Investigation Into Ramie Whiskers Reinforced Arylated Soy Protein Composites

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Abstract

Whiskers were prepared from ramie fibers and were characterized by transmission electron microscopy to evaluate their dimensions. By incorporating different weight content (wt%) of the whiskers into soy protein isolate (SPI), we prepared the SPI/whiskers composites designated as SW. 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", coded as SW-B. The SW and SW-B composites were characterized, and their morphologies, mechanical properties, thermal stability, optical transmittance, and water uptake were 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) microparticles on the surface. This work provided a novel method to increase the water resistance of protein based composites.

Key Words: soy protein, ramie whiskers, water uptake, arylation, composites

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1. Introduction

Due to the very high stability of synthetic fibers and matrices the reuse of classical fibers reinforced composites are not possible. To get rid from these types of composites we use landfill disposable systems. Due to increasing population, lots of nonbiodegradable wastes are generated and simple landfill disposable systems are not sufficient. Therefore, environmentally compatible alternatives are thought for and examined, e.g. recovery of raw materials, or more importantly biodegradation of materials in certain circumstances. Recently, the fabrication of soy protein isolate (SPI)/natural fiber composites have 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 to be very promising reinforcing materials for composites, because of their high stiffness and strength [8]. Due to small diameter, whiskers are nearly free of internal defects, thereby yielding strength 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 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 China grass. Ramie fibers are widely cultivated plant of industrial importance. We have shown previously the successful use 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 SPI matrix with TDG as a plasticizer has been 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 the renewed interest of preparing water resistant and environmentally-friendly bio-composites with protein as a matrix.

2. Experimental

2.1 Materials

SPI with a protein content of about 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^{o}C, mol. wt. = 122.19 g/mol and density = 1.182 g/mL) (Sigma) were used as received. Ramie fibers were purchased from Hubei province.

2.2 Preparation of ramie whiskers

Ramie whiskers were prepared by method as reported elsewhere [19]. The ramie fibers were cut in small dimensions. The small ramie fibers were washed four times in boiling 2wt% aqueous NaOH for 4 h under mechanical stirring. The fibers were filtered and rinsed with distilled water in between each treatment step. The fibers were

subsequently dried for 24 h at 50^{o}C in a convection oven. The dried treated fibers were dispersed in 65wt% sulfuric acid in water (4wt% ramie). This suspension was held at 60^{o}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 10,000 rpm and 10^{o}C until a turbid supernatant became visible (3 times). Dialysis against distilled water was performed to remove free acid in the dispersion. This was verified by neutrality of the dialysis effluent. Complete dispersion of the ramie whiskers was obtained by a sonication step. The dispersions were stored in the refrigerator after filtration and 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 0.025 M having pH 9.5~10. Different content (wt%) of the whiskers was added to SPI-TDG dispersion. The whiskers and the matrix were mixed to coat the fibers uniformly. The resulting mixtures were then poured on the glass plate to prepare the composites by solution casting method. The composites were peeled off after drying in an oven at 60^{o}C for 24 h. In the second stage, the peeled off composites were subjected to hot press at 140^{o}C for 20 min under pressure of 15 MPa. By controlling the wt% of whiskers in SPI as 0, 2.5, 5, 7.5, 10, 15, 20, and 25, the composites were coded 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, 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 = ~25℃) using MAClever type II probes (spring constant = 2.8 N/m, resonant frequency = ~75 kHz, Molecular Imaging, USA). Scan rates were about 1.5 line/s. The images were rastered at 256 × 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_r) of the SW and SW-B composites was measured with a UV-vis spectrophotometer (Shimadzu UV-160A, Japan) from a wavelength of 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 % RH for three days at room temperature before performing the experiment. An average value of five replicates of each sample was taken.

Water uptake of the samples was evaluated according to ASTM D570-81. The composites were preconditioned at 50^{o}C for 24 h, then cooled in desiccators and

weighed (W_o). 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^oC to evaporate the water. The residuals were the water-soluble contents (W_r). The weight gain of the samples (W_t) plus the weight of the water-soluble residuals was counted as the total absorbed water. An average value of three readings has been reported.

3. Results and discussion

3.1 Morphology and structure

Figure 1 shows 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 the SW15 (Figure 2a,b) and SW15-B (Figure 2c,d) composites. The SW composites exhibited uniform surface, whereas the microparticles of diphenylhydroxymethane (DPHM) was observed on the surface of the SW-B composites. It has been reported by us that 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 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 TEM, which resulted from charge concentration effects due to the emergence of whiskers from observed surfaces [6].

