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Modified natural halloysite/potato starch composite films

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ABSTRACT

Halloysite/potato starch composites were prepared by adding modified natural halloysite nanotubes into potato starch matrices to reenforce the mechanical properties of potato starch films. The halloysite/potato starch films were characterized by X-ray diffraction, scanning electron microscope and infrared spectrometry. Meanwhile, the mechanical properties and transparency of the films were studied. The results show that the modified halloysite nanotubes can be well distributed in the starch matrix and thus the tensile strength of the films was clearly enhanced. The flexibility of the films could be improved through adding glycerol although at the cost of reducing tensile strength. But incorporation of PVA could further improve the tensile strength of the halloysite/potato starch films.

1. Introduction

As one type of nanoclay, halloysite is a kind of natural aluminum-silicate hollow cylinder with a length of 0.5–1 μm, a outer diameter of about 50 nm and a lumen of 15 nm (Ismail, Pasbakhsh, Ahmad Fauzi, & Abu Bakar, 2008a). Halloysite is able to entrap a range of molecules with specific sizes and can be used as a viable nanocage for active molecules, owing to its empty space inside the nanotubes. For example, halloysite was reported as a carrier for the controlled release of anticorrosion coating agents, herbicides, and fungicides (Price, Gaber, & Lvov, 2001; Shchukin et al., 2006a; Shchukin & Mohwald, 2007b; Shchukin et al., 2008c). Furthermore, halloysite was once used as a support to immobilize catalyst molecules such as metallocomplexes (Machado, Castro, Wypych, & Nakagaki, 2008). Like montmorillonite nanosheets, halloysite nanotubes can be incorporated into polymers to modify their properties (Ismail et al., 2008a). Composites of halloysite/plastics (Marney et al., 2008), halloysite/rubber (Pasbakhsh, Ismail, Ahmad Fauzi, & Abu Bakar, 2009b, 2010c; Rooj et al., 2010) and halloysite/hydrogel (Zheng & Wang, 2010) have been studied. These composites can be widely used for drug deliveries (Hughes & King, 2010; Vergaro et al., 2010), nanotemplates (Ismail et al., 2008a) and reinforcing materials (Ning et al., 2007).

Plastic waste has been considered as one source of environmental pollution. Thus, researches have been devoted to developing biodegradable plastics as substitute materials. Some familiar biodegradable polymers, such as polyglycoloic acid, polycaprolactone, and polylactic acid have been widely used as biomaterials (Bengtsson, Koch, & Gatenholm, 2003), but they are too expensive to be used to replace synthetic polymers. So it is an urgent task to find cheap, renewable resource-based and environmental friendly materials to reduce plastic pollution (Das et al., 2010).

Starch has been proved to be one of the most promising biodegradable polymers since it is abundant, nontoxic, biodegradable and of low-cost and so on (Belhassen et al., 2009; Réti, Casetta, Duquesne, Bourbigot, & Delobel, 2008; Shen, Wu, Chen, & Zhao, 2010; Ziegler, Creek, & Runt, 2005). Starch films, as packaging materials, have been prepared from different starch sources (Mao, Imam, Gordon, Cinelli, & Chiellini, 2000; Sreedhar, Chattopadhyay, Karunakar, & Sastry, 2006; Zou, Qu, & Zou, 2007). The mechanical properties of potato starch are relatively better than most of other kinds of starch, but it still can hardly meet the application demand. To make commercially acceptable starch films modification or blending with other materials has been tried. Poly(vinyl alcohol) (PVA) (Cinelli, Chiellini, Lawton, & Imam, 2006) and polyethylene (Arvanitoyannis, Biliaderis, Ogawa, & Kawasaki, 1998; Borghei, Karbassi, Khoramnejadian, Oromiehie, & Javid, 2010; Gupta & Sharma, 2010; Kim, 2003b; Kim & Lee, 2002a) are often incorporated into potato starch to improve its properties. In order to maintain the biodegradability, natural polymers such as chitosan (Shen et al., 2010), sucrose (Zhou et al., 2009), cellulose derivatives (Lee, Baek, Cha, Park, & Lim, 2002; Shishonok et al., 2007), alginate (Djabali, Belhaneche, Nadjemi, Dulong, & Picton, 2009), pullulan (Barnett, Smith, Scanlon, & Israilides, 1999), gelatin (Cui,

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Liu, Wu, & Bi, 2009) and proteins (Ito, Hattori, Yoshida, & Takahashi, 2006) have been added to improve mechanical and other properties of potato starch films. Moreover, Potato starch can also composite with clays to modify its properties (Chiou, Yee, Glenn, & Orts, 2005; Cyras, Manfredi, Ton-That, & Vázquez, 2008; Kvien, Sugiyama, Votrubec, & Oksman, 2007; Zeppa, Gouanvé, & Espuche, 2009).

