

Characteristics of Vermiculite-Reinforced Thermoplastic Starch Composite Films

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ABSTRACT: The thermoplastic starch–vermiculite (VER) composite films were prepared by solution-casting technique in this study. First, the VER was used as the filler reinforcement for thermoplastic starch to enhance its properties. The modification of VER and the structure of films were investigated and characterized by X-ray diffraction and scanning electron microscope technology. Moreover, the Fourier transform infrared spectra confirmed that the VER particles formed strong hydrogen bond interactions with starch matrix.

According to TGA, differential scanning calorimetry study, and water absorption testing, the starch–VER composite films exhibited better improvement properties than did the starch matrix. It provides information on the use of VER to reinforce the properties of starch-based materials. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: thermoplastic starch; vermiculite; urea; composite films

INTRODUCTION

In the last decade, many environmental problems brought about by petrochemical wastes have already drawn close attention from researchers and experts in diverse areas. Many researchers have put forward the use of biodegradable polymers to obtain environmentally friendly materials. Recently, more attention has been paid on starch because of its complete biodegradability in soil and water and its worldwide availability at low cost. Several authors have already obtained the good performance of thermoplastic starch with the presence of clay and plasticizers.^{1–4} However, it is difficult to achieve industrialization production because of poor mechanical performance and their water sensitivity.⁵ Therefore, the starch-based materials have to be modified physically or chemically to take the place of conventional petroleum-based polymers.

Starch-based nanocomposites are a new class of materials with great potential developments. These

nanocomposites are prepared by the addition of low amounts of clay to the starch matrix, exhibiting the excellent properties of nanocomposites.^{6–8} The most commonly used clays in starch matrix were layered silicates, and especially on montmorillonite, as the reinforcing phase for starch-based materials. However, there is no literature about starch–vermiculite (VER) system. Recently, VER has been proved to be a promising reinforcing agent for biopolymer nanocomposites.^{9,10} VER is a natural hydrous magnesium silicate mineral with $(\text{Mg}, \text{Ca})_{0.7}(\text{Mg}, \text{Fe}, \text{Al})_{6.0}[(\text{Al}, \text{Si})_{8.0}](\text{OH}_{4.8}\text{H}_2\text{O})$ as the theoretical unit cell formula. VER belongs to the 2 : 1 layered structure composed of two tetrahedral silica sheets enclosing a central sheet of octahedral magnesia. Adjoining layers are held together by a combination of electrostatic and van der Waals forces.¹⁰ Furthermore, the increased presence of silanol groups on VER surface is noteworthy, which easily establish strong hydrogen bond interactions with hydroxyl groups in polymers such as starch and chitosan (CS).

In this study, starch–VER composite films were prepared by the solution-casting process with the addition of different VER types. Urea, which improves water resistance properties of starch-based materials and prevents the recrystallization of starch during the storage and transportation process, was used as the plasticizer of starch-based composites in this study. The uniformly dispersed composites were obtained,

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and the morphology of different composites was investigated and characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscope (SEM). Furthermore, the effect of various clay types and concentrations on the thermal properties and water absorption of starch-VER composite films are discussed.

EXPERIMENTS

Materials

The wheat starch (WS) was bought from Qinhuangdao pengyuan starch Co., LTD. The vermiculite (VER) was purchased by Chenxin vermiculite Co., LTD. The CS in powder form (a deacetylation degree greater than 75%) was obtained by Sigma-Aldrich (Shanghai, China). The inorganic cations in the VER were ion exchanged with sodium ions according to the reported literature,⁹ and Na⁺-VER powder obtained was denoted as NVER. Acetic acid (HAc) and Urea (U) were obtained from aladdin-reagent (Shanghai). Other reagents used were all analytical grade and used as received.

Preparation of CS-modified VER

VER (5 g, 400 mesh) was dispersed into 100 mL water solution with stirring for 12 h at 60°C. At the same time, CS (1 g) was dissolved in 1% (w/v) acetic acid with stirring for 2 h at 60°C to prepare the CS solution. The resulting solution was slowly added into the VER suspensions under stirring at 3 days at 60°C, and then the precipitates were washed with distilled water three times. The solids obtained were dried at 60°C overnight in a vacuum oven to obtain CS-modified VER (CVER) powder.

