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Research article

Thermoplastic modification of polyvinyl alcohol for preparing water-splittable sea-island fiber

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Abstract. Polyvinyl alcohol (PVA) is a type of water-soluble polymer that is a candidate for ‘sea’ polymer to prepare sea-island fibers in industry. In this study, two types of polyols (sorbitol ether and neopentyl glycol) were mixed in different proportions and used to prepare thermoplastic PVA (TPVA) as a compound plasticizer. When the plasticizer was introduced, a blue shift occurred on the characteristic band of hydroxyl in the Fourier transform infrared spectroscopy (FTIR) pattern. The melting temperature (T_m) of the corresponding TPVA decreased, and their initial decomposition temperature (T_d) increased to some degree. The addition of compound plasticizer made PVA show an improved T_d up to 273.1 °C. Moreover, it led to an increment of the melting flow index and improved the resistance to oxidation at a temperature higher than 200 °C. The increased spinnability enabled TPVA in PVA-PLA sea-island fiber making. PLA superfine fibers were obtained after splitting in water at 95 °C for just 3 min.

Keywords: *fiber, textile processing, fiber spinning, melt-blowing, polyvinyl alcohol*

1. Introduction

Polyvinyl alcohol (PVA) is a type of water-soluble and biodegradable polymer that is commonly used in fields such as textile, medicine, and architecture, to name a few [1–3]. PVA fibers are usually prepared through a wet-spinning technique, which generates a large amount of industrial wastewater [4, 5]. As a comparison, melting-spinning shows a higher spinning efficiency, and organic solvents are avoided during spinning. However, a large quantity of hydroxyls in PVA molecules forms strong intra/intermolecular hydrogen bonding. This makes PVA lose its thermoplastic processing window.

On the other side, thermoplastic PVA (TPVA) was desirable to be used as a ‘sea’ polymer to prepare sea-island fibers in industry. The involved sea-island fibers would be split into ultra-fine fibers through an energy-saving and efficient water-reduction process [6, 7]. Nevertheless, there are rare reports on research or industrial practice to our best knowledge. Ultra-fine fiber is generally defined to have a diameter of less than 0.55 dtex. Owing to small fineness, the rigidity of fiber decreases exponentially, and the specific surface area of fiber increases [8, 9]. Corresponding textile products normally show a novel softness and excellent absorption or filtration properties [10–12].

The thermoplastic modification of PVA could be realized via a chemical copolymerization or physical blending. The former method introduces a second monomer to break the macromolecular tacticity of PVA. It will reduce the crystalline degree as well as the melting temperature of PVA [13, 14]. The latter strategy is more frequently reported owing to a facile operation and higher production. The addition of plasticizers with polar functional groups, such as

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polyols [15], is one of the most effective methods to improve the thermoplastic processing property of PVA. Generally, various plasticizers, such as glycerol or water, are blended with commercial PVA pellets in a screw extruder. This will reduce inter-molecular interaction between PVA molecules. The melting temperature of PVA usually decreases, generating a proper thermoplastic processing window [16]. Xu *et al.* [17] prepared a pseudo-ionic liquid as a plasticizer to modify the thermoplastic behavior of PVA. The cations, anions, and hydrogen bond acceptors in the plasticization system formed stronger hydrogen bonds with the hydroxyl groups of PVA. Melt-spun PVA fibers with smooth surfaces and uniform cross-sections were prepared. However, the content of plasticizer is usually higher than 30 wt%, which will significantly decrease the crystalline ability of PVA fiber. In addition, owing to the evaporation behavior, the plasticizer is easy to migrate during melt-spinning, affecting the rheological property of TPVA [18]. How to reduce the usage doge of plasticizers and meanwhile maintain their spinnability are urgent problems for TPVA.

Poly (lactic acid) (PLA), with good biodegradability, has become one of the most popular materials in some fields, such as tissue engineering, scaffolding, and packing [19–21]. PLA fiber and corresponding textiles raise great interest as a biodegradable candidate for realizing carbon neutralization. In this study, two types of polyols were mixed in different proportions to make a compound plasticizer that was used to prepare TPVA. The influence of plasticization on the thermal properties of PVA and hydrogen bonding interaction was studied. In addition, PVA-PLA sea-island fibers were prepared, and corresponding PLA superfine fibers were obtained after water splitting. It is of significant importance to promote the efficient and green splitting of sea-island fibers during the making superfine fibers.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA, trademark 098-05) pellets were supplied by Anhui vinylon factory of Sinopec Co. Ltd. (Wuhu, China). Sorbitol ether (SE) and neopentyl glycol (NPG) were purchased from Aladdin Agent Co. (Shanghai, China). Polylactic acid (PLA) pellets were brought from Fengyuan Co. Ltd. (Bengbu, China).

