The Investigation Plasticizing Mechanism on Poly (vinyl alcohol)/Water/Caprolactam System and the Preparation of Raw PVA Fibers by Melt Spinning

Yongjing Xu, Youfu Wang, Liming Zou, Jiongxin Zhao, Wengang Li, Guoping Liu

1State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, 2999 North People Road, Shanghai 201620, People’s Republic of China
2Shanghai Luoyang New Material Technology Co. LTD, Shanghai 200092, People’s Republic of China
*Corresponding author’s e-mail: lmzou@dhu.edu.cn; zjxin@dhu.edu.cn

Abstract. A novel plasticizer system water/caprolactam (W/CPL) was applied in thermal processing of poly (vinyl alcohol) (PVA), water as the primary plasticizer and caprolactam as coplasticizer. The plasticizing mechanism of PVA/W/CPL system was investigated and the raw PVA fibers was prepared by melt spinning. The result showed that the melting temperature of PVA polymers decreased and the window of thermal processing has broaden due to W/CPL plasticizer. In addition, the raw melt-spun PVA fibers with circular structure and uniform structure had great potential application prospects in cement-based reinforcement.

1. Introduction

Poly (vinyl alcohol) (PVA), as an environmentally friendly polymer, with good biodegradability and water-solubility, great mechanical and thermal properties, excellent adhesive performance and gas barrier property, has been extensively used in packaging, adhesives, building materials[1], medicine[2], and so on. Due to the strong intra-/intermolecular hydrogen bond interactions resulting by the abundant hydroxyl groups in PVA chains, the melting temperature is close to its decomposition temperature as well as the high crystallinity of PVA[3], leading to the narrow processing window. Herein, the melting processing of PVA polymers is difficult to achieve and the industrial applications (PVA films, PVA fibers) are limited to complex solution processing, which is time-consuming and unenvironmental. While melt spinning can completely avoid the above problems. Therefore, how to broaden the window of thermal processing and achieve the melt spinning of PVA, will be tremendous advance in the development of PVA fibers in 21 century.

In the last few years, addition of plasticizer has gained more attention to broaden the narrow processing window of PVA because the plasticizer can form new hydrogen-bond interaction with the hydroxyl groups of PVA and then destroy the inter-/intra- hydrogen bonding[4]. Water as “green solvent” is the ideal plasticizer for PVA, but the low boiling point can evaporate rapidly under the melting temperature, affecting the spinnability of PVA fibers. While caprolactam (CPL) as co-plasticizer, not only can form the hydrogen bonding interaction with PVA chains, but also can be kept inside PVA fibers without extraction processing. Therefore, the water/caprolactam (W/CPL) was selected as plasticizing
system for melt-spun PVA fibers, which could increase the boiling point of water, achieving the melt spinning of PVA.

The aim of this paper is to study the plasticizing mechanism of W/CPL on PVA polymers and prepare the raw PVA fibers by melt spinning. All samples were characterized by Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), thermal analysis (TG-DTG), X-ray diffraction (XRD), and mechanical properties. It is worth mentioning that, the large diameter PVA fibers with melt spinning has broken the barrier that wet spinning can only produce small diameter PVA fibers, and that has potential application prospect in cement-based reinforcement materials.

2. Materials and methods

2.1. Materials
Poly(vinyl alcohol), with degree of polymerization 1700 and degree of alcoholysis 99%, was provided by Anhui Wanwei Factory, China. Caprolactam (TW-100) was purchased from Sinopharm Group Co. LTD. Before use, all materials were dried in a vacuum oven at 65℃ for 48h to remove moisture.

2.2. Preparation of PVA/W/CPL Composites
PVA polymers were added in the W/CPL (90/10, wt%) solution and transferred in the sealed container. And then, the composites were placed in the oven at 60℃ with fully swelling. Finally, the modified PVA polymers were prepared by the twin-screw extruder.

2.3. Preparation of Raw PVA fibers
PVA raw fibers were prepared by melt spinning machine (ABE Ф25, Japan), and the specific spinning parameters were as follows: screw diameter 25mm, number of spinneret holes 36, spinning temperature 160℃, and spinning speed 15m/min.

3. Results and discussion

3.1. FTIR spectra of PVA/W/CPL Composites
The FTIR spectra of pure PVA and PVA/W/CPL was illustrated in Figure 1, and the bending vibration of -OH and C-O were presented in Figure 2B and 2C. For pure PVA, the 3300 cm\(^{-1}\) and 1659 cm\(^{-1}\) peaks are assigned to the stretching and bending vibration of -OH, respectively, the 1420cm\(^{-1}\) and 1325 cm\(^{-1}\) peaks are corresponding to the bending and rocking vibration of -CH\(_2\), respectively, the 1142 cm\(^{-1}\) peak is assigned to the bending vibration of C=O, which are sensitive to the crystalline regions. For PVA/W/CPL, the 3374 cm\(^{-1}\) peak is assigned to the stretching vibration of -OH, the 1628 cm\(^{-1}\) peak is corresponding to the overlapping between bending vibration of -OH and C=O.