So far as is known, the inclusion of halloysite nanotubes in natural polymers has been rarely reported. Xie, Chang, Wang, Yu, & Ma (2011) had studied the halloysite/plasticized *Dioscorea opposite Thunb*. starch composites, but the mechanical strength of the composite films was not high enough to apply as packaging. Since halloysite nanotubes are easily aggregated, they do not easily disperse in polymer matrices. To solve this problem, pulverization is an effective way. Chang, Xie, Wu, & Ma (2011) took amylose to wrap the halloysite by ball-milling to obtain well dispersed starch/halloysite composites, but they did not study their appliance of the composites, especially in the preparing of halloysite/starch composites. Besides, the extraction of amylose is complicated and expensive, so we choose PEG as dispersing agent to mill, modify and disperse halloysite nanotubes in different solvents, and then added the modified natural halloysite nanotubes as fillers to prepare halloysite/potato starch films and studied their properties.

2. Materials and methods

2.1. Materials

Potato starch (PSt) was obtained from Tianjin TingFung Starch Development Co. Ltd.; halloysite was supplied by Hunan Xiangtan Kaolin Industry Co. Ltd.; glycerol, sodium bromide, polyvinyl alcohol (PVA) and polyethylene glycol (PEG 4000) were all from Tianjin Chemical Reagent Co.

2.2. Treatment of halloysite by planetary ball-milling in the presence of PEG

15.0 g halloysite, together with 0.30 g PEG, was put into 150 mL distilled water or distilled water/ethanol mixture of different ratios. The halloysite suspension was made by ball-milling for 4 h at a speed of 800 rpm and followed by centrifugal treatment to get precipitate. The precipitate was rinsed with distilled water or water/ethanol mixture (50/50, v/v) for several times to remove the free PEG macromolecules and then dried in a freezing dryer to get modified halloysite powder. The halloysite powder was redispersed in distilled water after ultrasonic treatment for 15 min by cells grinding apparatus to get aqueous suspension of halloysite nanotubes.

2.3. Preparation of halloysite/potato starch films

Halloysite/potato starch composite films were prepared as following. Starch slurry was first prepared by dispersing 10 g PSt in 100 mL distilled water, ultrasonic treatment for 15 min using cells grinding apparatus and gelatinizing at 85 °C for about 1 h, and then a certain amount of glycerol, halloysite suspension and aqueous PVA solution (if needed) were added. The mixture was stirred to obtain a homogenous paste that was cast on the stainless-steel plate, and dried at 30 °C for about 24 h to acquire halloysite/potato starch composite films. Three sets of halloysite/potato starch films were prepared, and they are symbolized as PStH, loading with different amount of halloysite at the 20 wt.% content of glycerol; PStH-G containing different amount of glycerol and 5 wt.% amount of halloysite; and PStH-P, having different amount of PVA besides a fixed amount of halloysite (5 wt.%) and glycerol (20 wt.%).

2.4. Characterization of the halloysite/potato starch films

2.4.1. Scanning electron microscope (SEM) observation

The morphology of halloysite nanotubes and their distribution in the halloysite/potato starch films was observed by SEM. The samples were gold coated using a sputter coater (Desk–II; Denton Vacuum), put onto the stage in the chamber and observed under SEM (JEOL-6700F ESEM, Japan).

2.4.2. X-ray diffraction analysis

The X-ray powder diffraction spectra of halloysite/potato starch films were measured using an X-ray diffractometer (X'pert, PANAlytical, Netherlands) with a reference of target: Cu-Kα radiation ($\lambda = 1.73$ Å), voltage: 45 kV, current: 30 mA. They were measured at an angular range from 5° to 80° (2θ) with steps of 0.007° and a measuring time of 5 s/step.

2.4.3. Infrared spectroscopic (IR) analysis

IR spectra of the samples were measured with a BIO-3000 FT-IR spectrometer in the range of 500–4000 cm^{-1}. Each FT-IR spectrum was the average of 16 scans.

