Mechanical and water resistance properties of chitosan/poly(vinyl alcohol) films reinforced with attapulgite dispersed by high-pressure homogenization

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HIGHLIGHTS
- APT by high-pressure homogenization can well disperse in the CS/PVA matrix.
- Mechanical properties of CS/PVA/APT films increase due to disaggregate of crystal bundles.
- Water resistances of CS/PVA/APT films are improved according with homogenization pressures.
- Introduction of APT into CS/PVA matrix nearly not affected the optical property.

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Abstract
Attapulgite (APT) is a natural one-dimensional nanorod with higher mechanical strength and shows great potential as an effective reinforce filler for deriving nanocomposites. The dispersion degree and aspect ratio of APT are keys to decide the performance of nanocomposites. However, natural APT cannot develop its nanometer reinforce advantages because it usually appears as a crystal bundle or aggregate. In this work, we effectively disaggregate the crystal bundles of APT by a simple high-pressure homogenization technology at various pressures. The obtained nanometer APT as an ideal reinforce filler was introduced into chitosan (CS)/poly(vinyl alcohol) (PVA) matrix to derive a series of nanocomposites by the solution casting method. The CS/PVA/APT nanocomposites were characterized by field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FTIR). Tests results indicated that the nanometer APT can enhance the mechanical properties and water resistance of nanocomposites more obvious than pristine APT. The nanocomposites also were shown to be highly transparent and the introduction of APT into CS/PVA matrix nearly not affected the optical property of the films.

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1. Introduction
Organic/inorganic nanocomposites have attracted considerable attentions in the past decades because the incorporation of nanoscale inorganic filler into polymer matrix brings surprising hybrid performance superior to their individual components [1–4]. Attapulgite (APT) is a natural nanometer rod-like hydrated magnesium aluminum silicate mineral, consisting of two double chains of the pyroxene-type (SiO3)2̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈̈的一面
strength, elongation at break of polyimide were sharply increased by introducing organized APT. Yin et al. prepared PAN/APT nanocomposite films with different clay contents [8]. The results showed that small amount of APT nanorods in the matrix could concurrently improve both the tensile strength and the toughness of the matrix.

Generally, the dispersion degree of the inorganic fillers in the polymer matrix is critical to decide the final performance of the nanocomposites [9–11]. However, natural APT usually appears as a bundle or aggregate of randomly oriented rod crystals due to the action of van der Waals’ interactions among the APT rods [12]. Unlike individual rod-like single crystal, the crystal bundles or aggregate do not have the characteristics of nanometer materials, and so the advantages of APT as a reinforce filler cannot be fully developed and its extensive application was limited. Therefore, the high-efficient disaggregation of APT aggregates into individual rods becomes a key to utilize the nanometer properties and develop the high-performance product. Conventionally, the disaggregation or dispersion of APT bundles can be realized by adding various chemical dispersants, but this method can only partially disaggregate the bundles, the process is complex and the undesirable chemicals may be introduced inevitably. So, a physical method that can effectively disaggregate the bundles is highly desirable. In our previous work, we have disaggregated and dispersed APT crystal bundles effectively by a simple high-pressure homogenization process [13]. The dispersed nanometer rod-like single crystals shows the characteristic of one-dimensional nanometer materials, and so they would be a good candidate for reinforcing polymeric materials effectively.

Biodegradable materials have attracted considerable attentions due to the growing concerns on the environmental problem resulting from non-biodegradable materials especially in the area of food packing [14–16]. Among these materials, chitosan (CS) is one of the most promising biopolymers because it is the only basic polysaccharides with unique properties [17]. CS anticipates to be applied in many fields such as pharmaceutics [18], fuel cell [19], wastewater treatment [20,21], due to its biodegradability, biocompatibility, antimicrobial activity, and excellent film-forming ability. However, CS is only partially crystalline due to the strong intra- and intermolecular hydrogen bonding, and so CS-based films are too brittle with a weak strain at break and are hardly to be used as a food packing material.

