Preparation of high molecular weight polyvinyl alcohol by emulsifier-free emulsion polymerization

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Abstract. In this report, high molecular weight polyvinyl alcohol (PVA) was prepared by emulsifier-free emulsion polymerization, using the redox initiator of potassium persulfate (KPS) / N,N-dimethyl ethanolamine (DMEA). The structure and property of PVA were studied by using ubbelohde viscometer, fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance hydrogen spectroscopy (^{1}H-NMR), X-ray Diffraction (XRD), differential scanning calorimeter (DSC) and thermo gravimetric analysis (TGA). The results showed that the viscosity-average degree of polymerization (DP) of PVA 7506, which was much higher than that of PVA commonly used in industrial production. The syndiotacticity and crystallinity of PVA was 54.2 % and 35.6 %, respectively.

1 Introduction

High-performance polyvinyl alcohol (PVA) fibers show additional advantages, such as good acid resistance, high Young's modulus, strong adhesion and good dispersion [1, 2]. PVA fibers have been widely used as reinforcing materials in cement, rubber and bullet-proof materials [3]. The theoretical values for 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 [1]. However, the maximum tensile strength of a commercial PVA fiber was reported approximately at 2.1 GPa, that is only nearly 10% of the theoretical calculation of strength. The significant difference between practical and theoretical strength of PVA fibers attracted many researchers' interest.

It is known that the relative molecular weight is one of the important factors that affect the property of PVA fiber. The preparation of high molecular weight PVA is one of the effective methods to obtain the PVA fiber with high breaking strength and high Young's modulus [4]. At present, the preparation method of industrial production of PVA is free radical polymerization with vinyl acetate (VAc) as raw material and azodiisobutyronitrile or benzoyl peroxide as initiator. This method is difficult to get high molecular weight PVA because of chain transfer. In order to prepare high molecular weight PVA, many researchers used suspension polymerization, solution polymerization, emulsion polymerization or radiation polymerization to control chain transfer [5]. However, these methods also have some disadvantages, such as complex process conditions, impurity residues and so on.

The preparation of high molecular weight PVA by emulsifier free emulsion polymerization can not only reduce the chain transfer, but also overcome the residual problem of emulsifiers [6]. In this work, high molecular weight PVA was prepared by emulsifier-free emulsion polymerization, using the redox initiator of potassium persulfate (KPS) / N,N-dimethyl ethanolamine (DMEA). The structure and property of PVA were investigated by using ubbelohde viscometer, fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance hydrogen spectroscopy (^{1}H-NMR), X-ray Diffraction (XRD), differential scanning calorimeter (DSC) and thermo gravimetric analysis (TGA).

2 Experimental

Materials. VAc was obtained from Sinopharm Chemical Reagent Co., Ltd. KPS and DMEA were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All the other reagents were supplied by Sinopharm Chemical Reagent Co., Ltd. All reagents were analytical grade and used as received. The water used in experiment was purified with double distillation.

Preparation of Polyvinyl acetate (PVAc). A 500 mL round-bottomed three-necked flask equipped with a mechanical stirrer and condenser was immersed in a thermostatic water bath. The polymer temperature was controlled to 5 °C. A prescribed amount of double distilled water and VAc were charged to the flask and stirred for 30 minutes under nitrogen, and the dosage of VAc was 35 wt % of water. The solution of KPS and DMEA was dropwise added into the flask. The molar ratio of KPS to DMEA was 1 : 3. The dosage of KPS was 0.5 wt % of VAc. The polymerization was stopped by adding

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hydroquinone solution (0.5 g/L) after reaction 8 hours. The latex was frozen to demulsification. After thawed out, the product (PVAc) was washed and filtered, and the sample was dried to a constant weight under vacuum at 40 °C.

Preparation of PVA. PVAc was dissolved in methanol at 60 °C, the concentration was 10 wt %. After PVAc was completely dissolved, 10 wt % KOH solution in methanol was dropwise added into the mixture while stirring. After KOH solution was added up, the saponification reaction continued for another 3 hours at 60 °C. The product was washed and filtered several times with water and methanol. Then the sample (PVA) was dried to a constant weight under vacuum at 40 °C.

Acetylation of PVA. A mixture of PVA, pyridine and acetic anhydride were stirred in a conical flask at 100 °C for 24 hours. Then the mixture was poured into cold water to precipitate PVAc, which was filtered and purified by repeating the reprecipitation from ethanol and water.