2.4.4. Transparency of the halloysite/potato starch films

The halloysite/potato starch films were cut into a certain size of samples (8 mm × 30 mm); put on one side of cuvette after their thickness was measured, and the spectra were measured in double beam UV–vis spectrophotometer (TU-1901). The transmittance (T_m) was determined at the wavelength range of 200–800 nm, taking the blank cuvette as reference. The relative transmittance (RT) was calculated according to the following equations. All the data were the mean values of three independent measurements.

$$\text{RT\%} = \frac{T_m}{d_r} \times 100 \tag{1}$$

$$d_r = \frac{d_m}{d_o} \tag{2}$$

where T_m is the measured value of transmittance of the halloysite/potato starch films; d_r and d_m are the relative thickness and the actual thickness of the films, respectively, and d_o is the thickness of one film in a set of films and used as a control.

2.4.5. Mechanical property of the halloysite/potato starch films

For each of the halloysite/potato starch films, over six specimens in stripe shape with a size of 80 mm × 12 mm were cut from

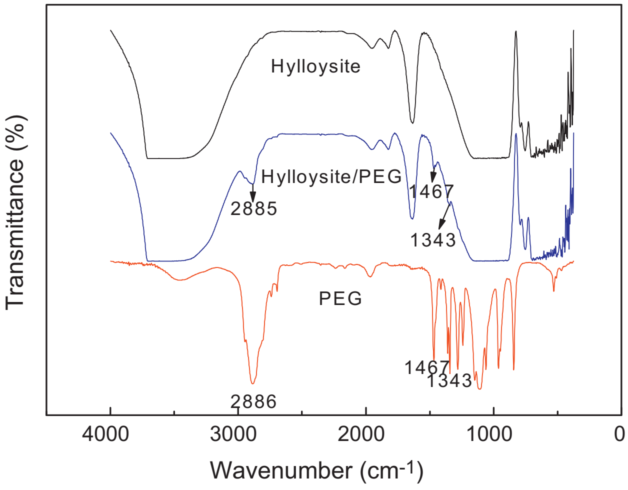

Fig. 1. IR spectra of halloysite and the treated halloysite.

the films. The samples were conditioned in 58% RH (a saturated NaBr solution) at 25 °C for 24 h in an incubator and their thickness was measured with a micrometer before test. The data of thickness were taken at five different positions for each sample and the average value was calculated. The tensile strength and elongation at break were measured using the material testing machine (The Testometric Company Ltd. United Kingdom) with 10 kg load cell, according to ASTM Standard Method D882–88. The initial grip separation was 40 mm and cross-head speed was 5 mm/min. The tensile strength is calculated by dividing the maximum force exerted on the film during fracture by the cross-sectional areas, and percentage elongation at break is expressed as percentage of change of the original length of a specimen between grips at break.

2.4.6. *Thermogravimetric analysis (TGA) of the halloysite/potato starch films*

The halloysite/potato starch films were dried to a constant weight in a vacuum at 60 °C, and then thermograms of the films were measured with a Rigaku-TD-TDA analyzer using a heating rate of 6 °C/min.

3. Results and discussion

3.1. *IR spectra of halloysite and the treated halloysite*

As a kind of clay, halloysite easily aggregates owing to its large specific surface areas and polar functional groups, and this causes halloysite nanotubes poorly dispersing in polymer matrix. To solve this problem, we took water as a medium to mill halloysite power and hoped to obtain well dispersed halloysite nanotubes, but this was not successful. Then we chose water/ethanol mixture of different ratios as the media and PEG as the dispersing agent to treat halloysite, and found a suitable water/ethanol ratio of 50/50, at which the halloysite power of aggregated nanotubes was thoroughly broken, and the treated halloysite could be well dispersed in distilled water or water/ethanol.

Fig. 1 shows the IR spectra of halloysite, PEG as well as the halloysite modified by PEG. The characteristic peaks of halloysite were at 3618 cm^{-1}, 1636 cm^{-1}, 1038 cm^{-1}; while the characteristic peaks of PEG were at 2885 cm^{-1}, 1468 cm^{-1}, 1343 cm^{-1}. The halloysite modified by PEG has the characteristic peaks of both halloysite and PEG. This indicates that some PEG was still on the surface of halloysite even after it was rinsed with water.