The blending of two or more polymers has been developed to obtain new composite materials exhibiting excellent properties because of synergistic effects of components [22–24]. Poly(vinyl alcohol) (PVA) is a highly biocompatible, nontoxic synthetic polymer with high water solubility due to the hydroxyl groups in the polymer side chain, which shows many applications in membrane [25,26], medical [27], and so on. The blending of PVA with CS is favorable to enhance the physical properties of CS due to the formation of hydrogen bonds between CS and PVA [28,29]. However, the mechanical properties and water resistance of CS/PVA composite should be improved to meet the demand of practical applications.

For developing new CS/PVA-based packing materials with improved mechanical properties and water resistance, a nanocomposite strategy was used by introducing nanometer APT pre-dispersed by high-pressure homogenization technology at different pressures. The APT-reinforced CS/PVA films were characterized by field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FTIR). The effect of homogeneous pressure on the dispersion of APT in the matrix, the mechanical properties and water resistance of the nanocomposites was investigated, and the structure–properties correlation between APT and the polymer matrix was established.

2. Materials and methods

2.1. Materials

PVA (degree of polymerization, 1700 ± 50, degree of hydrolysis, 99%) was purchased from Lanzhou Chemical Reagent Co. Ltd. (Gansu, China). CS (90% degree of deacetylation and molecular weight of 6 × 105) was from Yuhuan Ocean Biology Company (Zhejiang, China). APT mineral was obtained from Jiuchuan Technology Co., (Jiangsu, China). It has the composition of 1.29% CaO, 10.47% Al2O3, 1.52% Na2O, 20.41% MgO, 64.31% SiO2, 0.13% K2O and 0.87% Fe2O3 (determined by a MiniPal 4 X-ray fluorescence spectrometer, PANAlytical Co.). Glycerol and acetic acid were analytical grade commercially available, and used without further purification.

2.2. Preparation of CS/PVA/APT nanocomposite films

Five types of APT samples were obtained by homogenizing the suspension of APT with a high-pressure homogenizer at different pressures (10, 30, 50, 70 and 90 MPa) as the procedure described in our previous work [13]. The nanocomposite films were prepared by the solution casting method. Typically, PVA was dissolved in distilled water at 95 °C with stirring for 2 h to form 10 wt% PVA solutions, and then the solutions were filtered by a filter for the subsequent use. CS was dissolved in 1 wt% acetic acid aqueous solution at room temperature with stirring to obtain 2.0 wt% CS solutions. Afterward, 63 mL 10 wt% PVA solutions was added into the 135 mL 2.0 wt% CS solution to obtain a PVA/CS mixture with weight ratios of 7/3. APT samples including pristine and five types of APT dispersed by high-pressure homogenization (denoted as APT0, APT10, APT30, APT50, APT70 and APT90) was dispersed in distilled water under mechanical agitation at 500 rpm for 1 h at room temperature to obtain the suspension with various contents of APT. The obtained APT dispersion was added slowly to the CS/PVA solutions (1%, 2%, 3%, 4%, and 5% w/w) clay loadings with respect to polymer weight. Then, glycerol was added into the system at 10% loadings with respect to polymer weight and the mixture was stirred at 500 rpm for 4 h to obtain homogeneous solution. After that, the mixture was poured into a glass dish (10 cm × 10 cm) and evaporated at atmosphere for 48 h, and the resulting films were dried in a vacuum oven (at 70 °C) for 6 h to remove traces of the solvents. The obtained films were fully dried under ambient conditions and subsequently kept in a desiccator for further treatments. CS/PVA film was prepared according to a similar procedure except without addition of APT. Before characterization, all films were kept in a conditioning cabinet at 50% relative humidity (RH) and 25 °C to ensure the stabilization of their water content.