Table 1. The components' ratio setting of each sample granule.

Sample ID	PVA [wt%]	SE [wt%]	NPG [wt%]
1:1	94	3	3
2:1	94	4	2
4:1	94	4.8	1.2
1:2	94	2	4
A	94	6	0
B	94	0	6

2.2. Thermoplastic modification of PVA

The raw PVA was plasticized using SE and NPG. The content of the plasticizer was 6 wt%, respectively. SE/NPG (A/B) proportion was 4:1, 2:1, 1:1 and 1:2, respectively. The details are included in Table 1. All components were homogeneously blended and then matured for 2 h at 80 °C. A twin-screw (RXT2, Ruiya, Nanjing, China) with a diameter of 25.4 mm, *L*/*D* ratio of 40, and a speed of 250 rpm was employed. The processing temperature was controlled at different zones of the extruder to obtain an ascending temperature profile from 110 to 190 °C. Those prepared granule were named thermoplastic PVA (TPVA). TPVA obtained by adding a single component of SE (A) or NPG (B) were set as blank samples.

2.3. Preparation of PVA and sea-island PVA/PLA pre-oriented yarn

The prepared TPVA granule and PLA pellets were dried at 90 °C in a vacuum oven for 24 h before melt-spinning, respectively. The spinning of TPVA was conducted in a single-screw spinner. After undergoing temperature ascending in the extruder in different zones (210, 215, 220, 225, 230 °C), the melt was extruded from the spinneret with 48 filaments. The spinning speed was set as 1000 m/min. The sea-island spinning was conducted on a conjugated bicomponent spinning machine (Fangchen, Zhibo, China). TPVA was used as a 'sea' ingredient in extruder A (210, 215, 220, 225, 230 °C). PLA ('island' polymer) was sequenced out by extruder B (205, 210, 220, 230, 235 °C). The temperature of the die was set as 235 °C. The sea/island component mass ratio was set as 3:7. The rolling speed was set as 1000, 1200, 1500, and 2000 m/min, respectively.

2.4. Characterization

Molecular dynamics simulation was carried out using the Gromacs-4.6.7 software package. The details were described as follows. Two cubic boxes were built. One contained 100 chains of pure PVA. The other one was put in 100 PVA chains and 300 sorbitol ethers to get TPVA. The PVA was simulated at a temperature of 698 K and a pressure of 100 bar for 5 ns to enable the polymer chain to relax sufficiently. The equilibrium structure was then simulated at 298 K, 1 bar for 10 ns. All the all-atom MD simulations were based on a general AMBER force field with restrained electrostatic potential (RESP) charges [22]. The system was a relaxed liquid configuration at 298 K. We used the relaxed system as a starting configuration. As it is prior to system relaxation MD, energy minimization was carried out with a composite protocol of steepest descent using termination gradients of 100 J/(mol·nm). The particle Mesh-Ewald method [23] was used to compute long-range electrostatics within a relative tolerance of $1\cdot10^{-6}$. A cutoff distance of 1nm was applied to real-space Ewald interactions. The same value was used for van der Waals interactions. The Library of Integrated Network-Based Cellular Signatures (LINCS) algorithm [24] was applied to constrain bond lengths of hydrogen atoms. A leap-frog algorithm was used with a time step of 2 fs.