In appearance, arylated samples were hard and non-flexible compared to non-arylated ones. The T_r of the SW and SW-B composites at a wavelength of 800 nm was found 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 whiskers content increased to 25 wt%, the T_r for the SW-25 composites dropped, remarkably, to 35 %. Interestingly, T_r of the SW–B composites showed an increase in value indicating increased compatibility upon arylation. At higher wt% of the whiskers i.e., for SW25-B composites, Tr value almost remained 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

Figure 4a and 4b shows the tensile strength and modulus of the SW and SW-B composites, respectively with the different content (wt%) of the whiskers. 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 ~10-15 times increase in modulus for the SW-B composites, whereas increase in tensile strength was around 1.50-2 times. However, SW and SW-B showed decrease in the mechanical properties above optimum wt% of the fibers. Figure 5 shows the DTG curves of SW and SW-B composites. The onset temperature (T_{onset}) and final temperature (T_{final}) for degradation of SW-B composites increased from 133 to 195^{o}C and 376 to 396^{o}C respectively. Interestingly, SW-B showed single stage degradation as compared to SW showing 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 can be evaluated by 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 amount of whiskers. The water uptake of the SW-B composites (25±5 %) was significantly lower than that of SW composites. The significant improvement in the water resistance for SW-B composites could 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 improved significantly.

4. Conclusions

Ramie whiskers were used as a reinforcing agent for TDG plasticized SPI to obtain whiskers reinforced composites. Compared with non-arylated composites, the arylated ones showed significant improvement in water resistance, mechanical properties and thermal stability. We expect 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.

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List of Figures

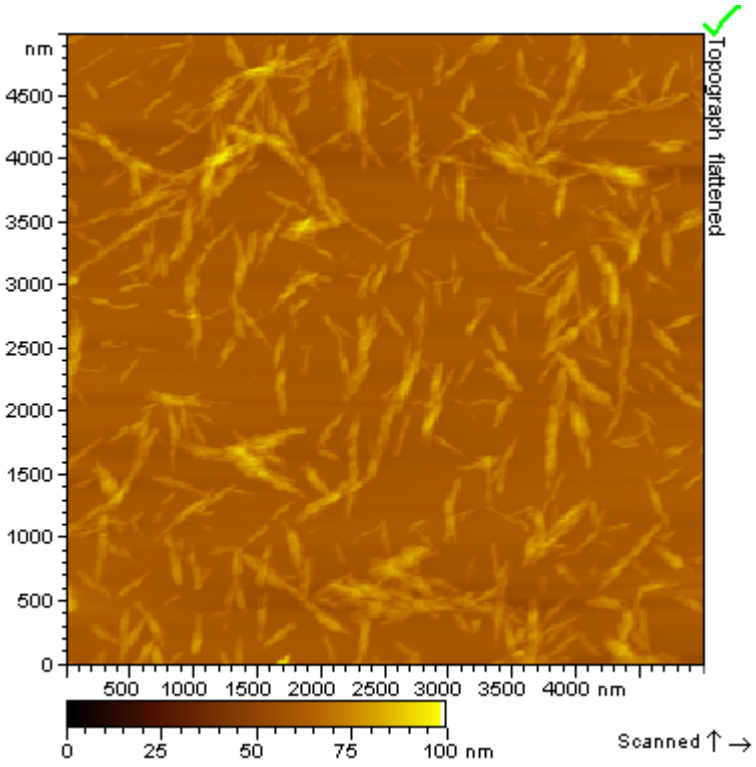

Figure 1 AFM image of the ramie whiskers.