2.3. Moisture uptake of nanocomposite films

The moisture uptake (MU) of nanocomposite films was determined on samples cutting into small pieces (3 cm × 2 cm). Then the samples were dried overnight at 70 °C. After weighing, the samples were conditioned for 4 days at 75% RH (NaCl saturated solution) to ensure equilibrium of the moisture before reweighing. The MU of the samples was calculated as follows:

\[
MU = \left| \frac{W_1 - W_0}{W_0} \right| \times 100\% 
\]

where \(W_0\) and \(W_1\) are the weight of the samples before exposure to 75% RH and at equilibrium, respectively. An average value of three replicates for each sample was taken.
2.4. Characterization

A FTIR Spectrophotometer (Thermo Nicolet, NEXUS 670) was used to measure the Infrared spectra of the nanocomposite films using the attenuated total reflectance (ATR) model in the range of 4000–400 cm⁻¹.

The fracture surface morphologies of nanocomposite films (CS/PVA/APT50) were determined using a field emission scanning electron microscope (FESEM, Hitachi S-4800) after coating the sample with a gold layer in a 13.3 Pa vacuum.

X-ray diffractions (XRDs) were carried out using a D8 Advance (Bruker) X-ray diffractometer with Cu Kα radiation (k = 1.5418 Å), running at 40 kV and 30 mA, scanning from 3 to 40 °C at 3°/min.

Tensile strength and elongation at break of films were measured using a New SANS universal material testing system (CMT4304) equipped with a 200 N load cell at room temperature with gauge length of 10 mm and crosshead speed of 2 mm/min. The experimental results were evaluated as an average of at least 6 measurements.

The UV/vis transmittance spectra of films were recorded with a UV/vis Spectrophotometer (Specord 200, Analytic Jena, Germany). The analysis conditions were 200–1000 nm spectral range and plot data were recorded every 1 nm at room temperature.

The contact angle (CA) of water was measured using a CA analyzer Kruss DSA 100 (Kruss Company, Ltd., Germany) apparatus at ambient temperature. A total of 5 µL was placed on the surface of films.

3. Results and discussion

3.1. FTIR analysis

FTIR spectroscopy is one of the most effective tools to study the interactions in polymer/clay composites. Fig. 1 shows the ATR-FTIR spectra of neat CS/PVA and nanocomposites. In the spectrum of CS/PVA (Fig. 1a), the stretching and bending vibration of the hydrogen bonding –OH group occurred at 3307 cm⁻¹. It can be seen from Fig. 1b that the peak (3307 cm⁻¹) nearly has no shift by incorporation of 1 wt% APT50. However, the peak (3307 cm⁻¹) is observed to shift to 3295 cm⁻¹ as shown in Fig. 1c when the amount of APT50 increased to 3 wt% in the polymer matrix. These results indicate that APT can interact with the polymers matrix, and partially destruct the hydrogen bonding between CS and PVA. A quite similar tendency was reported for exfoliated zirconium phosphate introducing into the PVA/starch matrix [30].

3.2. SEM analysis

Fig. 2a shows the SEM image of APT50. It is clear that the APT nanorods with the size of 50–100 nm in diameter and about 1 µm in length showed a better dispersion state with the arrangement of rod-like crystals after high-pressure homogenization process. Dispersion of the nanofillers is one of the most critical factors to achieve polymer reinforcement benefits [11]. Fig. 2b–e shows the effects of APT loading on the fractured surfaces section morphologies of nanocomposites. It can be seen that the CS/PVA sample (Fig. 2b) shows a homogeneous smooth surface, which implies that the pure CS/PVA film had good compatibility between the CS and PVA. Otherwise, all samples filled with APT showed much rougher fractured surfaces compared with neat CS/PVA.

Fig. 2c shows the microscopic morphologies of CS/PVA nanocomposite filled with 3 wt% APT0. It is clear that some crystal bundles appeared in the polymer matrix, which are consistent with the pristine APT reported in our previous work [13]. The APT50 as fillers were found dispersing well in the polymer matrix on a nanometer scale in the sample with 3 wt% APT content due to crystal bundles disaggregating well after homogenization at 50 MPa (Fig. 2d). A few agglomeration of APT appeared in the nanocomposite with 5 wt% APT50 content (Fig. 2e), which will induce negative effects on the performance of the nanocomposites and is consistent with the determination result of mechanical properties.