Characterization. The intrinsic viscosity of PVAc was determined with an ubbelohde viscometer. PVAc was dissolved in benzene with the concentration of 0.2 g/dL. The temperature was kept at 30 °C by a thermostatic water bath. The degree of polymerization (DP) of PVAc was calculated according to eq. (1) [7].

$$[\eta] = 8.91 \times 10^{-3}[P_n]^{0.62} \tag{1}$$

Where P_n was the viscosity-average DP of PVAc and $[\eta]$ was the intrinsic viscosity of PVAc. The DP of PVA was determined from PVAc that produced by acetylating PVA. FTIR in the range of 600~4000 cm^{-1} were obtained by a Nicolet 8700 Fourier transform infrared spectrometer (Thermo Electron, American), and under the averaging of 32 scans at a resolution of 4 cm^{-1}. ^{1}H-NMR was performed using an Avance3HD600 instrument (Bruker, Switzerland). XRD curve was acquired on a Powder X-ray diffractometer (Bruker, Germany), the scanning angle was 5-60 degrees. DSC was measured on a Q20 DSC instrument (TA, America) at a heating rate of 10 °C /min, under continuous nitrogen flowing. TGA was conducted with a TG 209 F1 Iris thermogravimetric analyzer (Netzsch-Geraetebau GmbH, Germany) under nitrogen flow, the sample (~3 mg) was heated from room temperature to 650 °C at the rate of 20 °C /min under nitrogen.

3 Results and Discussion

DP analysis. The DP of PVAc and PVA were shown in Table 1. The branching degree (BD) for acetyl group of PVAc was calculated by using eq. (2) [7].

$$BD = (DP_1/DP_2) - 1 \tag{2}$$

Where DP_1 was the P_n of PVAc and DP_2 was the P_n of PVA saponified of PVAc. As shown in Table 1, the DP of PVAc and PVA were 9757 and 7506, respectively, which were much higher than that of PVA commonly used in industrial production. And the BD of the sample was 0.30. These suggested that high molecular PVA could be prepared by emulsifier-free emulsion polymerization, by using the redox initiator of KPS / DMEA.

Table 1. DP of PVAc [a] and PVA

DP of PVAc	DP of PVA	BD
9757	7506	0.30

[a] The polymerization temperature was 5 °C, the mass ratio of KPS to VAc was 0.5 % and the final conversion was 75.2 %.

FTIR analysis. The FTIR spectra of PVA was shown in Figure 1. In the FTIR spectra, the characteristic absorption peak at about 3312 cm^{-1} was caused by the –O-H asymmetric stretching vibration band. In addition, the absorption peaks at about 2943 cm^{-1}, 1660 cm^{-1}, 1426 cm^{-1} and 1088 cm^{-1} were caused by –C-H stretching vibration, C-C framework stretching vibration, -C-H flexural vibration and C-O stretching vibration, respectively [8]. These indicated that the product prepared in this paper was PVA.
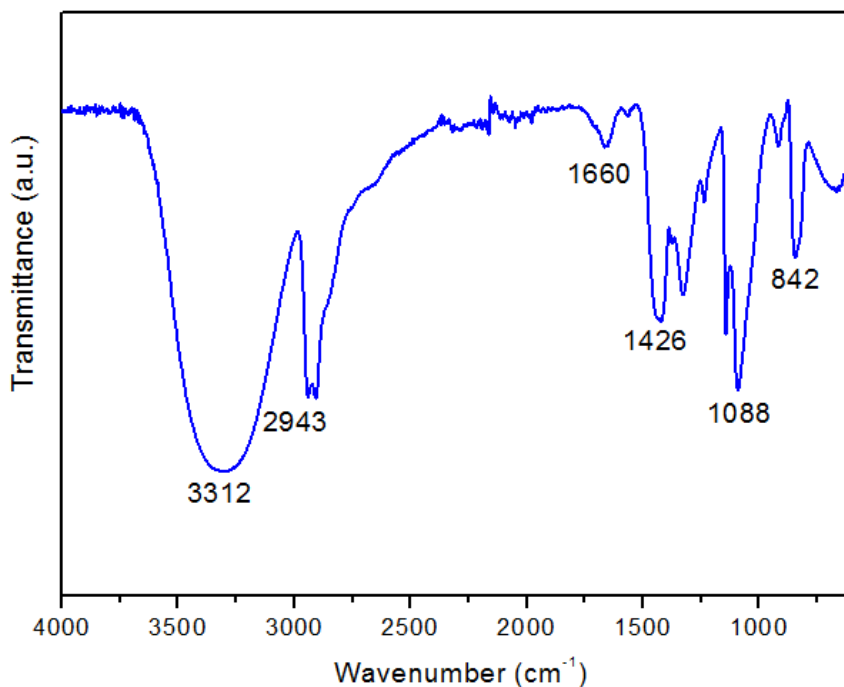
Figure 1. FTIR spectra of PVA

