

Investigation into ramie whisker reinforced arylated soy protein composites

Rakesh KUMAR (✉)^{1,2} and Lina ZHANG¹

Whiskers were prepared from ramie fibers and were characterized using atomic force microscopy to evaluate their dimensions. SPI/whiskers composites (SW) were prepared by incorporating different weight contents (wt.%) of the whiskers into soy protein isolate (SPI). Thiodiglycol was used as a plasticizer for the preparation of SW composites. The SW composites were arylated with 2,2-diphenyl-2-hydroxyethanoic acid through the process of “dip-coating” and coded as SW-B. In this paper, the characterization of SW and SW-B composites, such as their morphologies, mechanical properties, thermal stability, optical transmittance, and water uptake, are discussed. The results indicated substantial improvement in the water resistance, thermal stability, and the modulus of the SW-B composites after arylation due to the formation of hydrophobic diphenylhydroxymethane (DPHM) micro-particles on the surface. This work provides a novel method to increase the water resistance of protein based composites.

Keywords soy protein, ramie whiskers, water uptake, arylation, composites

1 Introduction

The reuse of classical fiber reinforced composites is not possible due to the very high stability of synthetic fibers and matrices. In order to get rid of these types of composites, we use landfill disposable systems. Due to the increasing population, however, many nonbiodegradable wastes are generated and simple landfill disposable systems are not sufficient. Therefore, environmentally compatible alternatives, e.g., recovery of raw materials, or more importantly, biodegradation of materials in certain circumstances, are being sought and examined. Recently, the fabrication of soy

protein isolate (SPI)/natural fiber composites has been reported [1–5]. Additionally, whiskers derived from natural fibers have also become one of the most promising means of dramatically increasing the physical properties of the composites [6–10]. Whiskers are considered as very promising reinforcing materials for composites because of their high stiffness and strength [8]. They are nearly free of internal defects because of their small diameter; thereby they yield strengths close to the maximum theoretical value predicted by the theory of elasticity. The extent of their reinforcement has been found to depend on several factors such as the nature of the matrix, the generation of a strong fiber matrix interface through physicochemical bonding, and the dispersion of the whiskers in the matrix [11–14].

Ramie is a plant fiber that has been used since ancient times and is commonly known as the China grass. Ramie fibers are widely-cultivated plants of industrial importance. We previously showed the successful usage of thiodiglycol (TDG) [15] and 2,2-diphenyl-2-hydroxyethanoic acid (DPHEAc) for the fabrication of relatively high water resistant soy protein films [16,17] and composites [18]. In this paper, the use of ramie whiskers as reinforcement materials in the SPI matrix with TDG as a plasticizer is reported. The SPI composites were arylated with DPHEAc through the process of “dip coating”, as mentioned elsewhere [18]. The morphologies, mechanical properties, and water resistance of the arylated and non-arylated composites were investigated. This work will generate renewed interest in preparing water resistant and environmentally-friendly bio-composites with protein as a matrix.

2 Experimental

2.1 Materials

SPI with a protein content of approximately 91% (dry basis) was purchased from Hubei Yunmeng Protein Technology Co. (Yunmeng, Hubei, China). Sulfuric acid, sodium hydroxide (Shanghai Chemical Co., Shanghai, China), DPHEAc, and TDG (bp = 164–166°C, mol. wt. = 122.19 g·mol⁻¹ and density = 1.182 g·mL⁻¹) (Sigma) were used as received. Ramie fibers were purchased from Hubei province.

