

M. LIU
B. GUO[✉]
M. DU
D. JIA

Drying induced aggregation of halloysite nanotubes in polyvinyl alcohol/halloysite nanotubes solution and its effect on properties of composite film

Department of Polymer Materials and Engineering, South China University of Technology, Guangzhou 510640, P.R. China

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ABSTRACT The polyvinyl alcohol (PVA)/halloysite nanotubes (HNTs) solution were prepared with the aid of ultrasonic treatment. The composite films were prepared through casting or coagulating the PVA/HNTs solution. The coagulation process was employed to obtain a composite film without aggregation of HNTs. It is shown that the particle size and distribution of HNTs in the PVA/HNTs solution is independent of the ratio between HNTs and PVA. It is also revealed that the aggregation of HNTs takes place during the drying process of the as cast film. Compared with the film by coagulation method, the HNTs in the as cast film show less profound effect on the nucleation of the crystallization of the PVA. The crystallization temperature initially increases with HNTs loading and overloading of HNTs tend to depress the improvement in the crystallization temperature. The glass transition temperature (T_g) of the composite film decreases with HNTs loading and the aggregation process shows practically no effect on the T_g . Inclusion of HNTs greatly depresses the decomposition of the PVA backbone, while it is not effective for improving the resistance to the abstraction of the side groups. The aggregation process at low concentration of HNTs has more significant effect on the thermal decomposition of composite films compared with that at high concentration.

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1 Introduction

Polyvinyl alcohol (PVA) is a biodegradable synthetic polymer used in paper coating [1–3], textile sizing [4–6], and flexible water-soluble packaging films [7–9], etc. PVA films have high tensile strength and abrasion resistance and applications in binder [10, 11], blood prosthetic devices [12], fuel cells [13], double layer capacitors [14], etc. Modification of PVA with inorganic fillers was common to improve its film performance such as mechanical strength, thermal resistance and permeability properties [15–18]. The surface characteristics of the filler which determine the interactions between the filler and the PVA are of primary

importance in the selection of filler for PVA composites. The inorganics with surface silanol groups such as montmorillonite (MMT) [15], silica [17], and attapulgite [18] have been demonstrated to interact with PVA via hydrogen bonding. The dispersion state of the inorganics in the polymer matrix is critical in determining the final performance of the composite film. As a consequence, the investigation of the dispersion of the inorganics and its effects on the performance of the composite film are of fundamental importance for the investigation of the PVA composite films. Solution coating and casting are commonly used in the preparation of PVA composite film [19–22]. During these processes, the well dispersed inorganics in the PVA solution may aggregate due to strong interactions among inorganic particles. Three kinds of interactions coexist in PVA/inorganics aqueous solution: the interaction between the inorganics and PVA, the interaction between the inorganics and water, and the interaction among the inorganics. During drying of the composite film with casting method, the water evaporates gradually and the interaction between water and the inorganics decreases. In addition, the concentration of the solution increases gradually with the evaporation of water. Beyond the solubility of PVA in water (normally not higher than 20 wt. %), the PVA molecules start to precipitate and this may reduce the interaction between PVA and inorganics. As a consequence, there is a critical point for the aggregation. Before this point, the solution is stable and the aggregation will not occur. Beyond this point, the unbalanced interactions trigger the aggregation. The aggregation during processing may have significant effects on the performance of the final composite films.

Halloysite nanotubes (HNTs) are a kind of aluminosilicate clay with hollow nanotubular structure mined from natural deposits in countries such as China, America, Brazil, France, Japan, South Korea and Turkey [23]. HNTs were used also as bioreactors [24], time-release capsules [25], catalysts of polymer degradation [26], templates [27], for high-tech ceramic applications [28], etc. Recently HNTs have been evaluated as polymer filler for higher mechanical and flame retardant properties of polypropylene [29].

The present work aims to incorporate HNTs into PVA to form a composite film and to disclose the drying induced aggregation of HNTs and its effect on the properties of the

✉ Fax: +86-20-22236688, E-mail: psbcguo@scut.edu.cn

composite film. The changes in the properties are correlated to the variation in the interactions between PVA and HNTs.

