Preparation and study of Polyvinyl Alcohol/Attapulgite nanocomposite fibers with high strength and high Young’s modulus by gel spinning

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Abstract
Polyvinyl alcohol (PVA)/Attapulgite (ATT) nanocomposite fibers with high strength and high Young’s modulus were prepared via gel spinning. The structures and properties of PVA/ATT nanocomposite fibers were investigated with Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimeter (DSC), thermo gravimetric analysis (TGA), x-ray diffraction (XRD), Environmental scanning electron microscope (ESEM), and mechanical testing. The results showed that ATT had a great influence on the structures and properties of PVA/ATT nanocomposite fibers. The melting temperatures, crystallinities, initial decomposition temperatures and maximum decomposition temperatures of PVA/ATT nanocomposite fibers increased firstly when ATT content was increased from zero to 3 wt%, however, they were then dropped when ATT contents were 5 wt% and 7 wt%. The highest melting temperature, crystallinity, initial decomposition temperature and maximum decomposition temperature of PVA/ATT-3 were 240.4 °C, 67.6%, 266.7 °C and 358.6 °C, respectively. Furthermore, ESEM observation indicated that ATT had good adhesion to PVA matrix. Mechanical tests showed that PVA/ATT-3 had the highest breaking tensile and Young’s modulus of 12.6 cN/dtex and 301.9 cN/dtex, respectively.

Introduction
Polyvinyl alcohol (PVA) has a planar zigzag structure like polyethylene and can be made into high-performance fibers with high strength and high modulus [1]. The repeating unit of PVA contains a hydroxyl group that easily forms intramolecular or intermolecular hydrogen bonds in PVA [2, 3]. The theoretical assumption of a PVA fiber’s tensile strength and Young’s modulus calculated using bond energy can be as high as 27 GPa and 255 GPa, respectively [4]. However, the maximum tensile strength of a PVA fiber that has been reported was approximately nearly 10% of the theoretical calculation of strength [2]. Great interest in developing high-performance PVA fibers has been primarily driven by this significant discrepancy between the practical and theoretical strength.

Up to now, many attempts have been made to develop PVA fibers with high strength and high modulus, such as enhancing the polymerization degree and tacticity of PVA and improving spinning methods and spinning processes of PVA fibers. Yamaura et al [5] prepared a PVA fiber via a gel spinning using a binary solvent composing of 80 vol % DMSO and 20 vol% water, resulting in a high Young’s modulus of 39 GPa. It is still not an easy job to reach the theoretical values in a majority of PVA fiber production. One major problem was associated with intermolecular hydrogen bonding commonly found in PVA macromolecules, resulting in challenges in molecular orientation development at both fiber spinning line and post drawing process [6, 7]. Moreover, the addition of inorganic materials may provide an effective way to improve the mechanical properties of PVA fibers. Jo et al [8] obtained a PVA fiber with high tensile strength and Young’s modulus of 23.1 g d−1 and
Attenuated total internal reflection Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR measurements were performed using a Nicolet 6700 obtained in the range 600–4000 cm$^{-1}$ by averaging 32 scans at a resolution of 4 cm$^{-1}$.

Differential scanning calorimetry (DSC)

DSC was measured on a Q20 DSC instrument (TA, America) at a heating rate of 10 °C min$^{-1}$, under continuous nitrogen flowing. In each experiment, the sample (~3 mg) was heated from room temperature to 250 °C.

Thermogravimetric analysis (TGA)

TGA were conducted with a TG 209 F1 Iris thermogravimetric analyzer (Netzsch-Geraetebau GmbH, Germany) under nitrogen flow. In each experiment, the sample (~3 mg) was heated from room temperature to 650 °C at the rate of 20 °C min$^{-1}$ under nitrogen.
X-ray diffraction (XRD)

XRD curves were acquired on a Powder x-ray diffractometer (Bruker, Germany) equipped with Cu Kα radiation (λ = 0.15418 nm, 30 kV, 10 mA), the scanning angle was 5–60 degrees.