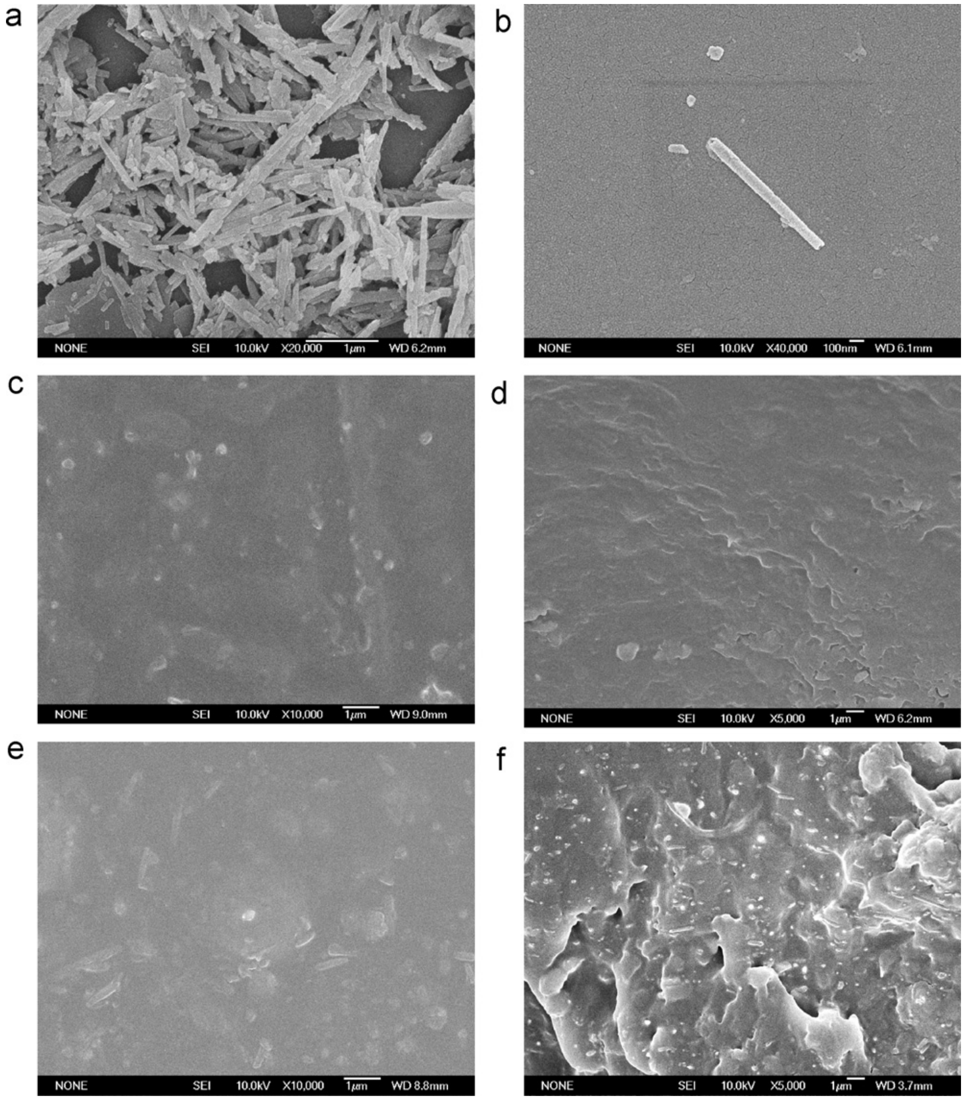

Fig. 2. SEM of treated halloysite (a and b) and halloysite/potato starch films with 3 wt.% (c and d) and 7 wt.% halloysite (e and f).

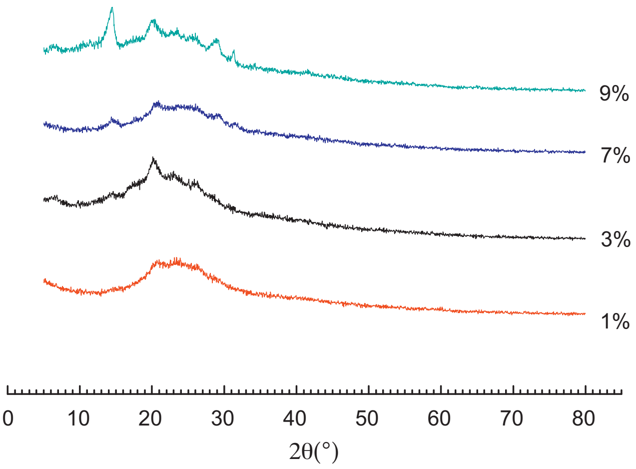

Fig. 3. XRD spectra of halloysite/potato starch films of different amount of halloysite (wt.%).