2.2 Preparation of ramie whiskers

Ramie whiskers were prepared by reported methods [19]. The ramie fibers were cut in small dimensions. The small ramie fibers were washed four times in boiling 2 wt.% aqueous NaOH for 4 h under mechanical stirring. The fibers were filtered and rinsed with distilled water between each treatment step. The fibers were subsequently dried for 24 h at 50°C in a

Received October 19, 2009; accepted November 24, 2009

1. Department of Chemistry, Wuhan University, Wuhan 430072, China

2. CSIR MSM, Port Elizabeth 6000, South Africa

E-mail: krrakesh72@gmail.com

convection oven. The dried-treated fibers were dispersed in 65 wt.% sulfuric acid in water (4 wt.% ramie). This suspension was held at 60°C under mechanical stirring for 15 min to allow ramie hydrolysis. The suspension was subsequently diluted with an equal part of cold water and washed by successive centrifugation at 10000 rpm and 10°C until a turbid supernatant became visible (3 times). Dialysis against distilled water was performed to remove free acid in the dispersion, which was verified by the neutrality of the dialysis effluent. Complete dispersion of the ramie whiskers was obtained after a sonication step. The dispersions were stored in refrigerator after filtration and the addition of several drops of chloroform. The ramie whisker yield was approximately 30% of the original ramie weight.

2.3 Preparation of soy protein composites

Whisker reinforced composites were prepared in two stages. In the first stage, 30% of TDG w.r.t. SPI was mixed for about 1 h in a concentration of 0.025 mol·mL⁻¹ of pH 9.5–10. Different amounts (wt.%) of the whiskers were added to the SPI-TDG dispersion. The whiskers and the matrix were mixed to coat the fibers uniformly. The resulting mixtures were then poured onto the glass plate to prepare the composites by the solution casting method. The composites were peeled off after drying in an oven at 60°C for 24 h. In the second stage, the peeled off composites were subjected to hot press at 140°C for 20 min under a pressure of 15 MPa. We controlled the wt.% of whiskers in SPI as 0, 2.5, 5, 7.5, 10, 15, 20, and 25 and coded the composites as SW0, SW2.5, SW5, SW7.5, SW10, SW15, SW20, and SW25, respectively. The SW composites were arylated by immersing the samples in DPHEAc solution (0.5% w/v) for 26 h. This sample was coded as SW-B [18].

2.4 Characterization

Atomic force microscopy (AFM) image of whiskers was performed on a PicoScan atomic force microscope (Molecular Imaging, USA). Freshly prepared samples were mounted on AFM stage and imaged under MAC Mode in air (relative humidity = 40%–50%, $T = \sim 25^\circ\text{C}$) using MAClever type II probes (spring constant = 2.8 N·m⁻¹, resonant frequency = ~ 75 kHz, Molecular Imaging, USA). Scan rates were about 1.5 line·s⁻¹. The images were rastered at 256 pixels × 256 pixels, unfiltered and flattened when needed. Scanning electron microscope (SEM) images of the surface of SW and SW-B composites were taken on a FESEM (Sirion USA) electron microscope at an accelerating voltage of 20 kV. The optical transmittance (T_T) of the SW and SW-B composites was measured using a UV-vis spectrophotometer (Shimadzu UV-160A, Japan) with the wavelength from 400 to 800 nm.

The tensile strength, elongation at break, and Young's modulus of the composites were measured on a universal testing machine (CMT6503, Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China) with a tensile rate of 5 mm·min⁻¹ according to ISO527-3: 1995 (E). The samples were preconditioned at 57% relative humidity (RH) for three days at room temperature before performing the experiments. For each sample, an average value of five replicates was studied.

Water uptake of the samples was evaluated according to ASTM D570-81. The composites were preconditioned at 50°C for 24 h, then cooled in desiccators and weighed (W_0). The preconditioned specimens were immersed in distilled water at room temperature for 26 h. After the samples were removed from water, the containers were placed in an oven at 50°C to evaporate water. The residuals were the water-soluble contents (W_T). The weight gain of the samples (W_T) plus the weight of the water-soluble residuals was counted as the total absorbed water. The average value of three readings is reported.