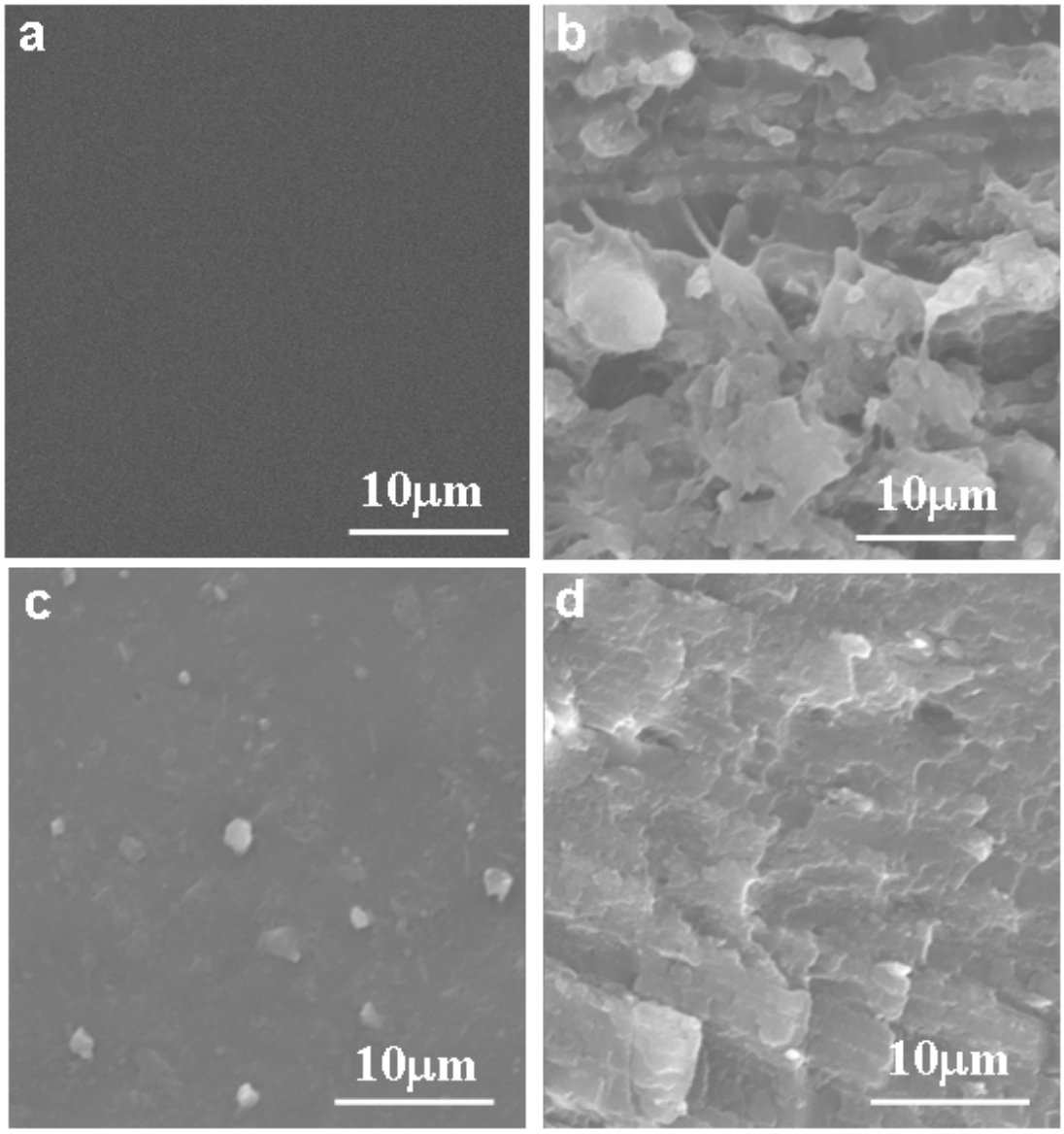

Figure 2 SEM photograph of the surface (left) and cross section (right) of the SW (a,b) and SW-B (c,d) composites.