Environmental scanning electron microscope (ESEM)

ESEM images were observed on a Quanta-250 (FEI, Czech) at an accelerating voltage of 10 kV.

Tensile stress testing

Tensile strength and Young’s modulus were measured on XQ-1A (China) yarn strength tester. The length of fixture was 2 cm and the stretching speed was 10 mm min⁻¹. The reported tensile strength and Young’s modulus were the average value of 20 samples.

Results and discussions

FT-IR analysis

The ATR-FTIR spectra of pure ATT and PVA/ATT nanocomposite fibers are shown in figure 1. In the spectra of pure ATT, the characteristic absorption peaks at 3553, 1655, 1196 and 982 cm⁻¹ were assigned to hydroxyl groups of coordinated water in the tunnels of ATT, bending vibration of zeolite water, Si–O vibrations and asymmetric stretching of Si–O–Si bonds [19], respectively. In the spectra of PVA/ATT nanocomposite fibers, the absorption peaks near 3313–3327 cm⁻¹ were characteristic for the –OH asymmetric stretching vibration band. In addition, the absorption peaks at about 2937 cm⁻¹, 2908 cm⁻¹, 1660 cm⁻¹, 1428 cm⁻¹ and 1091 cm⁻¹ were caused by –CH₂ asymmetric and symmetric stretching vibration, C–C framework stretching vibration, –CH flexural vibration and C–O stretching vibration, respectively [20, 21]. In a comparison of the spectra of PVA/ATT nanocomposite fibers with different ATT contents, although the characteristic absorption peaks of other groups had little change, the OH stretching vibration absorption peaks at about 3298 cm⁻¹ moved toward higher wavenumber with the increase of ATT content, indicating that hydrogen bonding in the PVA/ATT nanocomposite fibers was weaker than that in the pure PVA fiber. It is well-known that the presence of Si–OH groups on ATT surface would allow the formation of hydrogen-bonding interaction with the hydroxyl groups in the PVA nanocomposite fibers [16, 17].

DSC analysis

DSC measurements were used to study the thermal properties of the PVA composite fiber [22]. Figure 2 shows the DSC curves of PVA/ATT nanocomposite fibers. An endothermic peak of melting temperature at around 225 °C–245 °C was found on the DSC curve of pure PVA (PVA/ATT-0). With the addition of ATT, the melting point of PVA/ATT nanocomposite fibers was increased from 234.1 °C to 240.0 °C when ATT content was increased from 0 wt% to 3 wt%. However, the melting temperatures were then dropped at high ATT content (5 wt% and 7 wt%). The melting temperatures suggested a critical change when ATT content was 3 wt%. Table 1 showed melting temperature, heat of fusion, and degree of crystallinity of PVA/ATT nanocomposite fibers. The
The degree of crystallinity of the PVA component was calculated based on the following equation (1) [20]:

$$\chi_c = \frac{\Delta H_m^0}{\omega \Delta H_m}$$

Where $\Delta H_m^0 (161 \text{ J g}^{-1})$ is the melting enthalpy for 100% crystalline PVA, and $\omega$ is the weight fraction of the PVA component in the nanocomposite fibers. Both the heat of fusion and the crystallinities of PVA/ATT nanocomposite fibers were increased when the ATT was increased from zero to 3 wt%, however, they were decreased when the ATT contents continued to increase from 3 wt% to 7 wt%. The highest crystallinity of PVA/ATT-3 was 67.7%, which was 8.1% higher than that reported in reference [17]. The hydroxyl groups distributed in the surfaces of ATT might work as nucleation sites [16, 23]. The strongest nucleating effect exists at an optimal ATT content that was most likely about 3 wt%. Nevertheless, for higher ATT contents, phase separation may occur, leading to ATT agglomerates and affecting fiber integrity.