3 Results and discussion

3.1 Morphology and structure

Figure 1 shows the AFM image of the ramie whiskers. Ramie whiskers existed separately as well as in the form of aggregates at some places. The average diameter and length were found to be approximately (30 ± 5) nm and (250 ± 50) nm, respectively. Figure 2 shows the SEM photograph of the surface (left) and cross section (right) of SW15 (Figure 2(a),(b)) and SW15-B (Figure 2(c),(d)) composites. The SW

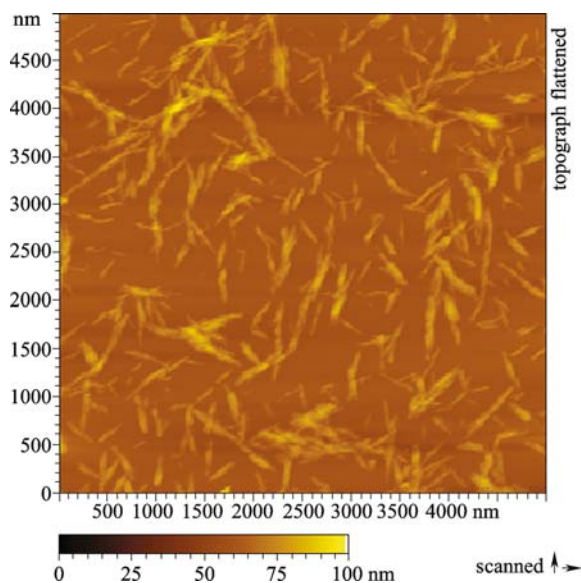


Figure 1 The atomic force microscopy image of the ramie whiskers.

composites exhibited uniform surfaces, whereas the micro-particles of diphenylhydroxymethane (DPHM) were observed on the surface of the SW-B composites. We have reported such observation previously in the presence of water. DPHM is formed due to the loss of CO_2 from DPHEAc upon interaction with SPI [16]. A relatively uniform distribution of whiskers in the SPI matrix with a compact structure was observed for the cross-section of SW-B composites. However, the cross-section of SW composites showed agglomerates of the whiskers. The diameter of the whiskers determined by SEM was larger than that identified by AFM, which resulted from charge concentration effects due to the emergence of whiskers from the observed surfaces [6].

In appearance, the arylated samples were hard and non-flexible compared to the non- arylated ones. The T_r of the SW and SW-B composites at a wavelength of 800 nm was acquired and shown in Figure 3. With an increase in the content of the whiskers from 0 to 15 wt.%, the value of T_r for the SW composites decreased from 57.7% to 42.2%. The obvious decrease in the T_r reflected the influence of the introduction of the whiskers on the interface structure. When the ramie whisker content increased to 25 wt.%, the T_r of the

SW-25 composites dropped remarkably to 35%. Interestingly, the T_r of the SW-B composites showed an increase in value, indicating an increased compatibility upon arylation. At higher wt.% of the whiskers i.e., for SW25-B composites, the T_r value remained almost the same as that of SW25. Similar to our earlier observation, in the SW-B composites, a strong band appeared at 700 cm^{-1} in the FTIR spectra [16]. The band at 700 cm^{-1} in composites was assigned to the out-of-plane deformation vibrations of the hydrogen atoms on the benzene ring, thus confirming the arylation of SPI with DPHEAc.

3.2 Properties of the composites

Figures 4(a) and 4(b) show the tensile strength and modulus of the SW and SW-B composites with the different amounts (wt.%) of the whiskers, respectively. The optimum wt.% of the whiskers for the reinforcement in the SPI composites was found to be 15 wt.%. Above this wt.%, there was no significant increase in the tensile strength and modulus. Interestingly, there was a ~ 10 – 15 times increase in the modulus for the SW-B composites, whereas increase in the ensile strength was around 1.5–2.0 times. However, SW and