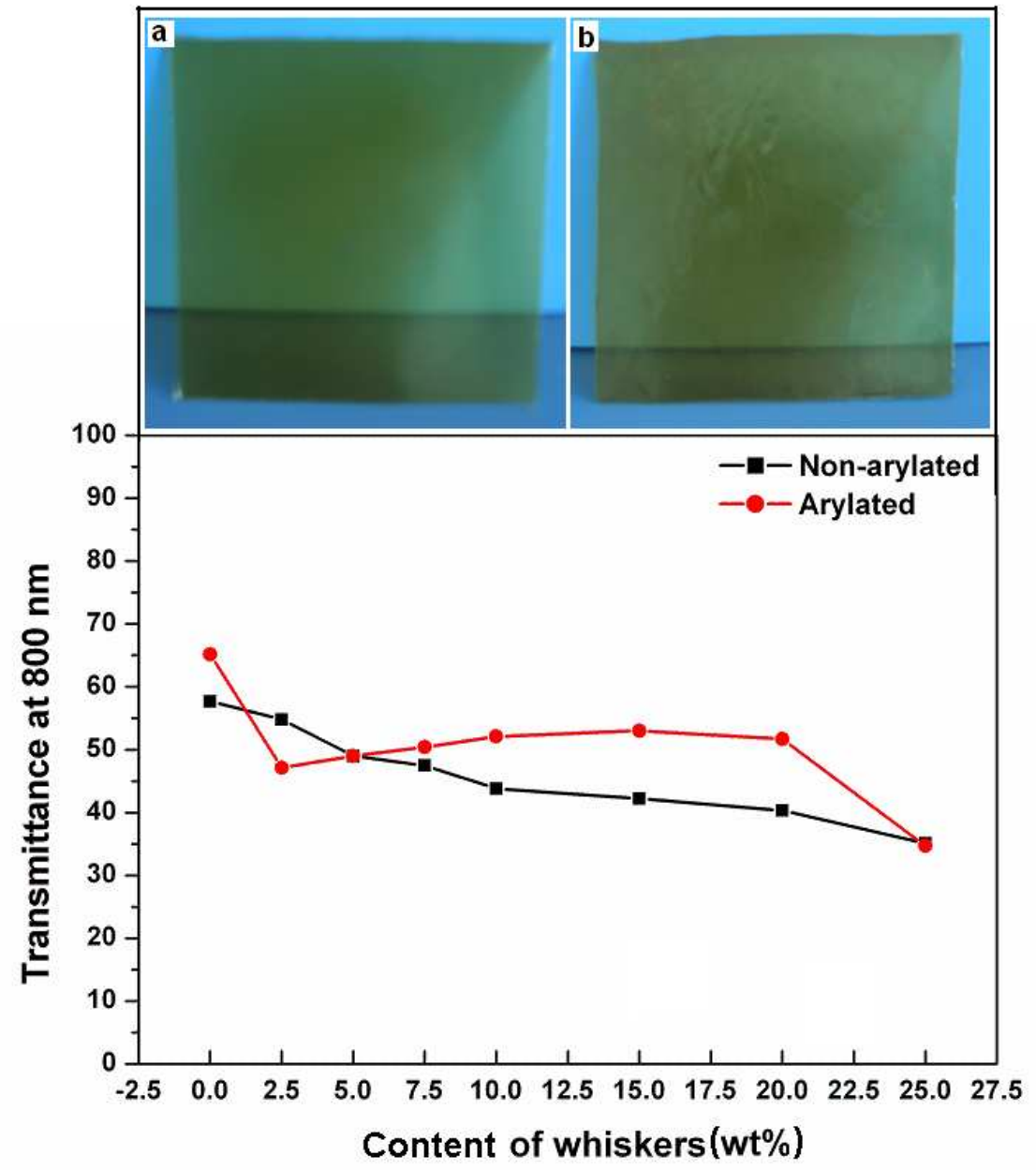

Figure 3 Photograph (top) of SW (left) and SW-B (right) composites. Dependence of the transmittance of arylated and non-arylated soy protein composites at 800 nm (bottom)

