. (2000) *J. Agr. Food Chem.*, 48, 4937–4941.
- Chabba, S. and Netravali, A.N. (2005) *J. Mater. Sci.*, 40, 6275–6282.
- Chabba, S. and Netravali, A.N. (2005) *J. Mater. Sci.*, 40, 6263–6273.
- Huang, X.S. and Netravali, A.N. (2008) *Ind. Crop. Prod.*, submitted.
- Huang, X.S. and Netravali, A.N. (2006) *Biomacromolecules*, 7, 2783–2789.
- Dicharry, R.M., Ye, P., Saha, G., Waxman, E., Asandei, A.D. and Parnas, R.S. (2006) *Biomacromolecules*, 7, 2837–2844.
- Salmoral, E.M., Gonzalez, M.E., Mariscal, M.P. and Medina, L.F. (2000) *Ind. Crop. Prod.*, 11, 227–236.
- Lodha, P. and Netravali, A.N. (2005) *Polym. Composite*, 26, 647–659.
- Lodha, P. and Netravali, A.N. (2005) *Ind. Crop. Prod.*, 21, 49–64.
- Stuchell, Y.M. and Krochta, J.M. (1994) *J. Food Sci.*, 59, 1332–1337.
- Jansson, P.E., Lindberg, B. and Sandford, P.A. (1983) *Carbohydr. Res.*, 124, 135–139.
- Doner, L.W. and Douds, D.D. (1995) *Carbohydr. Res.*, 273, 225–233.
- Banik, R.M., Kanari, B. and Upadhyay, S.N. (2000) *World J. Microb. Biot.*, 16, 407–414.
- Yang, L. and Paulson, A.T. (2000) *Food Res. Int.*, 33, 571–578.
- Sudhamani, S.R., Prasad, M.S. and Sankar, K.U. (2003) *Food Hydrocolloid*, 17, 245–250.
- Ciardelli, G., Chiono, V., Vozzi, G., Pracella, M., Ahluwalia, A., Barbani, N., Cristallini, C. and Giusti, P. (2005) *Biomacromolecules*, 6, 1961–1976.
- Mariniello, L., Di Pierro, P., Esposito, C., Sorrentino, A., Masi, P. and Porta, R. (2003) *J. Biotechnol.*, 102, 191–198.
- Lodha, P. and Netravali, A.N. (2005) *Compos. Sci. Technol.*, 65, 1211–1225.
- Fu, S.Y. and Lauke, B. (1996) *Compos. Sci. Technol.*, 56, 1179–1190.
- Pothan, L.A., Thomas, S. and Neelakantan, N.R. (1997) *J. Reinf. Plast. Comp.*, 16, 744–765.
- Chtourou, H., Riedl, B. and Aitkadi, A. (1992) *J. Reinf. Plast. Comp.*, 11, 372–394.
- Favier, V., Canova, G.R., Shrivastava, S.C. and Cavaille, J.Y. (1997) *Polym. Eng. Sci.*, 37, 1732–1739.
- Nakagaito, A.N., Iwamoto, S. and Yano, H. (2005) *Appl. Phys. A – Mater.*, 80, 93–97.
- Nakagaito, A.N. and Yano, H. (2005) *Appl. Phys. A – Mater.*, 80, 155–159.
- Nakagaito, A.N. and Yano, H. (2004) *Appl. Phys. A – Mater.*, 78, 547–552.
- Okubo, K., Fujii, T. and Yamashita, N. (2005) *JSME Int. J. A-Solid M.*, 48, 199–204.
- Samir, M.A.S.A., Alloin, F., Paillet, M. and Dufresne, A. (2004) *Macromolecules*, 37, 4313–4316.
- Bledzki, A.K. and Gassan, J. (1999) *Prog. Polym. Sci.*, 24, 221–274.
- Mohanty, A.K., Misra, M. and Hinrichsen, G. (2000) *Macromol. Mater. Eng.*, 276, 1–24.
- Fukuda, H. and Chou, T.W. (1982) *J. Mater. Sci.*, 17, 1003–1011.