Preparation of thermoplastic starch-VER composite films

The thermoplastic starch-VER composite films were prepared by solution-casting technology. The clay was stirred in distilled water (10 mL) for 1 h at room temperature. At the same time, urea (30% w/w, relative to starch on dry basis) was added to the starch solution (20 mL) with stirring 1 h at room temperature. Subsequently, the clay suspensions were added into the starch solution. The mixture was then heated to the gelatinization temperature of starch and continuously stirred at this temperature for 1 h. The hot solution was then poured onto Teflon-coated Petri dishes, and the solvent was allowed to evaporate slowly to dryness at about 50°C. The dried films were removed and conditioned according to the different requirements of the test method used. The symbols of starch composites are listed in Table I.

TABLE I
The Symbol of WS-VER-U Composites

Samples	Starch (wt %)	Urea (wt %)	CVER		
			NVER (wt %)	CS (wt %)	NVER (wt %)
WS-U	100	30	–	–	–
WS-1CVER-U	99	30	0.83	0.17	–
WS-3CVER-U	97	30	2.5	0.5	–
WS-5CVER-U	95	30	4.2	0.8	–
WS-7CVER-U	93	30	5.8	1.2	–
WS-3NVER-U	97	30	–	–	3
WS-5NVER-U	95	30	–	–	5

Characterizations and measurements

The XRD data were recorded by using an X-Ray diffractometer, Rigaku D/Max-Rc, equipped with a Cu K α radiation ($\lambda = 0.154060$ nm) source generated at 40 kV and 40 mA. The diffraction spectra were obtained in the range of 2°–50° at a scan rate of 2°/min (step size = 0.02°).

The FTIR spectra were performed by a Nicolet 380 FTIR spectrometer using a resolution of 4 cm⁻¹. The scanning coverage was from 4000 to 400 cm⁻¹. KBr was used as a background material, and disks of sample/KBr mixtures were prepared to obtain the FTIR spectra.

The morphology of the samples was observed by using JSM-5800 SEM. The surfaces of the materials were coated by sputtering with gold before observation.

The thermal behavior of film samples was determined by using DTG-60A thermogravimetric analyzer with flow rate of 50 mL/min. The samples were heated from room temperature to 600°C with a constant heating rate of 20°C/min. All the samples were dried at 50°C for 12 h prior to TGA tests, and the specimen weight was in the 5–10 mg range.

Differential scanning calorimetry (DSC) was carried out in DSC141 (Setaram, France) equipment with a cooler system of liquid nitrogen. About 10 mg of dried samples were placed in aluminum pans. Samples were gradually heated from –20 to 100°C under nitrogen atmosphere at a heating rate of 5°C/min. The glass transition temperature (T_g) was taken as the inflection point of the increment of specific heat capacity.

The film samples were dried in the oven at 100°C for 24 h and then immediately weighed to obtain the initial weight (W_1). The samples were stored at relative humidity conditions (RH = 100%) in a desiccator for 3 days at 25°C, and then taken out and immediately weighed to obtain the final weight (W_2). The moisture content (K) was calculated by the formula, $K = (W_2 - W_1)/(W_1) \times 100\%$. All measurements were performed in duplicate.