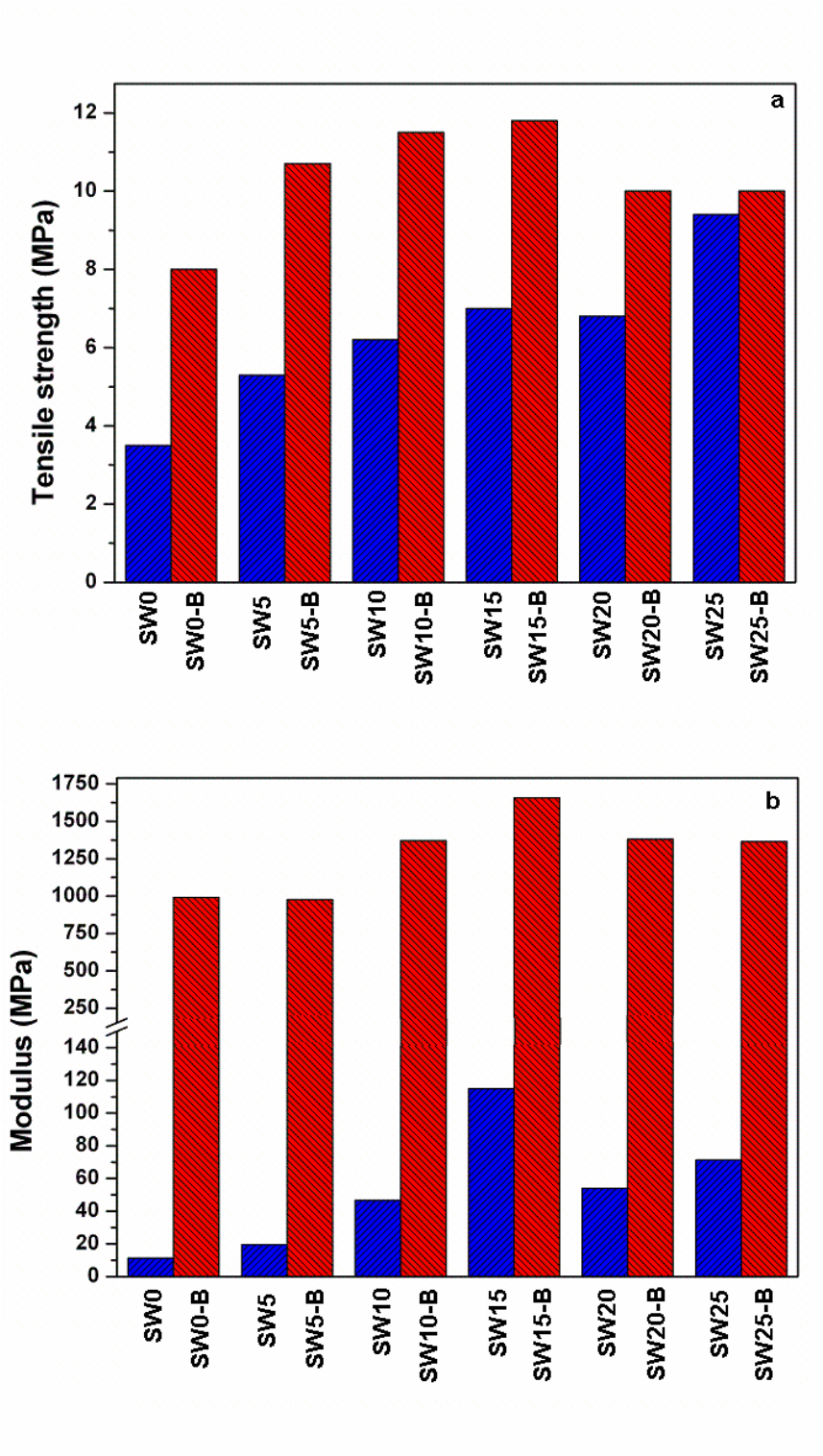

Figure 4 Tensile strength (a) and modulus (b) of SW and SW-B composites.