3.3. XRD analysis

Fig. 3 shows the XRD patterns of APT50 and CS/PVA/APT50 nanocomposites. The diffraction peaks at about 2θ = 19.2° are attributed to the diffraction of CS/PVA matrix [31], and the basal spacing (1 1 0) of the APT50 is approximately 10.4 nm which corresponds to 2θ = 8.4° [32]. It is clear that the peak of APT at about 8.4° is almost unchanged and other new diffraction peaks are not found after blending with CS/PVA. This behavior can be explained by the fact that polymer chains cannot intercalate into the APT layers. The intensity of the peak at about 8.4° gradually increases along with the increase in the APT content in the polymer matrix.

3.4. Mechanical properties

The results of the mechanical properties of CS/PVA/APT (APT0, APT10, APT30, APT50, APT70 and APT90) nanocomposites (APT amount varied from 0 to 5 wt%) are shown in Figs. 4 and 5, respectively. It is obvious that the mechanical behavior is greatly influenced by homogenization pressure and the addition amount of APT. As shown in Figs. 4 and 5, both the tensile strength, elastic modulus and elongation at break of nanocomposites filled with treated APT are significantly higher than the nanocomposite filled with pristine APT. It can be attributed to the fact that the crystal bundles of APT were disaggregated evidently by the high-pressure homogenization process [13] and thus the dispersion of APT in the polymer matrix was effectively improved. Among the nanocomposites filled with treated APT, the nanocomposites filled with APT50 show the highest tensile strength and elastic modulus, and the nanocomposites filled with APT30 show the highest elongation at break, respectively. Main reasons for the enhancement in the mechanical properties are ascribed to both the dispersion of APT in the polymer matrix and the aspect ratio of the APT. As known from our previous work, the crystal bundles of APT were effectively disaggregated with enhancing the pressures from 0 to 90 MPa and the length of individual fibrous crystals of APT decreased with enhancing the pressure to 70 and 90 MPa [13]. The tensile strength and elastic modulus increases sharply with increasing the homogenization pressure from 0 to 50 MPa due to the well dispersion of APT in the polymer matrix with the...
nanometer fibrous crystals. However, increasing the homogenization pressure from 50 to 90 MPa resulted in the decrease of tensile strength of the nanocomposites. This may be ascribed to the fact that the individual fibrous crystals were shortened by the high pressure. Bicerano et al. have reported that polyurethane was reinforced with microfibres having varying aspect ratios. The results indicated that the mechanical properties of flexible polyurethane elastomers were improved significantly by reinforcement with small amounts of microscopic fibers having high aspect ratios [33]. Liu et al. have also found that the higher aspect ratios of \( \alpha \)-zirconium phosphate could lead to significant improvements in modulus, tensile strength, elongation at break and heat distortion temperature [34]. Subsequently, the individual fibrous crystals with lower aspect ratio will decrease the efficiency of the stress transfer in a composite matrix.

As for the effects of the addition amount of clay on the mechanical properties, the tensile strength and elongation at break of nanocomposites films are significantly higher than that of the neat polymer with an increase in APT loading from 0 to 3 wt%. The tensile strength and elongation at break increased sharply by 62.61% from 36.01 to 58.54 MPa (CS/PVA/APT50) and by 32.88% from 99.92% to 132.87% (CS/PVA/APT30) with an increase in APT loading from 0 to 3 wt%, respectively. The elastic modulus increased sharply with an increase in APT loading from 0 to 4 wt%. This behavior can be explained by the facts as follows. Firstly, negative charges on the APT surface can interact effectively with the polycationic CS at slightly acidic pH through electrostatic attraction. Secondly, there might be plenty of intermolecular hydrogen bonds formed between APT and PVA, PVA and CS, CS and APT, which could form a three-dimensional network. Moreover, the large aspect ratio of

![Fig. 2. SEM micrographs of (a) APT50, (b) PVA/CS, (c) PVA/CS/APT0 containing 3 wt% of APT, (d) PVA/CS/APT50 containing 3 wt% of APT and (e) PVA/CS/APT50 containing 5 wt% of APT.](image)