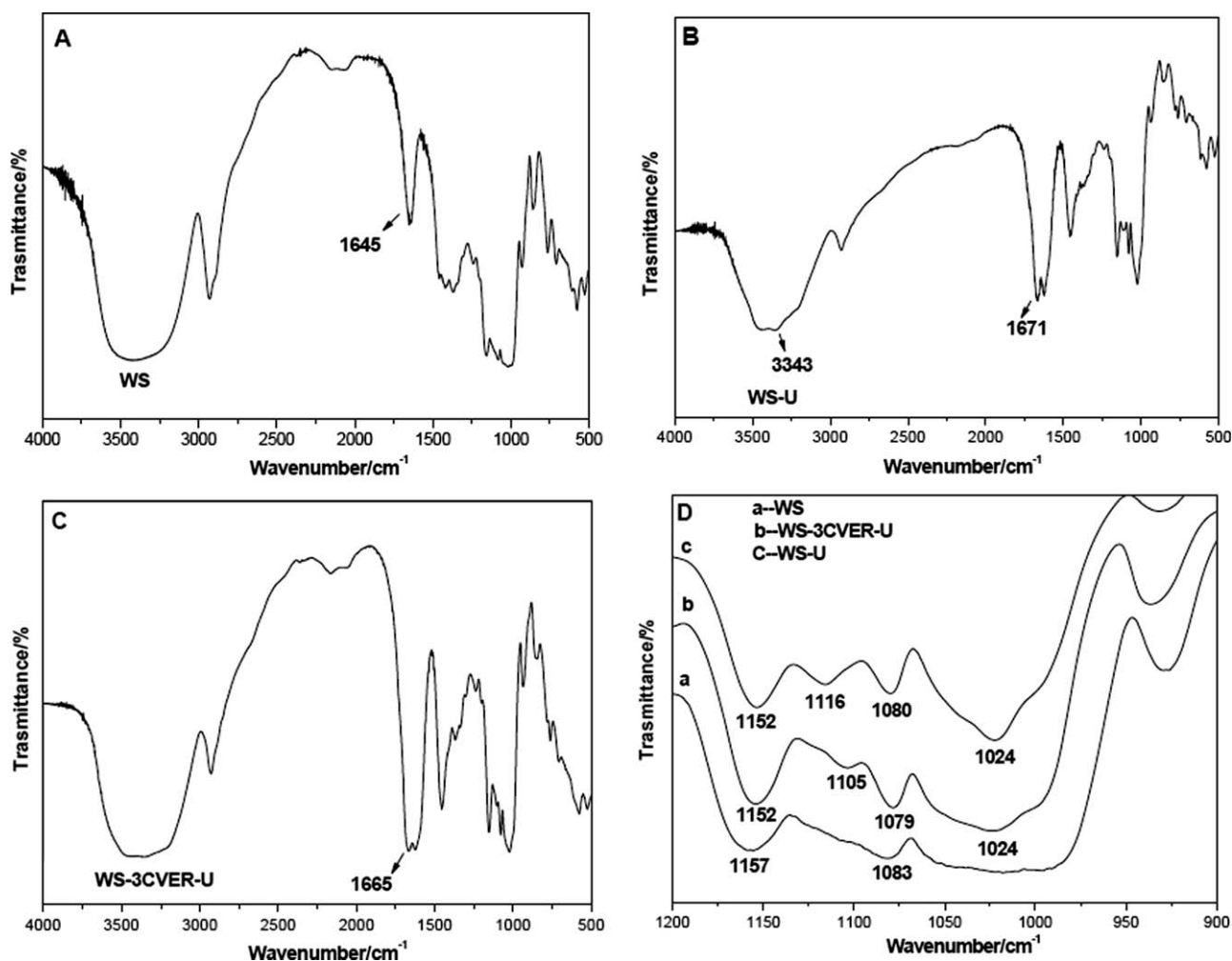


Figure 1 FTIR spectra of (A) WS, (B) WS-U, (C) WS-3CVER-U, and (D) FTIR spectra of samples between 1200 and 900 cm^{-1} .

Tensile tests were investigated using WDW-10 universal testing machine according to GB/T1040.1-2006 standard. The dumbbell-shaped specimens were conditioned at room temperature under 33% RH for 3 days before testing. The crosshead speed was 50 mm/min. Each measurement was performed for five specimens and averaged.

RESULTS AND DISCUSSION

FTIR analysis

The FTIR spectra of WS, WS-U, and WS-3CVER-U powders are shown in Figure 1. The characteristic peak registered at 1645 cm^{-1} is attributed to the $\delta_{\text{H-O-H}}$ vibration of bond water in the starch. Comparing the spectrum of WS and WS-U, the new peak at 3343 cm^{-1} related to the O-H stretching vibration band and another new peak at 1671 cm^{-1} attributed to the characteristic peak of ester group are observed in WS-U samples. The results indicate that starch can form strong hydrogen bonds with urea, and

even form part covalent bonds in the thermoplastic starch (TPS) processing. In comparison with the spectrum of WS-U film, a broader and stronger peak at lower frequency appears in WS-3CVER-U samples taking the place of the double peak in the WS-U, indicating that starch could establish strong interactions with hydroxyl groups on clay platelets in the TPS processing. Moreover, the peak related to the stretching vibration of ester group occurs at lower wave numbers (1665 cm^{-1}) in WS-3CVER-U samples. This may be in that the NH_2 of CS also intensively reacted with hydroxyl groups in starch, which made the stretching vibration of ester group shifted to lower frequency. This phenomenon confirms that the CS molecules adsorbed on the surface of clay particles could adjust the interactions of starch-clay system.