From Figure 2B, the peak of -OH of PVA/W/CPL moved to high wavenumber by contrast with pure PVA, indicating the weakening of inter-/intra- hydrogen bonding for PVA because of the W/CPL plasticizer. From Figure 2C, the intensity of C=O peak in 1142 cm\(^{-1}\) has weakened comparing with pure PVA causing by the addition of W/CPL plasticizer. This could be explained that the W/CPL could enter the crystal and amorphous regions of PVA, destroying the crystal structure and weakening hydrogen bonding of PVA. What is more, the intensity of C=O has strengthened comparing with pure PVA ascribing to volume effect of water and CPL and p-π conjugation effect caused by amide groups and C=O in CPL.
3.2. Thermal properties of PVA/W/CPL Composites

The DSC analysis and TGA analysis were demonstrated in Figure 2A and 2B. From the Figure 2A, it showed that the melt temperature of pure PVA was 227.2°C, and the melting interval was 13.8°C, as for PVA/W/CPL, there were two melting peaks, including the water (122.0°C) and modified PVA (218°C), and the melting interval was 41.0°C. In contrast with pure PVA, it can be seen that the melting temperature was decreased and the melting interval became wider for PVA/W/CPL. From the Figure 2B, the thermal decomposition of PVA/W/CPL (245.2°C) was slightly decreased with respect to pure PVA(247.2°C). In conclusion, the results of DSC and TGA from study illustrated that the window of thermal processing has been broaden for modified PVA by W/CPL plasticizer, which will be beneficial for melt spinning of PVA.

3.3. X-ray Diffractometry (XRD) of PVA/W/CPL Composites

The XRD of pure PVA and PVA/W/CPL was presented in Figure 3 and the parameters calculated by Scherrer Formulas (such as d-spacing, crystalline grain size and crystallinity) were displayed in the Table 1. From Figure 3, the pure PVA presented diffraction peaks at around 2θ 11.5°, 19.5°, 22.7° and 40.5°, ascribable to the (100), (101), (200) crystal planes and the overlapping with (1-11), (111), (2-10) and (210). While PVA/W/CPL showed obviously diffraction peaks at around 19.5°, 22.7° and 40.5°, and the intensity of peaks was weaken comparing with pure PVA, indicating that the crystal property of PVA was decreased due to the W/CPL plasticizer.
From the Table 1, it showed that the \( d \)-spacing and crystalline grain size of PVA/W/CPL were increased sharply than pure PVA, and the crystallinity of PVA/W/CPL was decreased in comparison with pure PVA. This can be explained that water as small molecule plasticizer and CPL with large volume of space could enter crystalline and amorphous regions, respectively, which could destroy the inter-/intra- hydrogen bonding of PVA by forming new hydrogen bond with PVA. As a result, the overall structure was damaged to a greater extent by water and CPL, leading to the increase of the crystallite size and the decrease of crystallinity.

| Samples       | Crystal plane | \( d \)-spacing (Å) | Crystalline grain size (Å) | Crystallinity (%) |
|---------------|---------------|----------------------|----------------------------|-------------------|
| pure PVA      | 101           | 4.55                 | 4.53                       | 64.91             |
|               | 200           | 4.00                 | 3.87                       |                   |
| PVA/W/CPL     | 101           | 8.66                 | 9.02                       | 33.93             |
|               | 200           | 7.12                 | 7.30                       |                   |

3.4. Light Microscope of raw PVA fibers

The cross section pictures of raw PVA fibers were showed in the Figure 4. As can be seen in the Figure 4, the raw PVA fibers had circular cross sections, and the structure was uniform. Comparing to the PVA fibers with waisted cross sections and small diameter produced by wet spinning, the circular structure and large diameter (melt-spinning) had great potential application in cement-based reinforcement.

4. Conclusion

W/CPL plasticizing system has been applied in achieving the PVA fibers by melt spinning. The results showed that the melt temperature of PVA decreased and the melting interval increased, causing that the
window of thermal processing has broaden for PVA. And the raw melt-spun PVA fibers with circular structure and uniform structure had great potential application prospects in cement-based reinforcement.

Acknowledgements
The authors would like to acknowledge the research center for analysis & measurement of Donghua University. This work is supported by National Key R&D Program of China (2016YFB0303200).

References
[1] Covelo, A., Gómez, K. K., Corona-Lira, P. (2018) Electrochemical characterization of PVA/SA nanofibers obtained by electrospinning processing. Surf Interface Anal, 50 (11):1012-1017.
[2] Ameer, Z. J. A., Al-Mutairi, N. H. (2018) Miscibility Improvement of LDPE/PVA Blends with Maleic Acid Additions. IOP Conference Series Materials Science and Engineering, 433, 012074.
[3] Priya, B., Gupta, V. K., Pathania, D. (2014) Synthesis, characterization and antibacterial activity of biodegradable starch/PVA composite films reinforced with cellulosic fibre. Carbohyd Polym, 109 (6): 171-179.
[4] Mohamed, S. A., Al-Ghamdi, A. A., Sharma, G. D. (2014) Effect of ethylene carbonate as a plasticizer on CuI/PVA nanocomposite: Structure, optical and electrical properties. J Adv Res, 5 (1):79-86.