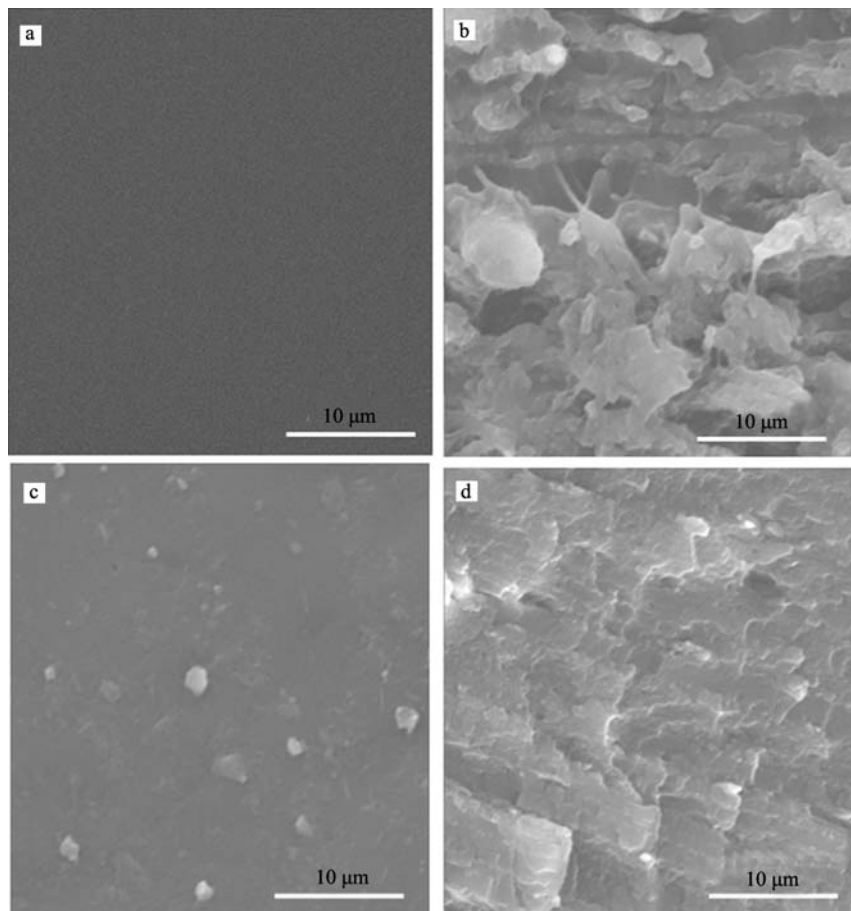


Figure 2 SEM photograph of the (a) surface and (b) cross section of the SW and (c) surface and (d) cross section of the SW-B composites.

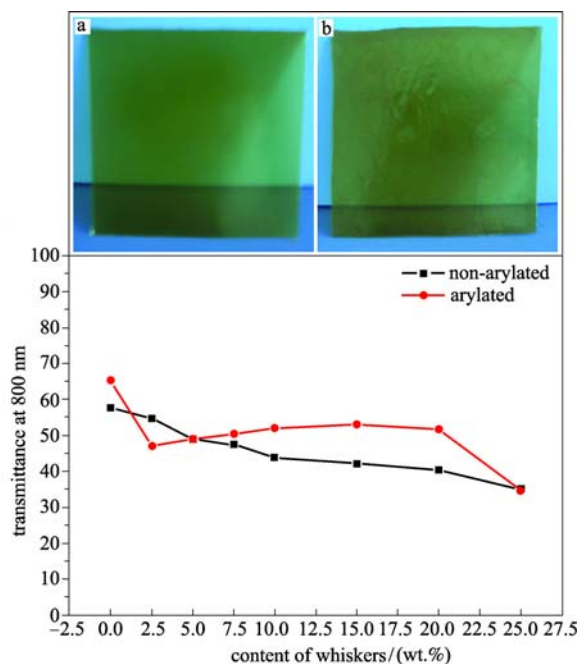


Figure 3 Top: Photograph of (a) SW and (b) SW-B (right) composites. Bottom: The dependence of the transmittance of arylated and non-arylated soy protein composites at 800 nm.