To better observe the shifts of groups related to the C-O bond stretching of samples in the TPS processing, the characteristic peaks of samples between 900 and 1200 cm^{-1} are shown in Figure 1(D). The peaks observed at around 1157 and 1083 cm^{-1} are related to the C-O bond stretching of C-O-H groups in

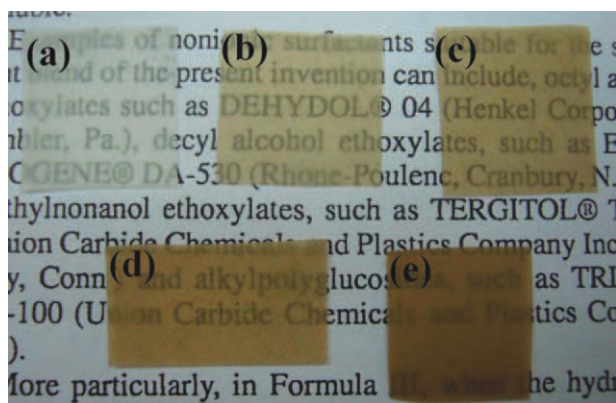


Figure 2 Optical images of starch films: (A) WS-U, (B) WS-1CVER-U, (C) WS-3CVER-U, (D) WS-5CVER-U, and (E) WS-5NVER-U. The thickness of each film is about 0.5 mm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

starch. It is apparent that these characteristic peaks of WS-U and WS-3CVER-U films appear at lower wave numbers than those of WS film. This is because both urea and clay could establish the strong hydrogen bonds with O of C—O—H groups in starch molecules. Furthermore, new peaks occurred between 1133 and 1100 cm^{-1} , associated with C—O bond stretching in WS-U and WS-3CVER-U composites. When compared with WS-U, the peak obviously shifted toward lower frequency, from 1116 to 1105 cm^{-1} , in WS-3CVER-U films, indicating the presence of the stronger interactions of starch–clay–CS in composites. Thus, the obvious shift of peak was not observed in the FTIR spectra of other starch–clay systems in our work. This observation implies that VER has an excellent compatibility with starch molecules. The broad peak observed between 990 and 1037 cm^{-1} is due to the C—O stretching vibration of C—O—C groups in starch molecules. Therefore, a conclusion can be drawn that the slight shifts of groups should be tightly associated with the stability and intensity of hydrogen bonds established among urea, clay, and C—O groups of starch in composites. The more stable and strong the hydrogen bonds were, the more the correlative peaks shifted and the peak styles changed.¹¹

Morphology

Figure 2 displays the optical images of the WS-U, WS-5NVER-U, and WS-CVER-U films containing different clay contents. It is clearly shown that all the WS-CVER-U films are homogeneous and transparent, similar to the WS-U film as confirmed by the fact that the words under the film can be clearly seen, and that the WS-5NVER-U film exhibits slight translucency. This demonstrates that the CVER particles with much smaller sizes than the pristine clay

are dispersed homogeneously in starch matrix through comparing two films with the same clay contents (Fig. 2, films d and e). The results indicate that the use of CS promoted the clay disaggregation as well as its better homogenous dispersion in starch matrix.¹² Obviously, the homogeneous and transparent characters of the starch films are advantages for application as packing materials.¹³ Figure 3 presents the SEM image of WS-3CVER-U films. It could be seen that clay particles are found uniformly dispersed in composite films. It was expected that the introduction of modifier CS enhanced the interactions of system and the dispersion of clay particles, thus improving both the thermal stability and water resistance properties of starch-based films as discussed below.

XRD analysis

To understand whether the added CS enters into the interlayer of clay minerals or not, XRD analyses were performed to measure *d*-spacing. Figure 4 shows the XRD patterns of NVER and CVER. The NVER exhibits characteristic diffraction peaks at $2\theta = 8.8^\circ$ (*d*-spacing = 1.00 nm) and 10.6° (*d*-spacing = 0.83 nm). After the addition of the modifier CS to the NVER suspension, the characteristic diffraction peak of CVER was not shifted, suggesting that the crystal structure of clay particles remains unchanged. However, the relative intensity of diffraction peaks ($2\theta = 8.8^\circ$) decreased dramatically, which is generally attributed both to poor intercalation and monolayered intercalation of CS chains into VER stacks.¹⁴ It can also be proved that the use of the modifier CS reduced the clay aggregation, leading to the smaller clay particles dispersed in starch matrix. As confirmed earlier, the transparency of WS-CVER-U film is obviously higher than that of WS-NVER-U film with the same clay loading.