2 Experimental

2.1 Materials

Polyvinyl alcohol (PVA), supplied by Shanghai Petrochemical, was 88% hydrolyzed, with a degree of polymerization of 1700. The halloysite, grade of ultra-fine, was provided by Imerys Tableware Asia Limited, New Zealand. The elemental composition is as follows (wt. %): SiO₂, 49.5; Al₂O₃, 35.5; Fe₂O₃, 0.29; TiO₂, 0.09. The Brunauer–Emmett–Teller (BET) surface area is approximately 28.7 m²/g.

2.2 Sample preparation

The stock solution of PVA (10.0 wt. %) and HNTs solution (0.1–10 wt. %) were prepared separately. PVA grains were fully dissolved in water by stirring at 70 °C for about 2 h. HNTs, which was dried for 8 h at 80 °C, was dispersed in water for 2 h by ultrasonic treatment. Then the solutions of PVA/HNTs were prepared by mixing the two stock solutions by stirring for 10 min and by ultrasonic treatment for 120 min, varying the HNTs content in PVA/HNTs composites from 2 to 53 wt. %.

The PVA film and PVA/HNTs composite films with 2, 10, 40 and 53 wt. % HNTs content were obtained by the casting and coagulation method. In the casting method, the solution was cast on a glass substrate and dried at room temperature for 48 h. In the coagulation method, the solution was added dropwise into plenty of acetone to precipitate the composite. The composite was then filtered and dried on the glass substrate at room temperature for 48 h. All the samples were kept in a vacuum desiccator at room temperature before any measurements were taken.

2.3 Sample characterizations

The particle size and distribution of HNTs solution and PVA/HNTs solution were characterized by a laser diffraction particle size analyzer LS13 320 of Beckman Coulter. The refraction index of HNTs was 1.55. Water was used as the flowing liquid. The specimens of the films were then cryogenically ultramicrotomed into thin pieces with thicknesses of about 10 nm with Leica EM UC6. Next, the transmission electron microscopy (TEM) observations were performed using a JEM-100CXII TEM machine at an accelerating voltage of 100 kV. Non-isothermal differential scanning calorimetry (DSC) tests of the composites were then carried out on a TA Modulated DSC 2910 instrument. The samples were heated from 30 to 230 °C and held at 230 °C for 3 min to eliminate the thermal history. The non-isothermal crystallization process was recorded from 230 to 50 °C and the glass transition process was recorded from 50 to 90 °C in the second heating process. The heating and cooling rates were set as 20 °C/min and nitrogen gas was used as the purging gas. Thermogravimetric analysis (TGA) was carried out under a N₂ atmosphere with NETZSCH TG 209 F1 at a heating rate of 10 °C/min from room temperature to 700 °C.

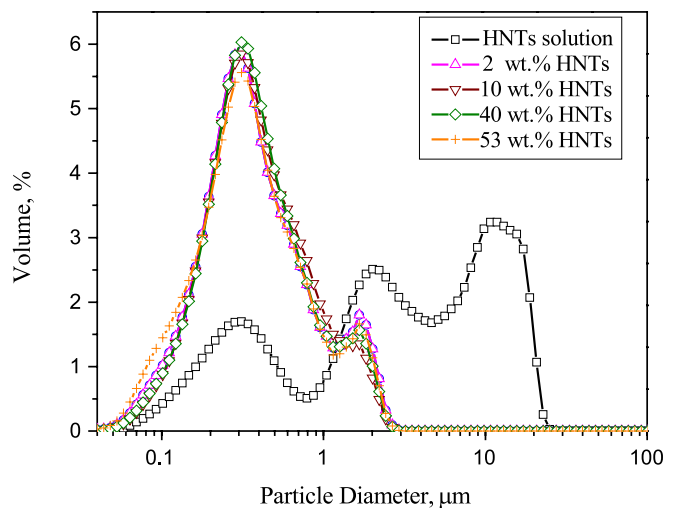


FIGURE 1 The result of particle size and distribution of HNTs in HNTs solution and in PVA/HNTs solutions

3 Results and discussion

The results of particle size and distribution of HNTs in the HNTs solution and PVA/HNTs solutions are shown in Fig. 1. It is shown that the HNTs particle size in PVA/HNTs solutions is significantly lower than that in the HNTs solution. The average particle diameter is lowered from 5.77 μm to about 0.55 μm. The particle size and distribution are practically independent from the composition of the PVA/HNTs solution. The decreased particle size may be attributed to the reduced aggregation of HNTs through forming the PVA/HNTs complex via hydrogen bonding. Macroscopically, the PVA/HNTs solutions in different compositions are very stable and no sedimentation is observed during long periods up to several weeks.