The prepared TPVA granules have undergone a series of characterizations. Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded using a Nicolet iS50 spectrometer (Thermo Fisher Scientific, USA) with 30 scans in the 4000 to 400 cm^{-1} range at room temperature. X-ray diffraction (XRD) analysis was conducted using a D8 Discover model X-ray diffractometer (Bruker, Germany) in the range of $2\theta = 5–40°$ at 40 kV and 30 mA of Cu K_α radiation. Differential scanning calorimetry (DSC) patterns were recorded on an equipment Model 200F3 (Netzsch, Germany). A 10 mg specimen was heated from 30 to 250 °C at a ramp rate of 10 °C/min. Thermogravimetric analysis (TGA) is conducted on the STA449F3 thermal analyzer (Netzsch, Germany). The sample was heated at 10 °C/min from 30 to 800 °C under N_2 atmosphere. The thermal oxidation property of prepared TPVA was evaluated by holding TPVA at 230 or 250 °C for 10 min in a TGA test in an air atmosphere (80% N_2 and 20% O_2). The rheological studies were carried out using an MCR302 (Anton Paar, Graz, Austria) rheometer having a disk geometry of 25 mm diameter. The rheometer instrument measure shear rate was up to 100 s^{-1}. The melt flow index (MFI) was measured using a MFI-1221 instrument (Jinjian instrument, Chengde, China) under 240 °C at a constant load of 2.16 kg.

The morphology of the prepared sea-island fibers was observed by using a scanning electron microscope model S4800N (Hitachi, Japan) after spraying with a layer of gold. The tensile properties of the prepared fibers were investigated using a universal testing machine model 3369 (Instron, USA) according to the test standard of GB/T 14337-2008. The grip distance of the head was set as 20 mm, and the speed was 40 mm/min. Each fiber was repeated for 15 specimens.

3. Results and discussion

3.1. Plasticization mechanism

The intermolecular and intramolecular H-bonding determine the thermal properties of PVA. It was studied by FTIR analysis, and the corresponding spectra are shown in Figure 1a. The peak located at 1250 cm^{-1} is ascribed to the C–C stretching. The band at 1650 cm^{-1} contributed to OH bending [25]. Raw PVA showed a characteristic band at 3326 cm^{-1} that contributed to OH stretching [26]. As a comparison, this band shifted to a lower wavenumber upon adding polyols to varying degrees. When a compound plasticizer composed of polyol A and polyol B was used, a larger blue shifting occurred. Moreover, the position of this band varied with the blending ratio of polyol A/B. When the weight ratio of polyol A and B reached 2:1, the position of the characteristic peak was around 3288 cm^{-1}. Such prominent blue shifts strongly indicated polyol addition decreased intermolecular H-bonding of PVA by breaking macromolecular interaction [27]. Polyol B has a smaller dimension and is more easily to penetrate PVA, generating a greater breaking effect to intra-molecular H-bonding of PVA, as illustrated in Figure 1b.

To further study the effect of plasticization on the interaction between PVA molecules, a molecular dynamic simulation was conducted on raw PVA and its modified counterpart. The corresponding conformation is shown in Figures 1c and 1d. Compared to the pure PVA system, the calculated root means square deviation (RMSD) of TPVA modified by SE was 24% higher (Figure 2a), the spin-back radius of the polymer increased from 5.5 to 6.1 nm (Figure 2b), and the number of hydrogen bonds between PVA decreased from about 7000 to 2000 (Figure 2c). The free volume fraction in the plasticizer system decreased by 0.9% relative to the pure