3.2. SEM analysis of the halloysite/potato starch films

Fig. 2(a and b) shows the SEM photographs of the treated halloysite. The halloysite nanotubes are separated and have a length of about 500–1000 nm and a diameter of 50–100 nm. This indicates that ball-milling can break the aggregated halloysite nanotubes and PEG can make the monotubes stably dispersed in the solvent. The ball-milling treatment may smash the halloysite nanotubes, so some short halloysite nanotubes are observed (about 100 nm long).

Fig. 2(c and d) (e and f) is the SEM photographs of surface (c and e) and cross section (d and f) of halloysite/potato starch films having 3 wt.% and 7 wt.% halloysite, respectively. The halloysite monotubes are evenly distributed in PSt matrix and well mixed with starch in these films, indicating that the modified halloysite monotubes and starch are compatible. PEG macromolecules contain –OH groups at the both ends of the macromolecules, and they can be adsorbed onto the halloysite nanotubes through the hydrogen bonds with the –OH groups on the surface of the nanotubes, and thus make the nanotubes well dispersed in water. When the modified halloysite nanotubes were added into starch paste, the PEG macromolecules could also form hydrogen bonds with the –OH groups on the starch macromolecules. So PEG seems acting as a bridge to connect the halloysite nanotubes and starch macromolecules, and this can effectively improve the compatibility of halloysite nanotubes and potato starch.

3.3. X-ray analysis of the halloysite/potato starch films

Fig. 3 gives X-ray diffraction (XRD) spectra of halloysite/potato starch films of different amount of halloysite. The peaks of potato starch range from 18° to 30°. As a crystalline material, halloysite has a peak at 14° in its X-ray spectrum. When small amount of halloysite nanotubes was added into PSt, there were just the crystalline peaks of starch. However, as the amount of halloysite nanotubes increased, its crystalline peak appeared and became more apparent, especially at the amount of 9 wt.%. Meanwhile, we find that the addition of halloysite nanotubes has no obviously effect on the X-ray spectra of PSt, indicating that the existence of halloysite nanotubes does not influence the crystallization of starch during the film preparation.

3.4. IR analysis of the halloysite/potato starch films

Fig. 4 is the IR spectra of potato starch films with different components, which consist of 9% halloysite (a), 30% glycerol (b), no addictives (c) and 9% PVA (d). None of them made significant changes to the IR spectra of potato starch films. The only difference was the intensity of the peaks of hydroxyl at about 3400 cm^{-1}, because PVA and glycerol have more hydroxyl groups than that of halloysite.

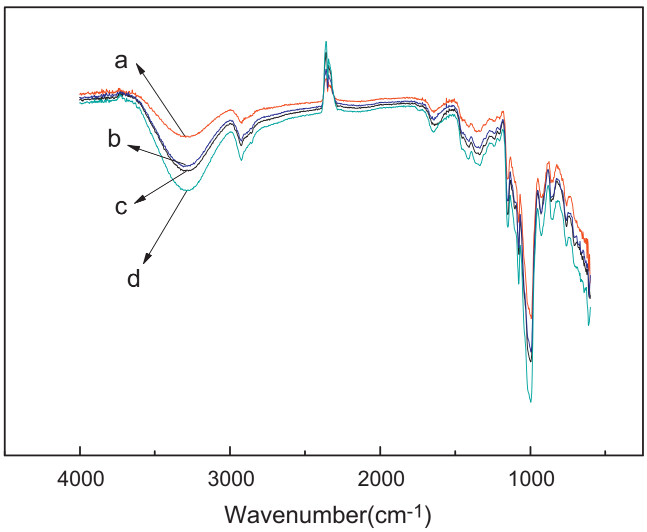

Fig. 4. IR spectra of potato starch films that contained 9% halloysite (a), 30% glycerol (b), no addictives (c) and 9% PVA (d), respectively.