1H-NMR analysis. The 1H-NMR spectra of PVA was shown in Figure 2. As shown in Figure 2, 1.26~1.63 ppm was the proton peaks of CH_2, 3.75~3.93 ppm was the proton peaks of CH. In addition, 4.25 ppm, 4.51 ppm and 4.68 ppm were the proton peaks of three different stereoscopic conformations of OH. The ratios of triad tacticity were estimated using the area of three peaks of OH proton. The syndiotacticity of PVA was 54.2%, it was in agreement with a previous report of a similar syndiotacticity (53 % ~ 54 %) of PVA prepared by the polymerization of vinyl acetate followed by saponification [9].
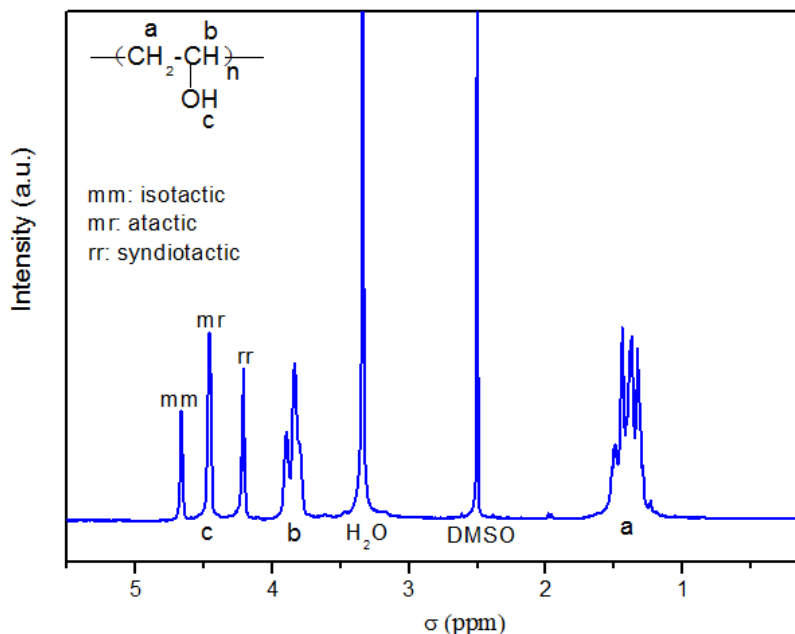

Figure 2. 1H-NMR spectra of PVA

XRD analysis. The XRD curve was used to characterize the crystallinity of PVA. The XRD curve of PVA was shown in Figure 3. There were obvious diffraction peaks at the diffraction angle of 11.4 °, 19.5 ° and 40.4 ° in Figure 3. These peaks were typical diffraction peaks of PVA [6]. The crystallinity of PVA was 35.6% calculated based on the areas of diffraction peaks.
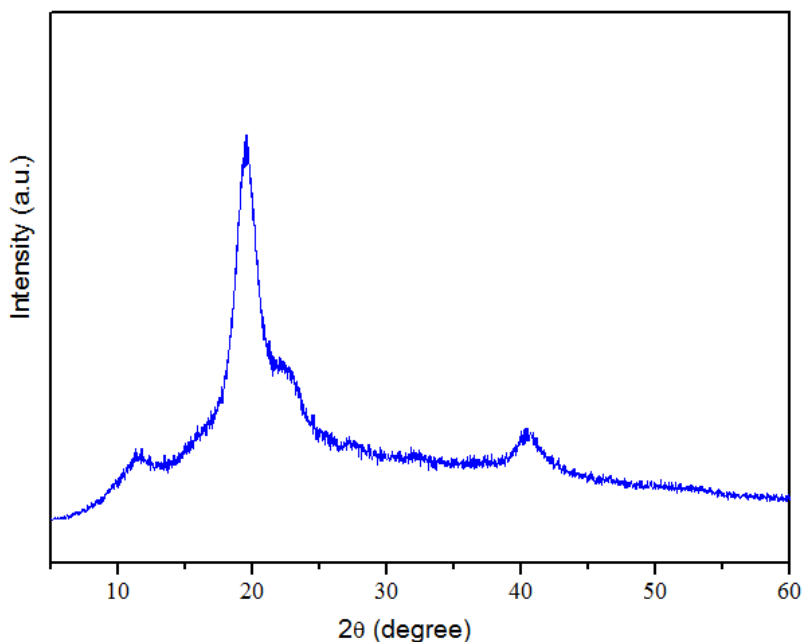
Figure 3. XRD curve of PVA

DSC analysis. The DSC curve of PVA was shown in Figure 4. The melting temperature of PVA was 233.4 °C as shown in Figure 4, and the melting enthalpy of PVA was 73.9 J/g. The degree of crystallinity was calculated based on the following Eq. (3) [8].