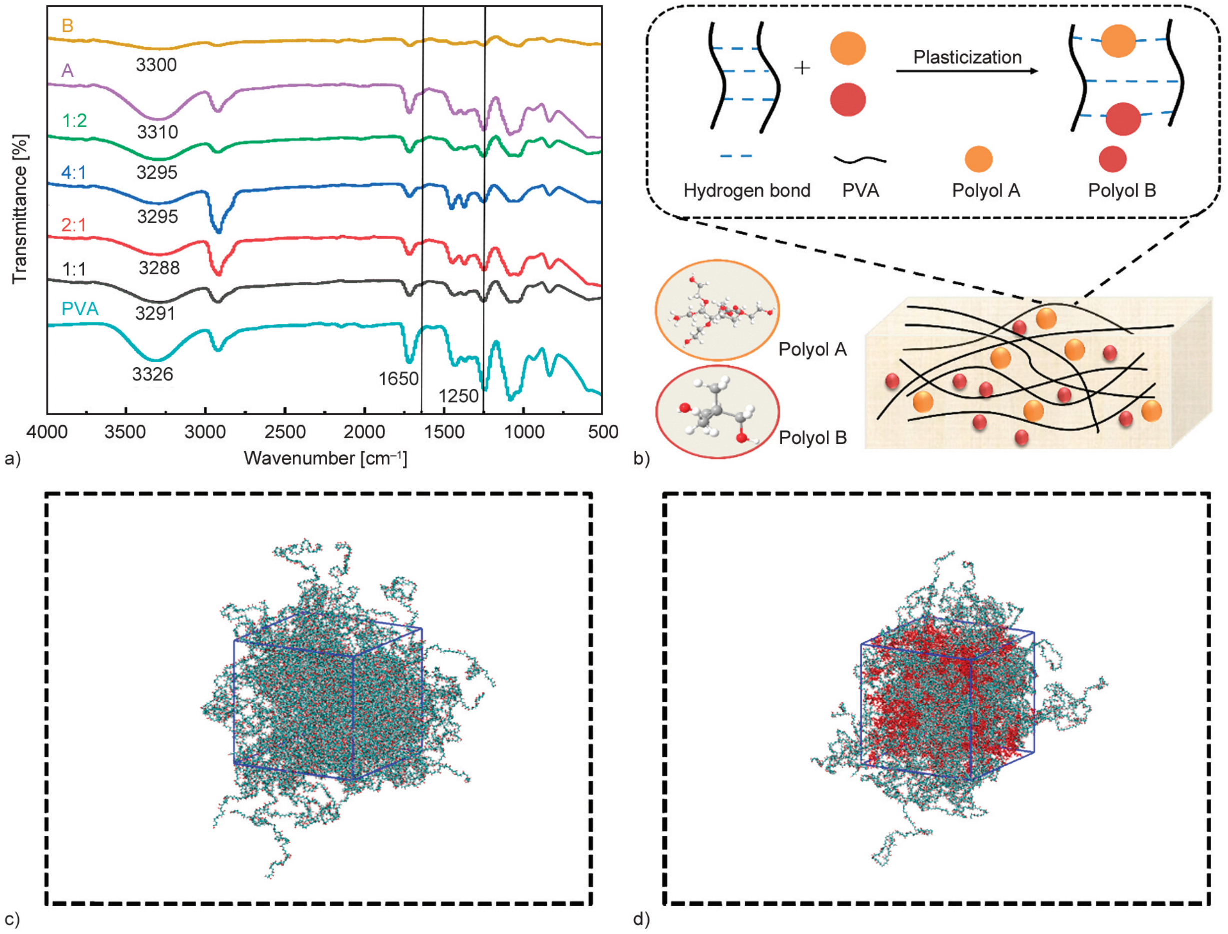

Figure 1. a) FTIR of PVA and TPVA modified with different ratios of polyols; b) mechanistic diagram of polyol-modified PVA; simulation conformation of PVA before (c) and after (d) polyol A addition.

Table 2. Free volume and internal potential energy of different polymer systems.

Samples		PVA	TPVA
Free volume fraction	[%]	11.7	10.8
Internal potential energy	[kJ/mol]	–1174.53	–1126.56

PVA polymer system, and the required internal potential energy decreased by 47.97 kJ/mol (Table 2). The simulation results effectively indicated that the plasticizer diffusion in PVA and the introduction of small molecules of plasticizer into PVA formed PVA-plasticizer hydrogen bonds so that intermolecular chain forces of PVA were disrupted to a large extent.

3.2. Thermal properties of TPVA

The effect of polyol A/B blending ratio on thermal properties was studied by DSC and TGA, as shown in Figures 3a–3c, respectively. The initial decomposition temperature (T_d) and melting temperature (T_m) are listed in Table 3. The raw PVA had a T_m of 199.8 °C. With the addition of plasticizers, the T_m of all obtained TPVA decreased. The reason was that the plasticizer penetrated PVA chains, which weakened the H-bonding of PVA. Compared to the role of a single polyol plasticizer, a synergistic plasticizing effect was observed between the compound polyol, further lowering the T_m of TPVA. When the ratio of SE and NPG is 1:1, the T_m of TPVA decreases to 185.6 °C. Polyol A has more OH bands than polyol B. It could form more H-bonding with PVA. When polyol A and B were blended as a compound plasticizer, modified TPVA showed multiple melting phenomena. It indicated there were different crystalline states in modified TPVA.