As indicated above, HNTs can be easily dispersed in PVA solution in virtue of the hydrogen bonding between surface silanols of the HNTs and the hydroxyl groups of PVA. Casting is a typical method for preparing the PVA films [20–22]. In the process of casting, however, the HNTs may aggregate again due to the strong hydrogen bonding between the filler particles. The re-aggregation may affect the structure and properties of the composite film. Recently, Winey et al. [30] have developed a coagulation method for the preparation of poly(methyl methacrylate) (PMMA)/carbon nanotubes (CNTs) composites with good dispersion of CNTs in the matrix. Through the coagulation method, the resulting PMMA/CNTs composites exhibited larger elastic modulus, higher electrical conductivity, and increased thermal stability with respect to pure PMMA. In order to reveal the aggregation of HNTs during the drying process in the casting method, the composite film without re-aggregation of HNTs was prepared through the coagulation method modified from that reported by Winey [30, 31].

Figure 2 shows the TEM photos of PVA/HNTs composite films with HNTs content of 2 wt. % prepared by the two methods. It can be seen that the composite film prepared by coagulation method has substantial uniform dispersion of HNTs compared with the as cast composite film. In the coagulation method, the well dispersed HNTs in the solution

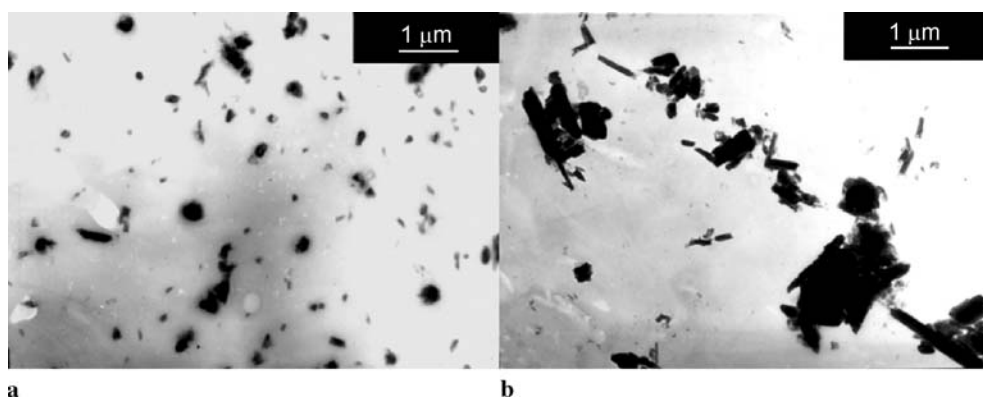


FIGURE 2 TEM photos of PVA/HNTs composite films (with 2 wt. % HNTs): (a) coagulation (b) as cast

are separated by the solidified PVA during the precipitation process and cannot re-aggregate. In the casting procedure, the water evaporates gradually and the concentration increases gradually. The reduced water content results not only in decreased interaction between water and HNTs, but also decreased interaction between PVA and HNTs as the PVA molecules start to precipitate. As a consequence, the HNTs start to re-aggregate.

PVA is a semicrystalline polymer in which high physical interchain and intrachain interactions exist, due to hydrogen bonding between hydroxyl groups. The introduction of nano-sized HNTs with hydroxyl groups alters the intramolecular and intermolecular interactions of the PVA chains. This may affect both crystallization behavior and the physical structure of PVA, resulting in the variations in properties of composite films. Figure 3 shows the DSC curves of neat PVA and PVA/HNTs composites in the cooling process. It is clear that the crystallization peak of PVA initially shifts to higher temperature with HNTs content, and the crystallization regime is prolonged compared with the neat PVA. The observed effects can be attributed to the nucleating effect of HNTs in the PVA crystallization process. Overloading of HNTs (53 wt. %)

in the composite, however, depresses the increase in the crystallization peak temperature. The overloading HNTs may aggregate in the PVA matrix and the aggregated HNTs have lower nucleating ability due to the reduced specific surface area. Similar results of the effect of nanosized inorganics on the crystallization of PVA have also been suggested [18]. Comparing the two preparation methods of composite films, the films prepared by the coagulation method have invariably higher crystallization onset temperature and crystallization peak temperature. This may be attributed to the better dispersion of HNTs in the PVA matrix with the method of coagulation, as indicated by the above-mentioned TEM results.