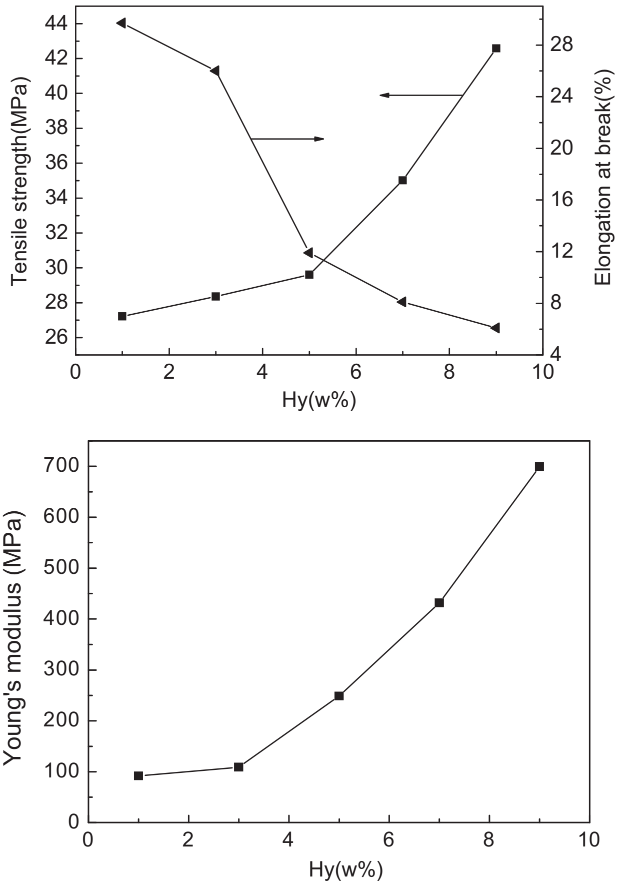

Fig. 5. Tensile strength, elongation at break and Young's modulus of PStH films with different amount of halloysite.

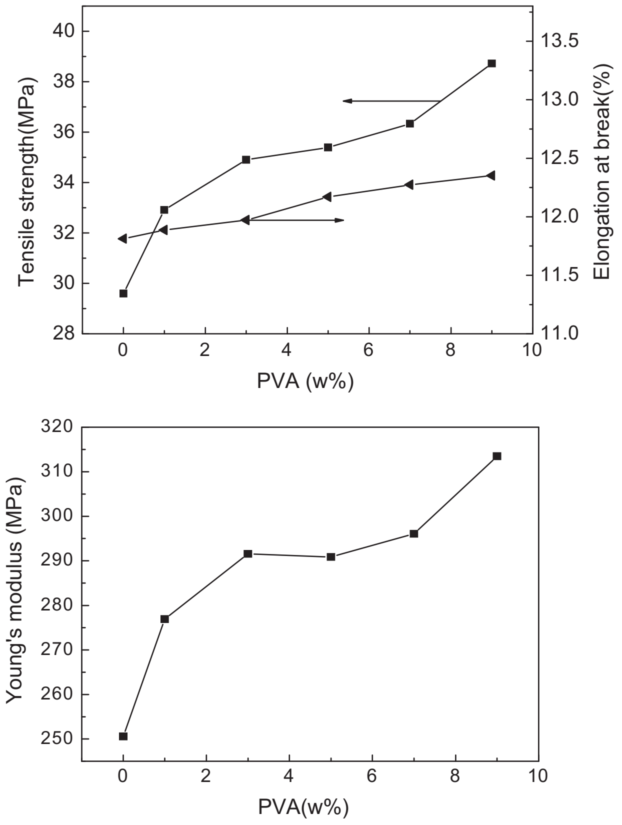

Fig. 6. Tensile strength, elongation at break and Young's modulus of PStH-P films with different amount of PVA.

3.5. *Mechanical properties of the halloysite/potato starch films*

Mechanical property is one of the most important parameters to evaluate materials. Natural polymers usually possess rigid or semi-rigid chains and they often show undesired flexibility. So its hard for starch, PSt included, to form successive soft films if no plasticizer is added. Here, we choose glycerol as plasticizer and study its effect on the mechanical properties of halloysite/potato starch films.

Fig. 5 shows the changes in tensile strength, elongation at break as well as Young's modulus of PStH films with different amount of halloysite. With the increase of halloysite, both tensile strength and Young's modulus increased, while elongation at break decreased. This phenomenon is common for polymer materials strengthened with inorganic fillers.