In general, the PVA macromolecules began to cleave when the temperature was higher than 200 °C [28]. The effect of the ratio addition of compound plasticizers on the thermal stability of PVA was also investigated. The initial decomposition temperature (T_d) of unmodified PVA was 214.7 °C. With the addition of plasticizer, the T_d of modified TPVA increased to 262.9 °C at least. This was because the hydroxyl of

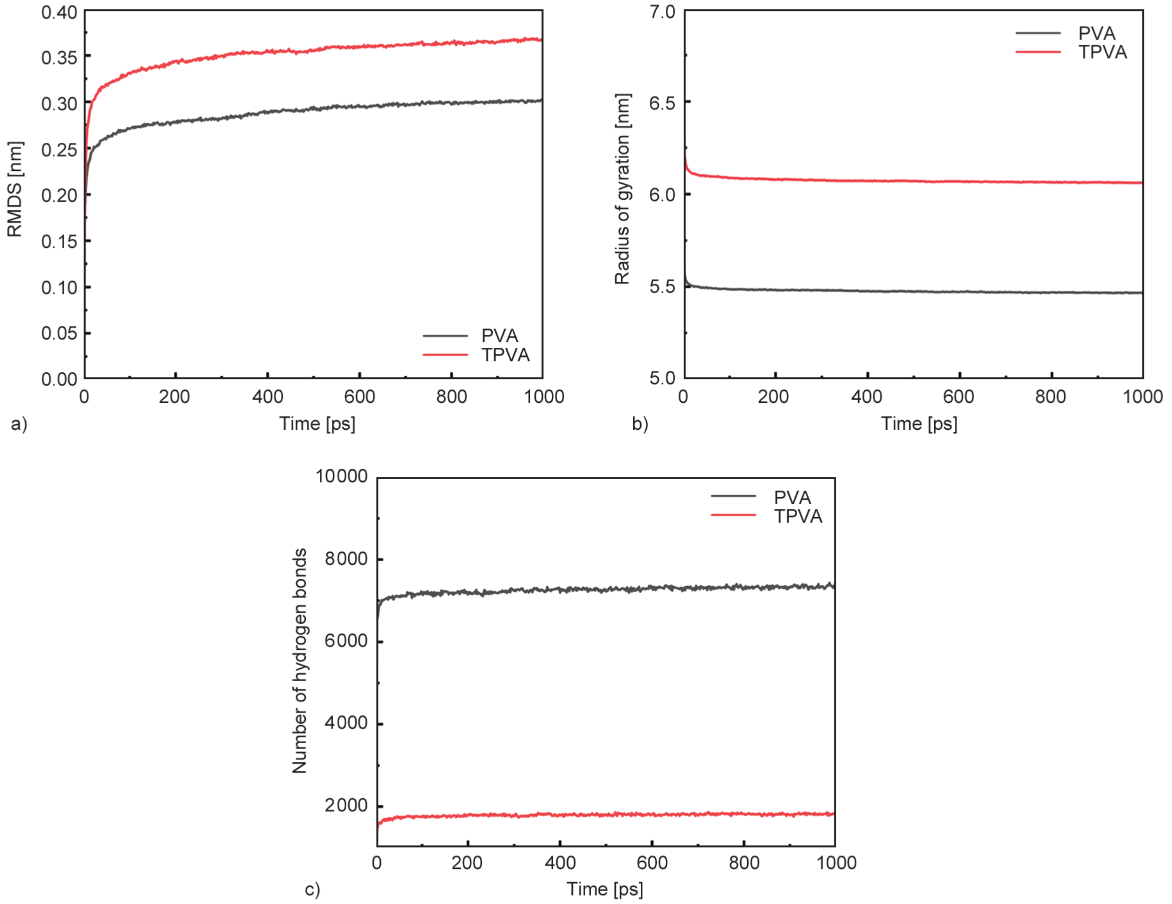

Figure 2. a) RMSD of different polymer systems; b) radius of gyration of different polymer systems; c) variation of the number of hydrogen bonds with time for different polymer systems.

polyol formed a new and stronger H-bonding with PVA [29]. The thermal processing window ($\Delta T = T_d - T_m$) was elevated to 81.5 °C when the SE/NPG mixing ratio reached 2:1, as shown in Table 3. This indicates that polyol blending is beneficial in improving the thermal stability of PVA. Even at temperatures higher than 260 °C, the weight loss of prepared TPVA did not exceed 5%. Moreover, the maximum decomposition rate (dW/dT) greatly decreased, and temperature at this rate increased by adding polyols.