Glass transition temperature (T_g) of composite variations are shown in Fig. 4. It can be seen that the T_g decreases slightly with HNTs content in the composite. It is to be noted that the preparation method shows practically no effect on the T_g of the PVA/HNTs composite film. The reported effects of nanoparticles on the T_g of PVA composites are somewhat contradictory. Incorporating silver (Ag) nanoparticles into the PVA matrix led to increases T_g [32], and the T_g of PVA increases with Ag content. With the Ag content of

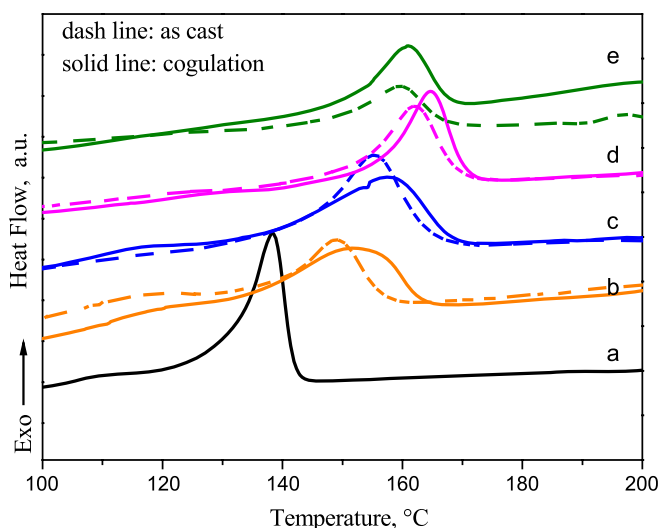


FIGURE 3 DSC cooling thermograms of neat PVA and PVA/HNTs composite films with different HNTs content: (a) 0 wt. % (neat PVA) (b) 2 wt. % (c) 10 wt. % (d) 40 wt. % (e) 53 wt. %