**TGA analysis**

The TGA and DTG curves were used to obtain ATT content in nanocomposite fibers and the detailed information of degradation process of PVA/ATT nanocomposite fibers (figure 3). The thermograms data were summarized in table 2. The temperature at which fiber weight loss is 5 wt% is defined as the initial decomposition temperature ($T_i$). The temperature at which the degradation rate reaches a maximum is defined.
as the maximum decomposition temperature ($T_m$). As shown in figure 3, a small weight loss at the beginning of the ATT was assigned to the loss of absorbed water in the air [24]. In the high temperature region even above 650 °C, ATT showed little weight loss and there was about 86.5 wt% residue at 650 °C, indicating that the ATT had a superior thermal stability. The DTG curve of neat PVA fiber shows two peaks at 272.7 °C and 342.7 °C that can be attributed to the decomposition of side chain and main chain of PVA fiber [25], respectively. The peak at 272.7 °C disappeared in the DTG curves of PVA/ATT nanocomposite fibers when ATT content was 3 wt% and more, indicating that there were no decomposition of side chain in PVA/ATT-3, PVA/ATT/5 and PVA/ATT-7. As shown in table 2, $T_i$ of PVA/ATT nanocomposite fibers was increased from 239.2 °C to 266.7 °C when the ATT content was increased from 0 wt% to 3 wt%. However, $T_i$ was then dropped at high ATT content (5 wt% and 7 wt%). The $T_i$ and $T_m$ of PVA/ATT-3 were improved 27.5 °C and 15.9 °C, respectively, compared with those of pure PVA fiber, suggesting that PVA/ATT-3 had the best thermal stability, these were consistent with the results of DSC. The enhancement of thermal stability was due to the strong interfacial interactions between ATT and PVA chains [16].

**XRD analysis**

XRD patterns were given in figure 4. Typical diffraction peaks of ATT were at 2θ = 8.3°, 13.7°, 19.9° and 26.7°, which were correspond to the primary diffraction of the (110), (200), (040), and 400 planes of ATT, respectively [24, 26]. The diffraction peaks of PVA fibers were clearly observed at about 2θ = 10.8° (100), 19.2° (101) [27]. The crystallinities of PVA/ATT nanocomposite fibers increased firstly and then decreased with increasing of
ATT content, this was consistent with the results of DSC. Nevertheless, the crystallinities of PVA/ATT-0, PVA/ATT-1, PVA/ATT-3, PVA/ATT-5 and PVA/ATT-7 obtained by XRD were 24.2%, 26.6%, 30.9%, 26.5% and 25.5%, that were lower than the crystallinities measured by DSC. That was because the heating process in DSC was able to further promote crystallization of PVA macromolecules [28].

Morphology and structure
The surface morphologies of PVA nanocomposite fibers were demonstrated in ESEM images. As shown in figures 5(a)–(c), the surfaces of PVA/ATT nanocomposite fibers were smooth and uniform when ATT contents were no more than 3 wt%. However, the defects and voids on the surfaces of PVA/ATT-5 and PVA/ATT-7 were found in figures (d) and (e), indicating that phase separation may occur when ATT contents were 5 wt% and

Figure 5. ESEM images of PVA/ATT nanocomposite fibers. (a) PVA/ATT-0, (b) PVA/ATT-1, (c) PVA/ATT-3, (d) PVA/ATT-5, (e) PVA/ATT-7, (f) cross section of PVA/ATT-3 without hot stretching.
7 wt%. It is well known that the properties of PVA/ATT nanocomposite fibers depend on the size and dispersion of ATT. Figure 5(f) was the ESEM image of the cross section of PVA/ATT-3 without hot stretching, large amounts of bright dots which were the ends of the embedded ATT can be found in figure 5(f). It can be found that ATT was enwrapped in the matrix of PVA, which was irregularly distributed, but some agglomerates can be observed. In addition, the interface between ATT and PVA matrix was not so clear, which means that ATT have good adhesion to PVA. The excellent adhesion between PVA matrix and ATT can be attributed to be the formation of hydrogen bonding between them [17].