PVA was rich in OH groups that were prone to be oxidized through a hydration reaction. This affected the processing, like rheological properties [30]. TGA test was conducted at a constant temperature under an air atmosphere to study the thermal oxidation behavior of TPVA. The one modified by SE/NPG = 2:1 was taken as a presentative example. The corresponding patterns are shown in Figure 3d. When PVA was kept at 230 °C for 10 min, a large weight loss of 5% was observed. At the same temperature, the thermal weight loss rate of TPVA was reduced by approximately 1%. This is because the addition of polyols depresses the oxidation of PVA. When the temperature was raised to 250 °C, 3% weight loss occurred, indicating that the prepared TPVA should be processed under 250 °C.

3.3. Rheological properties of TPVA

The rheological properties of TPVA were studied. The modified PVA showed a typical shear thinning behavior, as shown in Figure 4. At a constant temperature, the shear viscosity decreased with the increase of shear rate. This was because the secondary bonds between the molecules were broken by a larger shear force. Levering the temperature from 210 to 240 °C, the viscosity of the corresponding TPVA decreased due to the reduction of inter-molecular bonding. As the temperature increased, fluctuation appeared in the rheological curves of TPVA modified with polyol B. This was because polyol B had a boiling temperature lower than 230 °C. When the temperature was higher than 220 °C, the polyol began to evaporate and caused the change of rheological behavior of TPVA. Moreover, it was observed that the rheological properties of TPVA with polyol A/B = 2:1 were more