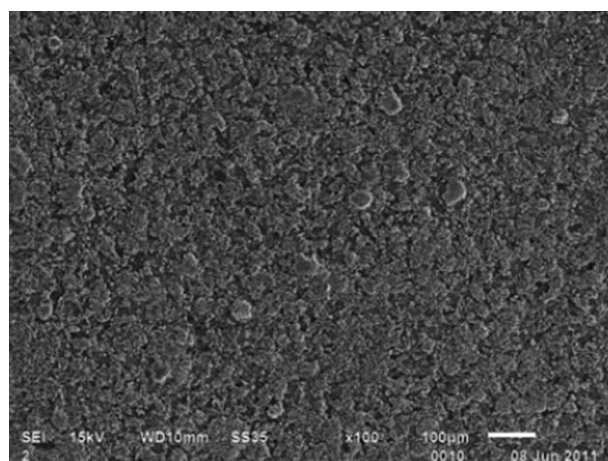


Figure 3 SEM image of WS-3CVER-U film.

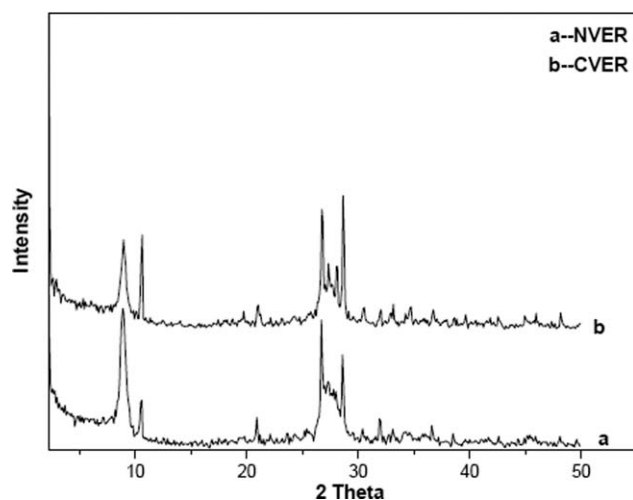


Figure 4 XRD patterns of (a) NVER and (b) CVER.

Moreover, the sharper diffraction peak located at 10.6° was observed for CVER when compared with NVER. We believe that this phenomenon is attributed to the strong hydrogen bonds formed between the clay surface and the hydrophilic CS, leading to the formation of some stacks of clay with small interlayer spacing. However, it may be noted that the aggregation degree is rather low. Figure 5 illustrates XRD patterns for the WS film and the composite films containing different clay contents. All the samples displayed two peaks at low 2θ angles, corresponding to the characteristic peaks of clay. No peak observed for the WS-1CVER-U was caused by the very low clay concentration, and an increase in this diffraction peak intensity was observed with the increase in clay concentration.¹ The presence of the characteristic peaks of clay revealed that these materials were composites.

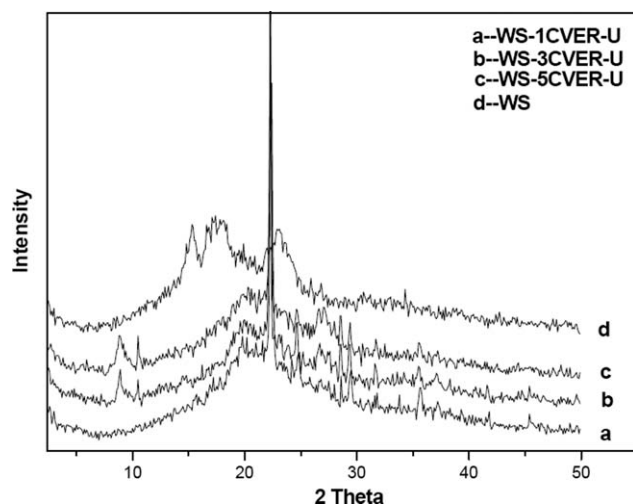


Figure 5 XRD patterns of WS and WS-CVER-U films with different clay contents.