In order to further increase the mechanical strength of the halloysite/potato starch films, PVA was incorporated and its effect is shown in Fig. 6. PVA is a hydrophilic polymer and contains plentiful –OH groups on the macromolecular chains. PVA shows high mechanical strength because the strong interaction among PVA macromolecules through hydrogen bonding. When it was added into starch, –OH groups on PVA macromolecules could form hydrogen bonds with those on PSt macromolecules and thus formed a compatible composite. Since PVA has high mechanical properties, the PVA loaded PStH-P has higher tensile strength and elongation at break than those of PStH. Tensile strength increased from 29.6 MPa to 35 MPa and the Young's modulus increased from 250 MPa to 291 MPa when PVA content increased to 3%, and then they increased slowly with further increasing of PVA to 8% and reached a higher tensile strength value of 39 MPa and Young's modulus value of 313 MPa at PVA loading of 9%, which were much higher than that previously reported (Xie et al., 2011). As for elongation at break, it was almost unchanged for PStH-P films. In terms of the biodegradability of the starch films, the loser the PVA level the better.

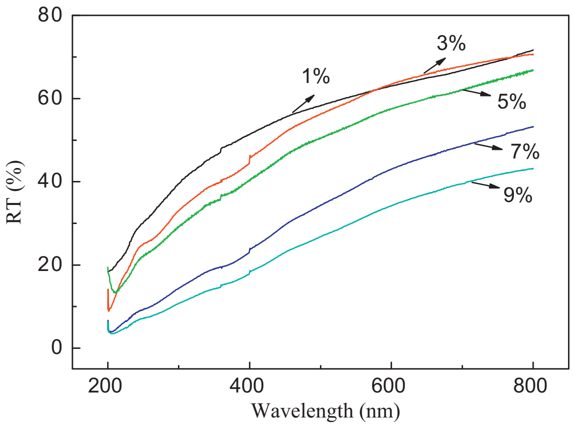

Fig. 7. Relative transmittances of PStH films with different amount of halloysite.

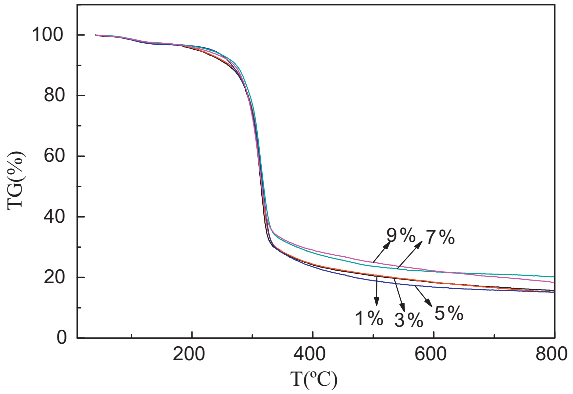

Fig. 8. TGA of the PStH films with different amount of halloysite.

3.6. *Transparency of the halloysite/potato starch films*

Fig. 7 shows the relative transmittances of PStH films with different amount of halloysite. The addition of halloysite obviously decreased the RT of the starch films. Meanwhile, the relative transmittances of PStH-G films and PStH-P films were determined as well. The addition of glycerol or PVA only caused slight changes in the transparency of the starch films.

3.7. *Thermogravimetric analysis (TGA) of the PStH films*

From the TGA of the PStH films with different amount of halloysite (shown in Fig. 8), we find that there was little weight loss below 200 °C. This loss may be caused by the volatilization of the adsorption water. When the temperature reached 310 °C, a massive decline appeared which was mainly caused by the thermal decomposition of starch and the volatilization of glycerol (whose boiling point was about 290 °C). Since halloysite has no weight loss at low temperature, the residue mass of the films increased as halloysite content raised.

4. Conclusion

Halloysite/potato starch films were fabricated from potato starch using modified natural halloysite nanotubes as fillers. The aggregated halloysite power could be thoroughly broken into halloysite nanotubes that was well dispersed in distilled water or water/ethanol after ball-milling treatment using 50/50 water/ethanol mixture as medium and PEG as dispersing agent. The treated halloysite nanotubes were well dispersed in potato starch matrix and the two phases showed good compatibility owing to the action of PEG. So the addition of halloysite could effectively improve the tensile strength of the PStH films. When small amount of PVA was incorporated, the tensile strength and Young's module of the composite films were further improved, and the elongation at break improved a bit as well. Since halloysite/potato starch films are biodegradable, low-cost and high strength, the enforced potato starch films will show great potential as green package materials.

Acknowledgments

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