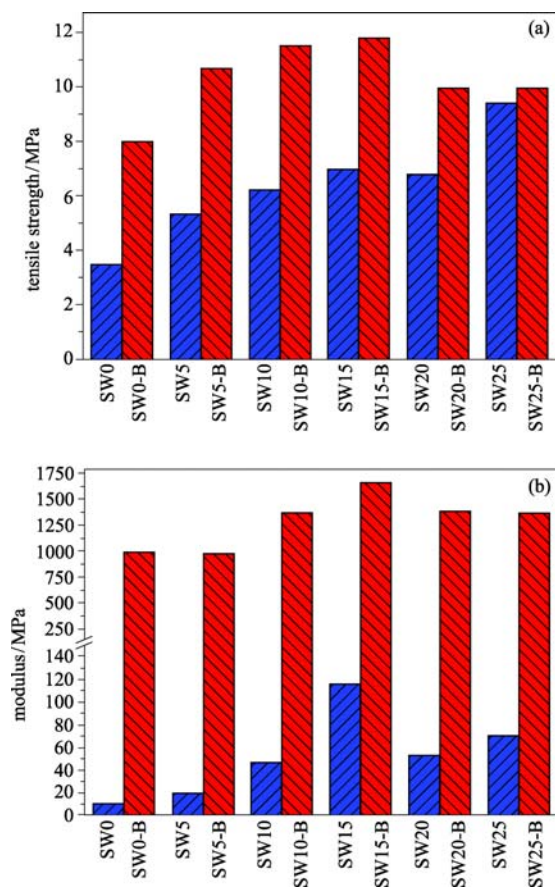


Figure 4 (a) Tensile strength and (b) modulus of SW and SW-B composites.

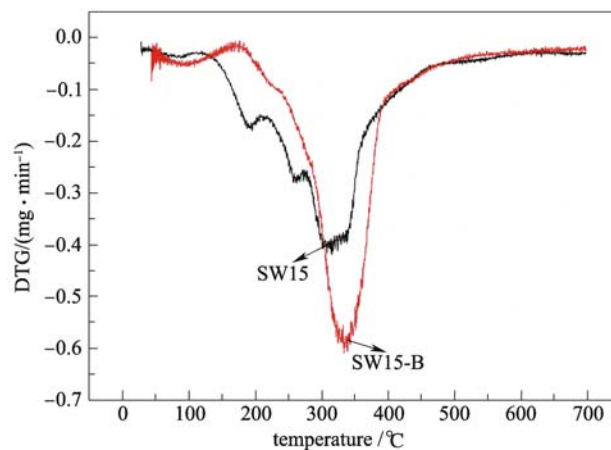


Figure 5 DTG curves of SW and SW-B composites.

SW-B showed a decrease in the mechanical properties above optimum wt.% of the fibers. Figure 5 shows the derivative thermogravimetry (DTG) curves of the SW and SW-B composites. The onset temperature (T_{onset}) and final temperature (T_{final}) for degradation of SW-B composites increased from 133°C to 195°C and from 376°C to 396°C, respectively. Interestingly, SW-B showed single stage degradation while SW showed three stages of degradation. The increase in the thermal stability indicated the effect of arylation on soy protein composites.

Water resistance of the SW and SW-B composites could be evaluated by the water uptake experiments (Figure 6). The water uptake decreased from 168% ± 5% for SW0 to 95% ± 5% for SW15, indicating the effect of whiskers on soy protein composites. The decrease in water uptake for SW-B composites indicated an increase in water resistance of the samples with an increase in the amount of whiskers. The water uptake of the SW-B composites (25% ± 5%) was significantly