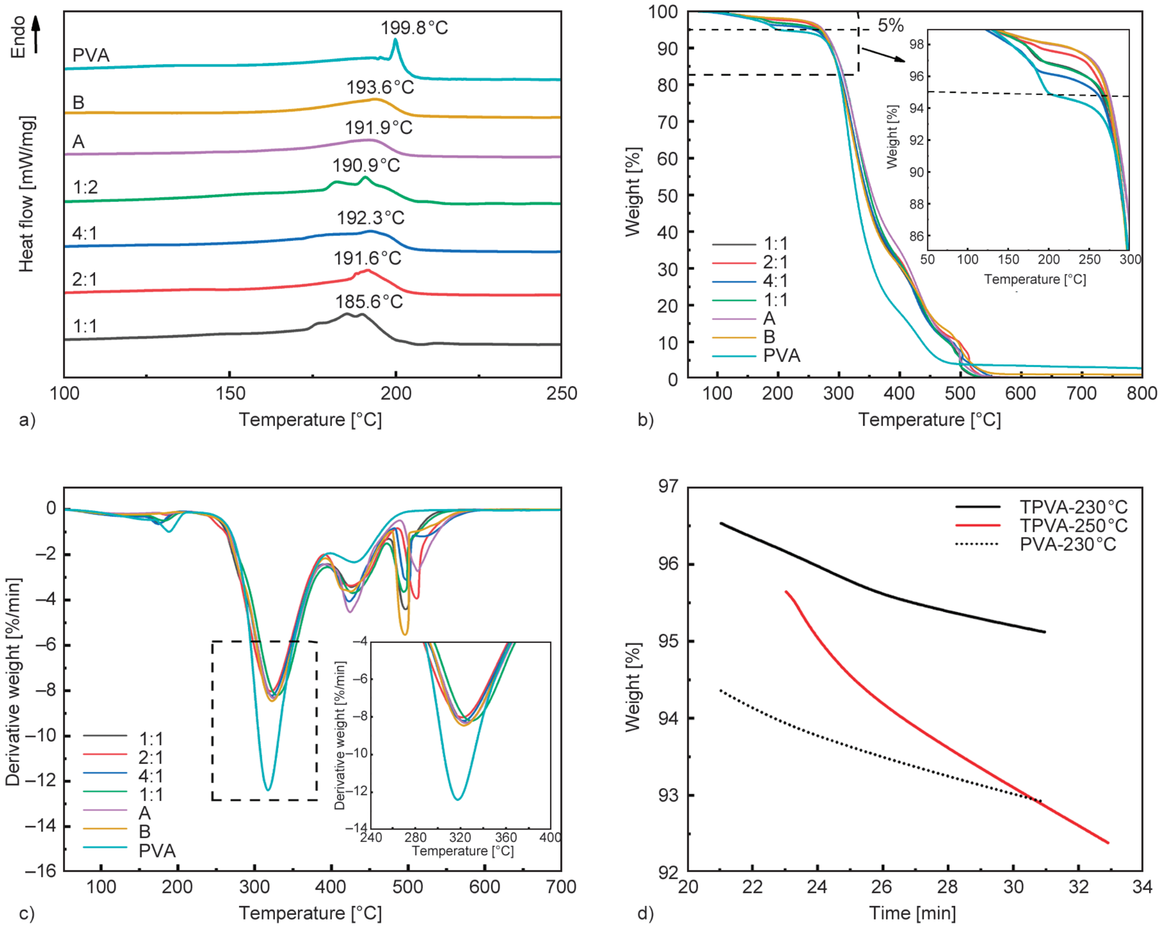

Figure 3. Thermal properties of PVA and TPVA modified with different ratios of polyols: a) DSC patterns; b) TGA curves and c) DTG patterns under N_2 atmosphere; d) thermal oxidation behavior of TPVA modified by 2:1 of polyol A/B under air atmosphere.

Table 3. Thermal properties of PVA and TPVA modified with different ratios of polyols.

Sample		PVA	1:1	2:1	4:1	1:2	A	B
T_m	[°C]	199.8	185.6	191.6	192.3	190.9	191.9	193.6
T_d	[°C]	214.7	266.5	273.1	262.9	269.1	271.1	272.7
ΔT	[°C]	14.9	80.9	81.5	70.6	78.2	79.2	79.1
$T_{d\,max}$	[°C]	317.9	324.9	321.5	322.5	329.5	324.6	322.9
dW/dT	[%/min]	12.4	8.31	8.03	8.22	8.20	8.33	8.46

sensitive to the temperature. This indicated the corresponding TPVA had a high flow activation energy.

3.4. Spinnability of TPVA

The MFI and spinnability of TPVA pellets, as described above, were studied. The corresponding results are shown in Table 4. Raw PVA and the one modified with polyol A did not show a value of MFI under the testing. This indicated the H-bonding in PVA was still maintained, and the prepared TPVA showed no melt-flowing behavior. It kept consistent with the investigation of FTIR spectra. When polyol B was introduced, the MFI of TPVA increased, and they were possibly processed in the melting state. The possible reason was listed previously. Polyol B was prone to penetrate the PVA amorphous region due to its small molecular size. However, it contained less –OH band than polyol A. Therefore, the interaction effect between polyol B and PVA was lower. The corresponding TPVA showed higher MFI. When a blended polyol was used, the TPVA showed a higher value of MFI. Especially when the polyol A/B ratio was higher than 1:2, the spinnability of prepared TPVA increases. A synergistic effect of plasticization was observed between polyols A and B. The tensile properties of TPVA fibers are also listed