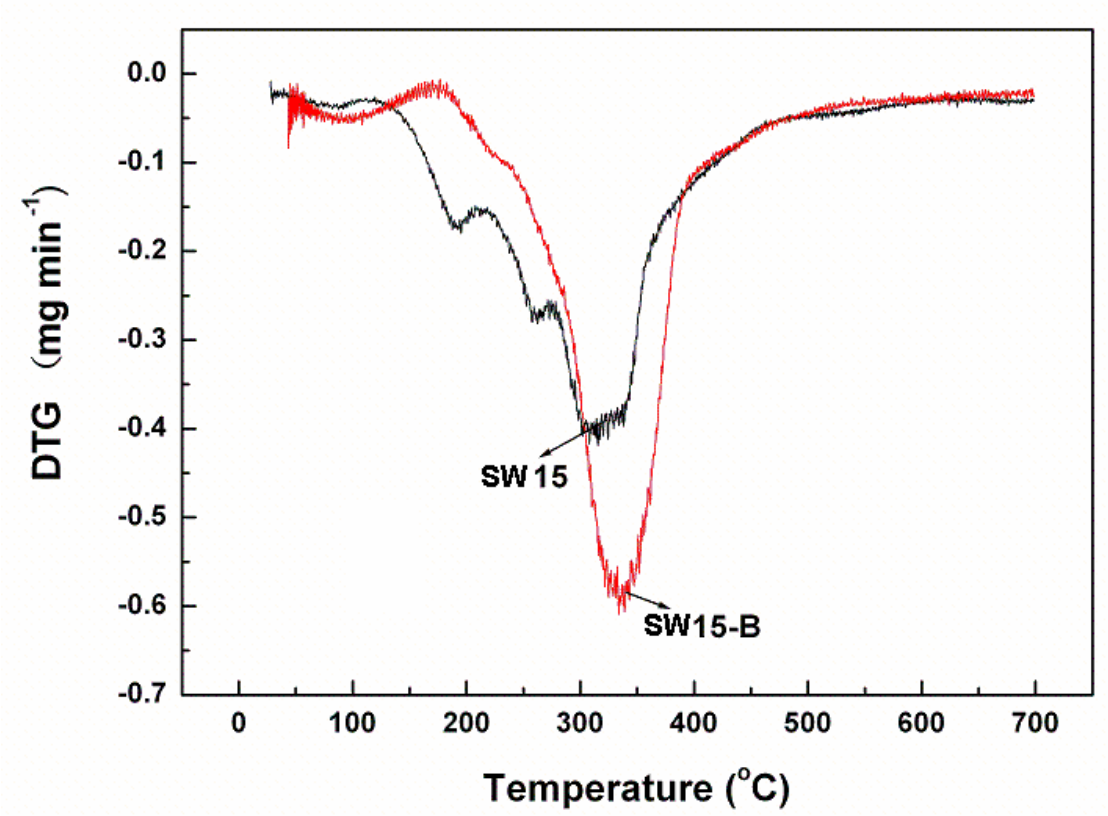

Figure 5 DTG curves of SW and SW-B composites

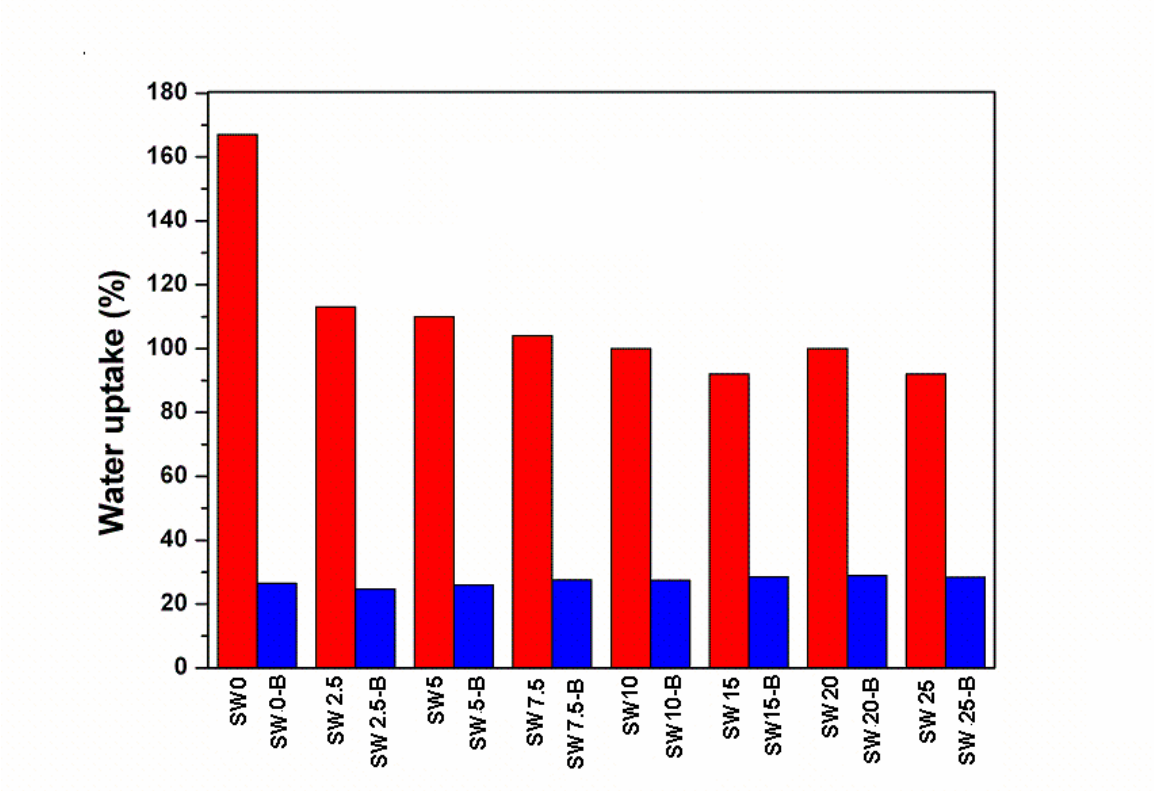

Figure 6 Water uptake of SW and SW-B composites.