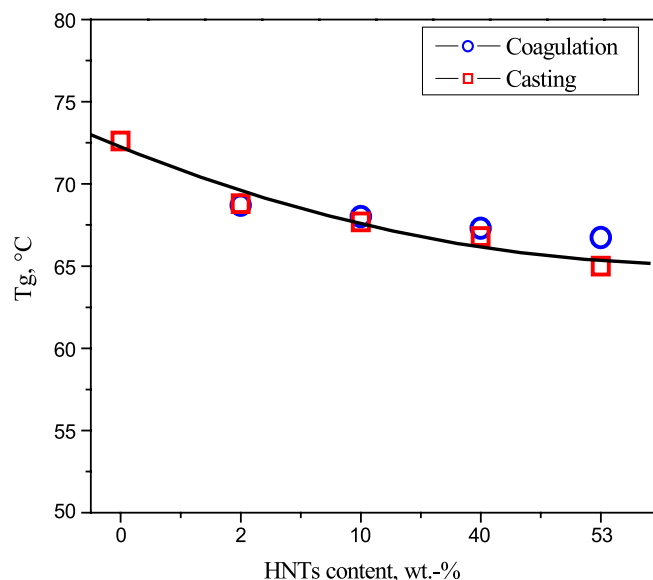


FIGURE 4 T_g curves of PVA/HNTs composite with different HNTs content

0.73%, the T_g of PVA increases at about 21 °C [32]. Incorporating the silica into PVA increased T_g of PVA only at relatively low silica content (lower than 33 wt. %) [17]. The work in [17, 32] attribute this phenomenon to the reduced mobility of polymer chains by incorporating the inorganics. Incorporation of nanoparticles into the polymer matrix may affect the distribution of chain segments, most likely due to a change in chain packing density in the vicinity of the surface of the nanofillers. It should be emphasized that the filler geometry may play the critical role in the effect of the T_g . Silica and silver have the sphere structure and are isotropic. A polymer chain may be absorbed or become entangled on the surface of the filler. The mobility of the polymer chain segment may be inhibited by the inorganics. However, incorporation of magnetite particles, with average diameters of 12–20 nm into the PVA matrix leads to decreased T_g [33], and this is consistent with the result of the present work. This may be due to the anisotropic character of magnetite and HNTs. For the sphere nanoparticles, the polymer chain could absorb onto or entangle with the nanoparticles as the diameter of the nanoparticles is comparable with the gyration radii of the polymer chains. This may lead to an increased packing density of the polymer chains. The restricted mobility originated from the denser chain packing results in higher T_g values. Although the diameter of HNTs is on the nanometer scale, their length is in the microscale and considerably higher than the typical gyration radii of polymer chains. As a consequence, the polymer chains could not wrap the nanotubes in three dimensions and many voids may exist around the nanotubes. The voids on a nanometer scale provide the free volume for the chain segments. As a result, the incorporation of nanotubes tends to lower the T_g of the polymer matrix.

Figure 5 presents the TGA curves of PVA, HNTs and PVA/HNTs composites. As observed in Fig. 5 the neat PVA exist in two weight loss steps. The weight loss around 350 and 450 °C was attributed to the decomposition of the side chain and backbone of the PVA, respectively [34–36]. It is shown that the decomposition of PVA at higher temperature stages is substantially restricted, although HNTs cannot im-

prove the initial decomposition temperature and restrict the decomposition at lower temperature stages. The fact that the HNTs do not affect the initial stage of decomposition of PVA is similar to the results of PVA/MMT nanocomposites. Manias [15] attributed this to the ability of supplying oxygen by PVA itself. Compared with MMT, HNTs do not exhibit inferior ability in blocking the thermal transfer. Therefore, the decomposition of the backbone of PVA is restricted. The preparation method of composite film has a slight effect on the thermal degradation of PVA. But the aggregation process at low concentration of HNTs has a more significant effect on the thermal decomposition compared with that at high concentration, which may be due to the fact that a change in dispersion state is more obvious at low concentration of HNTs.

4 Conclusions

The particle size and distribution of HNTs in the solution is independent of the HNTs/PVA ratio. It is revealed that the aggregation of HNTs takes place during the drying process within the casting of the film. Compared with the film through the coagulation method, the HNTs in the as cast film show a less profound effect on the nucleation of the crystallization of PVA. The crystallization temperature initially increases with HNTs loading and overloading of HNTs tend to depress the improvement in the crystallization temperature. The T_g of the composite film decreases with HNTs loading and the aggregation process shows practically no effect on the T_g . Inclusion of HNTs greatly depresses the decomposition of the PVA backbone but it is not effective for improving the resistance to the abstraction of the side groups. The aggregation process at low concentration of HNTs has a more significant effect on the thermal decomposition of composite films compared with that at high concentration.

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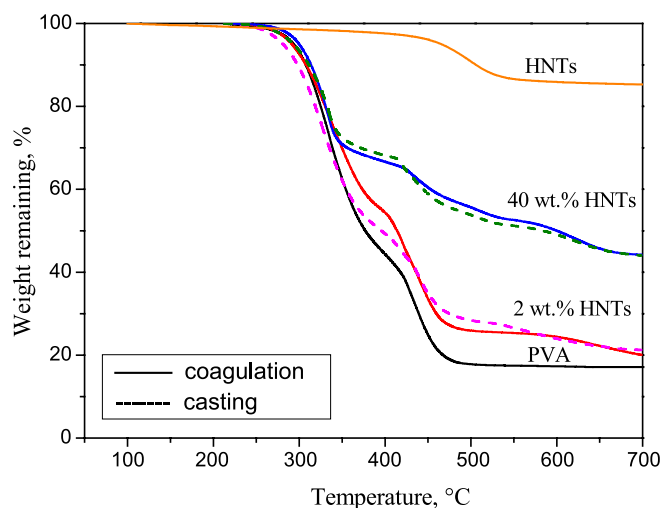


FIGURE 5 TGA curves of PVA, HNTs and PVA/HNTs composites

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