**Mechanical properties**

The mechanical properties of PVA/ATT composite fibers were studied. The stress-strain curves of PVA/ATT nanocomposite fibers were shown in figure 6. Table 3 showed maximum hot-drawing ratio, breaking tensile strength, Young's modulus and breaking elongation of PVA/ATT nanocomposite fibers. The breaking tensile strength and Young's modulus were increased when ATT content was increased from zero to 3 wt%. However, they were then dropped at high ATT content (5 wt% and 7 wt%), resulting in highest breaking tensile strength and Young's modulus measured in PVA/ATT-3 as shown in figure 6 and table 3. In addition, the breaking elongation of PVA/ATT-3 was relatively low. In general, PVA/ATT-3 showed the best performance among these PVA nanocomposite fibers. Furthermore, the breaking tensile strength of all PVA/ATT composite fibers were more than 10 cN/dtex, and PVA/ATT-3 had the highest strength of 12.6 cN/dtex, which was about twice as that reported in the reference [17]. From the structural characterization, it can be concluded that ATT work as rigid supports in the PVA matrix and the nucleating effect enhanced the Xc value of PVA/ATT nanocomposite fibers. All this is a response to a significant improvement of the mechanical properties of PVA/ATT nanocomposite fibers [16].

**Conclusions**

The structures and properties of a group of PVA/ATT nanocomposite fibers with different ATT contents were investigated using chemical and physical analysis. The results showed that ATT content had a great influence on
the structures and properties of PVA/ATT nanocomposite fibers. The melting temperatures, crystallinities, initial decomposition temperatures and maximum decomposition temperatures of PVA/ATT nanocomposite fibers increased firstly when ATT content was increased from zero to 3 wt%, however, they were then dropped when ATT contents were 5 wt% and 7 wt%. Furthermore, ESEM observation indicated that ATT were embedded in PVA matrix and combined closely, mechanical tests showed that the highest breaking tensile and Young’s modulus were PVA/ATT-3, which were 12.6 cN/dtex and 301.9 cN/dtex, respectively. These suggested that the strongest reinforcement exists at an optimal ATT content of 3 wt%.