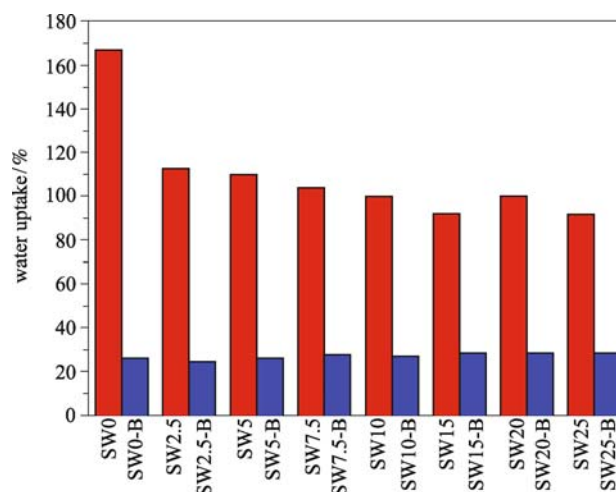


Figure 6 Water uptake of SW and SW-B composites.

lower than that of the SW composites. The significant improvement in the water resistance for SW-B composites can be attributed to the generation of hydrophobic DPHM microparticles upon arylation of SPI with DPHEAc [16]. In view of the water uptake results, the water resistance of the SW-B composites showed significant improvement.

4 Conclusions

Ramie whiskers were used as a reinforcing agent for TDG plasticized SPI in order to obtain whisker reinforced composites. Compared with non-arylated composites, the arylated ones showed significant improvement in water resistance, mechanical properties, and thermal stability. We expect that the arylation of protein materials could serve as a general motif to fabricate water resistant protein based composites, which is suitable for more diverse applications in the area of biocomposites.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant Nos. 59933070, 30530850, and 20474048) and the major program for Science and Technology (2006BA02A09).

References

1. Lodha, P.; Netravali A. N., *J. Mat. Sci.* **2002**, *37*, 3657–3665
2. Mohanty, A. K.; Khan, M. A.; Sahoo, S.; Hinrichsen, G., *J. Mat. Sci.* **2000**, *35*, 2589–2595
3. Otaigbe, J. U.; Goel, H.; Babcock, T.; Jane, J., *J. Elast. Plast.* **1999**, *31*, 56–71
4. Paetau, I.; Chen, C. Z.; Jane, J. L., *Ind. Eng. Chem. Res.* **1994**, *33*, 1821–1827
5. Liu, W.; Mohanty, A. K.; Askeland, P.; Drzal, L. T.; Misra, M., *Polymer* **2004**, *45*, 7589–7596
6. Lu, Y.; Weng, L.; Zhang, L., *Biomacromolecules* **2004**, *5*, 1046–1051
7. Wang, Y.; Cao, X.; Zhang, L., *Macromol. Biosci.* **2006**, *6*, 524–531
8. Tjong, S. C.; Meng, Y. Z., *J. Appl. Polym. Sci.* **1999**, *72*, 501–508
9. Angellier, H.; Boisseau, S. M.; Dole, P.; Dufresne, A., *Biomacromolecules* **2006**, *7*, 531–539
10. Chazeau, L.; Paillet, M.; Cavaille, J. Y., *J. Polym. Sci. Part B: Polym. Phys.* **1999**, *37*, 2151–2164
11. Chazeau, L.; Cavaille, J. Y.; Perez, J., *J. Polym. Sci. Part B: Polym. Phys.* **2000**, *38*, 383–392
12. Nair, K. G.; Dufresne, A., *Biomacromolecules* **2003**, *4*, 657–665
13. Nair, K. G.; Dufresne, A., *Biomacromolecules* **2003**, *4*, 666–674
14. Malkapuram R.; Kumar, V.; Negi, Y. S., *J. Reinf. Plast. Compos.* **2009**, *28*, 1169–1189
15. Kumar, R.; Wang, L.; Zhang, L., *J. Appl. Polym. Sci.* **2009**, *111*, 970–977
16. Kumar, R.; Zhang, L., *Biomacromolecules* **2008**, *9*, 2430–2437
17. Kumar, R.; Zhang, L., *Ind. Crops Prod.* **2009**, *29*, 485–494
18. Kumar, R.; Zhang, L., *Compos. Sci. Techn.* **2009**, *69*, 555–560
19. de Rodriguez, N. L. G.; Thielemans, W.; Dufresne, A., *Cellulose* **2006**, *13*, 261–270