Starch displays the A-type starch structure with characteristic peaks at $2\theta = 15^\circ, 17^\circ, 18^\circ,$ and 23° in Figure 5. All the composites exhibit a broad peak in the 2θ range between 10° and 35° corresponding to the amorphous structure. The data obtained indicate that the crystallinity of starch is affected by the addition of clay and U. It is explained by the fact that the complex interaction of original starch molecule chains was completely disrupted in the TPS processing, and the new, stronger 3D network structure was formed through the hydrogen bonds among WS, U, and VER in the composites. The sharp peaks observed at 22.3° for all the composites could belong to the urea crystal at the surface of samples, reflecting that the excess of urea would separate from the TPS.¹⁵

Thermal stability

The thermal stability of the samples was evaluated using TGA. The thermal stability of the WS-U and WS composites with different clay contents under nitrogen atmosphere is shown in Figure 6. In TGA curves, the parameters measured include the temperature of thermal degradation at 5% weight loss ($T_{5\%}$), the temperature of thermal degradation at 50% weight loss ($T_{50\%}$), and the yield of charred residue at 500°C (W_{500}). The summary of the important characteristic temperature obtained are listed in Table II. It is clear that all the samples exhibit two main stages. The weight loss between ambient temperature and 200°C was attributed to the volatilization of water molecules and plasticizers. The second stage of weight loss occurred between 200 and 400°C , with a maximum decomposition rate at 320°C corresponding to the starch decomposition.

It can be seen from Figure 6 that the addition of VER particles greatly improves thermal stability of starch matrix under nitrogen atmosphere when

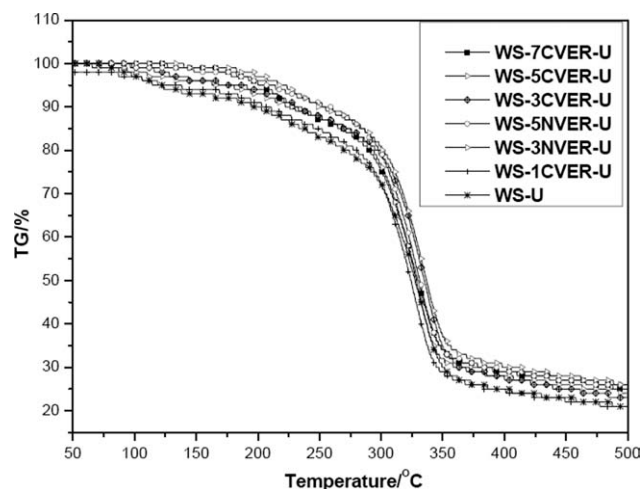


Figure 6 TGA weight loss curves for WS-U and the corresponding WS composites under nitrogen.

TABLE II
TGA Results for the WS-U and WS Composites in Nitrogen Atmosphere

Samples	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	W_{500} (%)
WS-U	114.3	327.6	21.1
WS-1CVER-U	140.4	323.4	21.6
WS-3NVER-U	223.5	336.9	26.2
WS-5NVER-U	214.2	331.4	26.8
WS-3CVER-U	191.3	334.7	23.3
WS-5CVER-U	180.6	328.7	24.1
WS-7CVER-U	206.6	330.1	25.9

compared with WS-U film. One reason may be resulted from the stronger structure formed between WS, U, and clay in composites than WS-U film as confirmed by the FTIR analysis. Additionally, it is well known that clay minerals exhibit better thermal resistance than polymers, which reduce the velocity of starch decomposition and promote the formation of char during thermal decomposition. Therefore, the higher thermal degradation temperature was obtained for all the composites in comparison with WS-U film. Chung et al.³ used CS as the compatibilizer of clay; however, the properties of starch-CS-modified clay nanocomposites were decreased due to the presence of larger agglomerates in the case of CS-modified clay. However, this difference from data in the literature is that the addition of CVER promoted clay disaggregation and improved the properties of starch composites in the study.