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

(3)

Where ΔH_m^0 (161 J/g) was the melting enthalpy for 100 % crystalline PVA. The crystallinity of PVA was 45.9 % calculated according to Eq. (3). The crystallinity was higher than that obtained by XRD, this was because the heating process in DSC was able to further promote crystallization of PVA macromolecules [10].
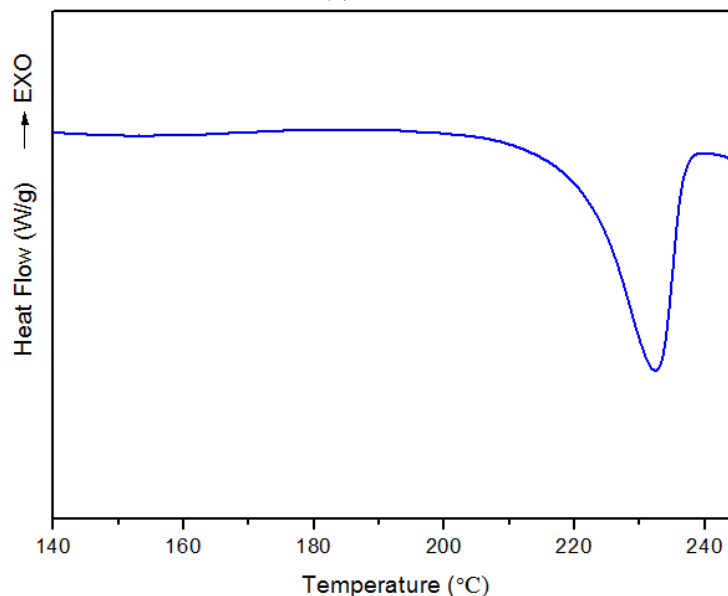

Figure 4. DSC curve of PVA

TGA analysis. The TGA curve of PVA was shown in Figure 5. The thermal decomposition process of PVA was divided into two phases. The first phase was initial decomposition due to the volatilisation and evaporation of the small molecules in PVA, and the second region was primarily the decomposition [6]. The initial decomposition temperature (T_d) of PVA was 243.1 °C and the final residual mass of PVA was 0.8 % at 650 °C.
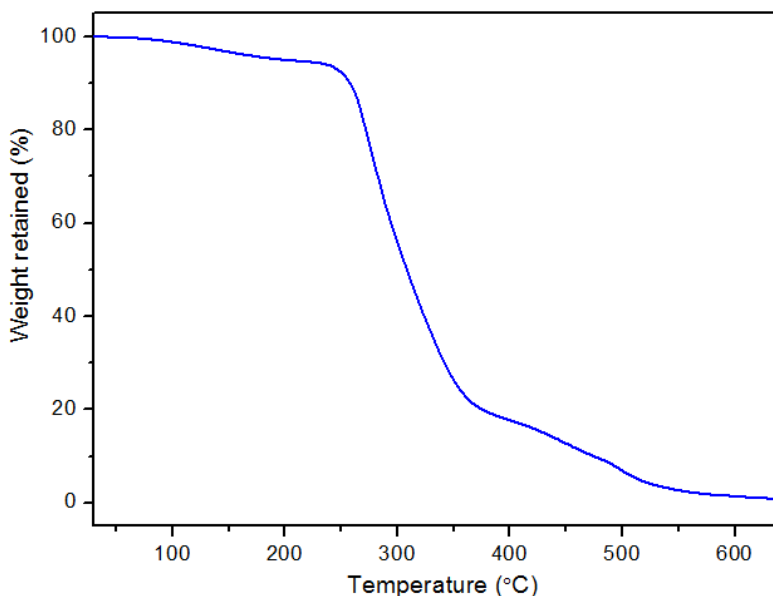
Figure 5. TGA curve of PVA

4 Summary

High molecular weight PVA was prepared by emulsifier-free emulsion polymerization, using the redox initiator of KPS /DMEA. The structure and property of PVA were studied by using FTIR, ^{1}H-NMR, XRD and DSC. The results showed that the DP of PVA was 7506, which was much higher than that of PVA commonly used in industrial production, and the BD was 0.30. The syndiotacticity and crystallinity of PVA was 54.2 % and 35.6 %, respectively. The melting temperature was 233.4 $^\circ$C and the initial decomposition temperature was 243.1 $^\circ$C.

Acknowledgments

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