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References

[1] Zha Y, Wu C X, Zhang Y W and Zhao J X 2013 Study on the chain entanglement of polyvinyl alcohol fiber during the dry-jet wet spinning process Fiber. Polym. 16 345
[2] Nawar A M, Mohammed M I and Yahia I S 2019 Facile synthesis and optical characterization of graphene oxide–doped TiO2/polyvinyl alcohol nanocomposites: optical limiting applications Mater. Res. Express 6 075054
[3] Suzuki M, Tanigami T, Matsuzawa S and Yamaura K 2002 Influence of molecular weight and syndiotacticity on the structure of high-performance poly(vinyl alcohol) fibers prepared by gel spinning J. Appl. Polym. Sci. 86 1970
[4] Lyoo W S and Ha W S 1996 Structure and properties of microfibrillar poly(vinyl alcohol) fibres prepared by saponification under shear force of poly(vinyl pivalate) Polymer 37 3121
[5] Yamaura K and Kumakura R 2000 Gel-spinning of partially saponified poly(vinyl alcohol). J. Appl. Polym. Sci. 77 2872
[6] Song D H and Lyoo W S 2007 Preparation of high molecular weight poly(vinyl pivalate) with high yield and high molecular weight poly(vinyl alcohol) by emulsion polymerization of vinyl pivalate and saponification J. Appl. Polym. Sci. 104 410
[7] Lyoo W S and Lee H W 2002 Synthesis of high-molecular-weight poly(vinyl alcohol) with high yield by novel one-batch suspension polymerization of vinyl acetate and saponification Colloid. Polym. Sci. 280 835
[8] Jo Y G et al 2009 Effect of gel spinning accompanied with cross-Linking using boric acid on the structure and properties of high-molecular-weight poly(vinyl alcohol) Fiber J. Appl. Polym. Sci. 113 1733
[9] Huang D, Wang W, Xu J and Wang A 2012 Mechanical and water resistance properties of chitosan/poly(vinyl alcohol) films reinforced with attapulgite dispensed by high-pressure homogenization Chem. Eng. J. 210 166
[10] Wang Q et al 2019 Preparation and electrochemical properties of NiCo2O4 nanorods grown on nickel foam filled by carbon-coated attapulgite for supercapacitors Mater. Res. Express 6 125524
[11] Niu X et al 2014 Rod-like attapulgite modified by bifunctional acrylic resin as reinforcement for epoxy composites Ind. Eng. Chem. Res. 53 16359
[12] Liu Z T et al 2017 Enhanced dehydrogenation of decabrominated diphenyl ether in aqueous solution by attapulgite supported Fe/Ni bimetallic nanoparticles: kinetics and pathways Mater. Res. Express 4 0485009
[13] Peng L et al 2011 Synthesis and properties of waterborne polyurethane/attapulgite nanocomposites Compos. Sci. Technol. 71 1280
[14] Shen L, Lin Y, Du Q and Zhong W 2006 Studies on structure–property relationship of polylamidé-6/attapulgite nanocomposites Compos. Sci. Technol. 66 2242
[15] Zhou Y, Lei L, Yang B and Li J 2017 Preparation of PLA-based nanocomposites modified by nano-attapulgite with good toughness-strength balance Polym. Test. 60 76
[16] Peng Z Q and Chen D J 2006 Study on the nonisothermal crystallization behavior of poly(vinyl alcohol)/attapulgite nanocomposites by DSC analysis J. Polym. Sci., Part B: Polym. Phys. 44 534
[17] Peng Z Q and Chen D J 2006 Alignment effect of attapulgite on the mechanical properties of poly(vinyl alcohol)/attapulgite nanocomposite fibers J. Polym. Sci., Part B: Polym. Phys. 44 1995
[18] Hong X Q et al 2018 Dry-wet spinning of PVA fiber with high strength and high Young’s modulus IOP Conf. Ser.: Mater. Sci. Eng. 439 042011
[19] Frost R L and Mendelowici E 2006 Modification of fibrous silicates surfaces with organic derivatives: an infrared spectroscopic study J. Colloid Interface Sci. 294 47
[20] Wei Y Z, Lai D P, Zou L M, Ling X L, Lu H W and Xu Y J 2018 Facile fabrication of PVA composite fibers with high fraction of multiwalled carbon nanotubes by gel spinning Polym. Eng. Sci. 58 1
[21] Huang D J, Wang W B, Kang Y R and Wang A Q 2012 Polym. Compos. 33 1693
[22] Luo Y Y, Wang F, Xu H, Zhu H L and Guo Y Y 2018 Effect of the degree of hydrolysis and polymerisation on the melting process of thermoplastic poly(vinyl alcohol) Plast. Rubber Compos. 47 1
[23] Xu W and He P 2001 Crystallization characteristics of polyoxyethylene with attapulgite as nucleating agent Polym. Eng. Sci. 41 1903
[24] Xia Y, Zha Y C, Zhou Y F,Nie W Y and Chen P P 2018 Polym. Compos. 39 560
[25] Ding H C, Lin S D and Li L 2017 J. Appl. Polym. Sci. 134 45437
[26] Wu T T, Dong J, Xu G F and Gan F 2019 Polym. 176 196
[27] Jia E, Su L, Liu P Q, Ye G D and Xu J J 2015 Fiber. Polym. 16 1964
[28] Nagara Y, Nakano T, Okamoto Y, Gotoh Y and Nagura M 2001 Properties of highly syndiotactic poly(vinyl alcohol) Polymer 42 9679