Moreover, it can be further observed that the thermal stability of all the composites are higher than that of WS-U film, especially the initial thermal degradation temperature as shown in Figure 6 and Table I. The composites exhibit an added value range of 26.1–109.2°C under a nitrogen flow in comparison with WS-U film when considering the 5% weight loss temperature as a point of comparison (Fig. 6 and Table I). It is also noted that WS-NVER-U composites exhibited higher thermal degradation temperature than did the WS-CVER-U composites under nitrogen flow. It may be caused by the fact that the modifier CS was not sufficiently intercalated in the clay layers and that the CS chains absorbed on the clay surface easily disintegrated during thermal decomposition, leading to the slight low thermal stability of starch matrix. The composites have a higher amount of char residue at 500°C. The $T_{50\%}$ value observed in the composites are similar to that of WS-U film, suggesting that the incorporation of clay particles has no effect on the decomposition mechanism of starch. Therefore, the increment of thermal stability obtained for TGA data is resulted from the uniformly distributed clay particles in starch matrix and the reduced mobility of starch chains brought about by strong interactions between starch and clay in the composites.

DSC analysis

The DSC measurements were performed to investigate the glass transition behaviors of materials. The glass transition temperature (T_g) of WS-U and the corresponding composites are listed in Table II. The T_g value of all the WS-NVER-U composites were the same as that of WS-U film. The WS-CVER-U films exhibited higher glass transition temperature with the increase in clay contents than did the WS-U film. The improved properties can be interpreted by the stronger hydrogen bonds in WS-CVER-U system and the uniformly dispersion of clay particles in the composites. As discussed earlier, CS chains restricted the mobility of starch molecule chains through hydrogen bonding, consequently enhancing the glass transition temperature of starch matrix.

Water absorption

Water absorption was an important property to decide the application of films.¹⁶ The results of water absorption experiments of the WS-U film and its composites containing different clay contents at RH = 100% are listed in Table III. It is apparent that the presence of CVER improved the water resistance of the starch matrix when compared with WS-U. It is attributed to the strong hydrogen bonds formed among WS, U, and CVER, which resulted in a 3D network structure and prevented water molecules from permeating into the materials, enhancing the water resistance of the corresponding composites. It is further observed that the water resistance of WS-CVER-U composites was better than that of WS-U and WS-NVER-U composites; especially, the WS-1CVER-U composite was improved by 160% when compared with WS-U film. We believed that the presence of CS promoted clay disaggregation and that the enlarged surface of clay particle increased the interface force with starch molecules. Therefore, the lower moisture absorption values of WS-CVER-U composites were obtained.

TABLE III
DSC and Moisture Sorption Results for WS-U and WS Composites

Samples	T_g (°C)	Moisture sorption (%)
WS-U	40	1.17
WS-3NVER-U	40	0.81
WS-5NVER-U	40	0.95
WS-1CVER-U	39	0.45
WS-3CVER-U	41	0.72
WS-5CVER-U	Not observed	0.80
WS-7CVER-U	46	0.84

The samples were conditioned at 100% RH before measurement.

TABLE IV
Mechanical Properties of Starch and Starch-Clay Composites Containing 3% Clay

Samples	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
WS-U	18.5	2.65	34
WS-3NVER-U	23.3	3.28	28
WS-3CVER-U	26.2	3.43	30

The samples were conditioned at 33% RH before measurement.

Mechanical properties

The mechanical properties of the starch film and the starch composites are presented in Table IV. The starch-clay composites with the CVER or the unmodified VER exhibit an improvement in Young's modulus and tensile strength when compared with the starch matrix; however, the decrease in the elongation at break of the starch films is also observed. The significant increases in modulus and strength are attributed to the strong hydrogen bond interactions formed between starch matrix and VER particles. Furthermore, it can be observed that the mechanical property of WS-3CVER-U film is higher than that of WS-3NVER-U film. This reflects that the chitosan improved the dispersion of VER particles in the starch matrix and increased the interface force with starch molecules.

CONCLUSIONS

The starch-VER composite films were prepared using NVER and CVER as the reinforcing phase. The modification of CVER and the structure of films were investigated by XRD and SEM technology. Although the CVER was not sufficiently intercalated

in the clay interlayers, the addition of modifier CS adjusted interactions of starch-clay interface and promoted clay disaggregation, thus enhancing the transparency of starch matrix. Moreover, the FTIR spectra analysis also revealed the formation of strong hydrogen bond interactions between starch and clay and the generation of some ester groups in the composites. The significant increase in starch-clay composites observed in the TGA, DSC, and water absorption clearly confirmed the use of VER as the reinforcement phase to improve the properties of starch-based materials.

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