![Fig. 3. The XRD patterns of (a) CS/PVA, (b-d) CS/PVA/APT50 containing 1, 3 and 5 wt% of APT50 and (e) APT50, respectively.](image)
the APT nanorods is also favorable to stress transfer. Therefore, the mechanical properties of nanocomposites are greatly improved even at low APT filler concentrations simultaneously. Yang et al. also have reported that the tensile strength and elongation at break of chitosan/graphene oxide nanocomposites were improved simultaneously with graphene oxide sheets as nanofillers [9]. The tensile strength and elongation at break began to decrease as the APT content was over 3 wt%, which possibly due to the aggregation of APT nanorods with higher surface energy in the polymer matrix.

3.5. MU of nanocomposite films

Fig. 6 displays the results of the MU of nanocomposites under 75% RH for 4 days. It is clear that the MU of neat CS/PVA in this RH is about 26.20%, which is higher than that of the other films containing APT. This indicates that the introduction of APT into the polymer matrix decreases the MU of the nanocomposites. This may be attributed to the following reasons: firstly, the formation of strong interaction through hydrogen bonds between hydroxyl groups of the polymer matrix and APT with high surface area improves the cohesiveness of polymer matrix and decreases the water sensitivity. Secondly, water resistance of APT is better than that of the polymers, the addition of APT reduces the diffusion of water molecules in the polymer matrix.

As increasing of the homogenization pressure from 0 to 90 MPa, there will be more hydrogen bonds forming in the system due to the well-dispersed APT in the polymer matrix with the well-disaggregated fibrous crystals, and thus result in the decreasing of the MU of the nanocomposites. With an increase of APT content, the MU decreases and reaches minimum at 3 wt% and 4 wt% APT loading and increases with more APT loading for the nanocomposites filled with APT0 and APT10, respectively. It can be explained by the fact that the APT0 and APT10 were not disaggregated effectively and the amounts of hydrogen bonds will decrease due to the aggregation of APT nanorods, which result in the increase of the MU. In addition, the MU of the nanocomposites filled with APT30, APT50, APT70 and APT90 decreases with increasing the amount of APT from 1 wt% to 5 wt% due to the well-disaggregated crystal bundles.

3.6. Water CA of nanocomposites

The CA of water droplet was measured to study the resistances of nanocomposites against liquid water. Fig. 7 shows the results of
water CA for various CS/PVA/APT (APT0, APT10, APT30, APT50, APT70 and APT90) nanocomposites with the APT at 3 wt% loading. It can be seen that the CA of nanocomposites is all higher than the CA of neat CS/PVA (68.5°), indicating that the introduction of APT into the polymer matrix increases the water resistance properties of the nanocomposites. The CA of nanocomposites increased from 80.6° to 93.5° with the increase in the pressure onto the APT from 0 to 90 MPa. Well disaggregated APT nanorods were achieved with enhancing the pressure on the pristine APT, and thus more hydrogen bonds formed between hydroxyl groups of the polymer matrix and APT, which result in the improvement of the surface hydrophobicity of the films.

3.7. Optical properties

The films of CS/PVA and CS/PVA/APT (APT0, APT10, APT30, APT50, APT70 and APT90) composites with 3 wt% APT were prepared with the thickness of 0.028 mm and used for optical property measurements. Fig. 8 shows the UV/vis spectra for CS/PVA and CS/PVA/APT nanocomposites. It can be observed that the CS/PVA/APT0 has the lowest light transmission in comparison with other nanocomposites. In addition, incorporation of treated APT into polymer matrix nearly does not affect the light transmittance of the resulting nanocomposites. It was attributed to the fact that the treated-APT dispersed well and pristine APT had some aggregates in the polymer matrix as an individual disaggregated fibrous crystals resulted in the decrease of MU and the improvement of the surface hydrophobicity of the nanocomposites. All films showed above 80% transmittance across the visible light regions (400–800 nm), indicating that the light transmittance of the resulting nanocomposites was slightly affected by the APT and this is favorable to its application in many fields.

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