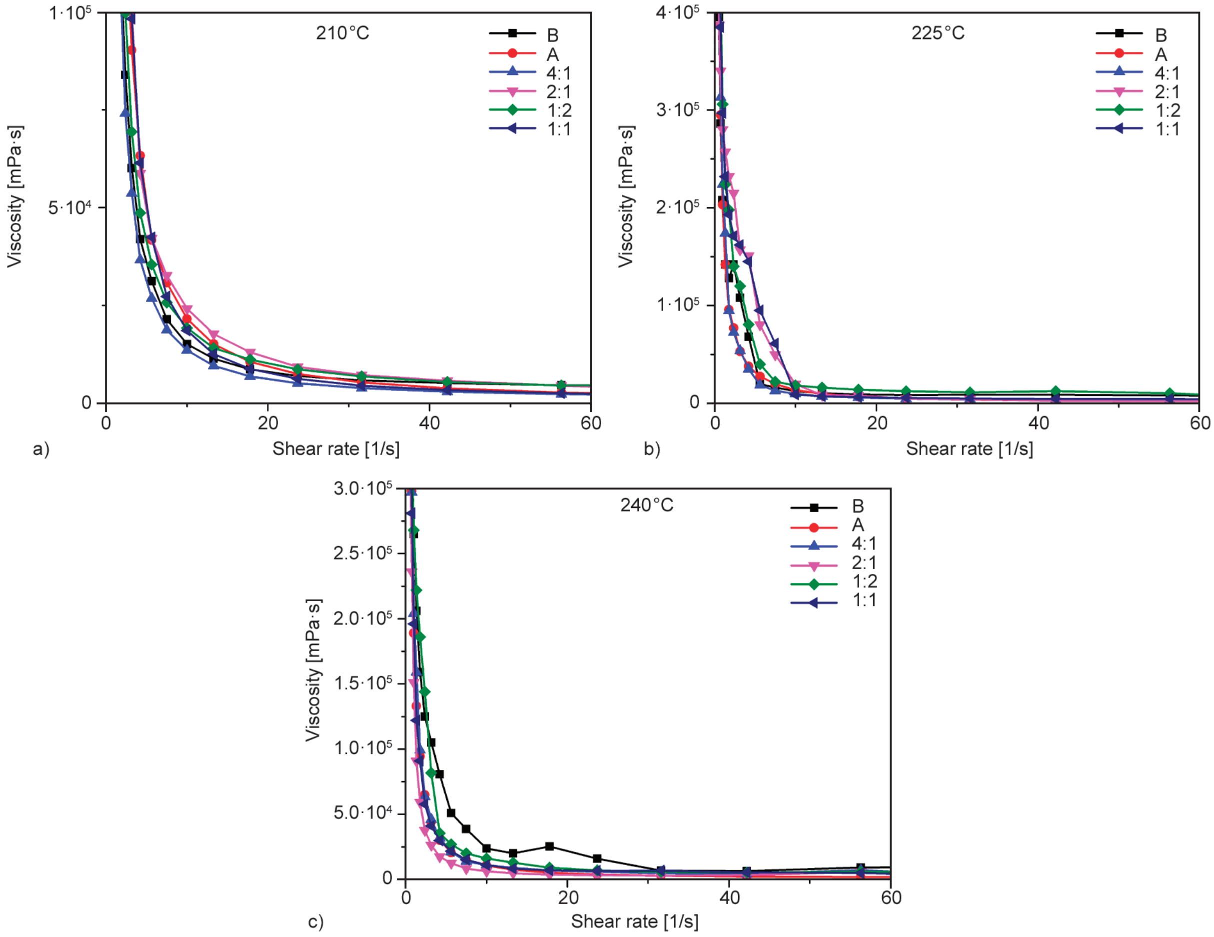

Figure 4. Shear viscosity change with shear rate at different temperatures a) 215 °C; b) 225 °C; c) 240 °C.

Table 4. Spinnability of TPVA pellets and tensile properties of prepared TPVA POY fibers.

Sample	Spinnability	MFI [g/10 min] (230 °C)	Elongation at break [%]	Breaking strength [cN/dtex]
PVA	×	/	/	/
1:1	√	30±3	65.3±6.1	0.73±0.07
2:1	√	35±2	76.7±6.6	0.85±0.08
4:1	√	32±2	72.1±5.6	0.81±0.09
1:2	×	29±2	/	/
A	×	20±3	/	/
B	×	27±3	/	/

in Table 4. When spinning at 230 °C with the polyol A and B ratio of 2:1, the melt flow index reached 35 g/10 min. The breaking strength and elongation at the break of corresponding TPVA fibers were also higher than those of PVA fibers modified by 1:1 or 4:1 polyol A/B.

3.5. TPVA-PLA sea-island fiber

The preparation of TPVA-PLA sea-island fibers is shown in Figure 5a. TPVA obtained from the polyol A and B blending ratio of 2:1 was selected as the 'sea' phase due to the large thermal processing window and good mechanical properties of corresponding PVA fibers. The effect of spinning speed on the tensile properties of sea-island pre-oriented yarns (POY) was studied, and the corresponding results are shown in Figure 5b–5d. As the spinning speed increased, linear density and diameter naturally decreased. When the spinning speed increased from 1000 to 1500 m/min, there was no significant change on the tensile strength of POY fibers (around 0.94 cN/dtex). This was possible because the crystallization of fibers was not affected at such a low spinning speed [31]. However, when the speed reached 2000 m/min, the mechanical strength reduced to 0.82 cN/dtex owing to the breaking of some filament in POY bundles during stretching. Breaking elongation of POY sustained at a high value of over 100% due to a lack of thermo-fixing treatment. The value decreased with the increase in spinning speed. Usually, a higher orientation was obtained once undergoing a higher spinning speed, which reduced the elongation at break.

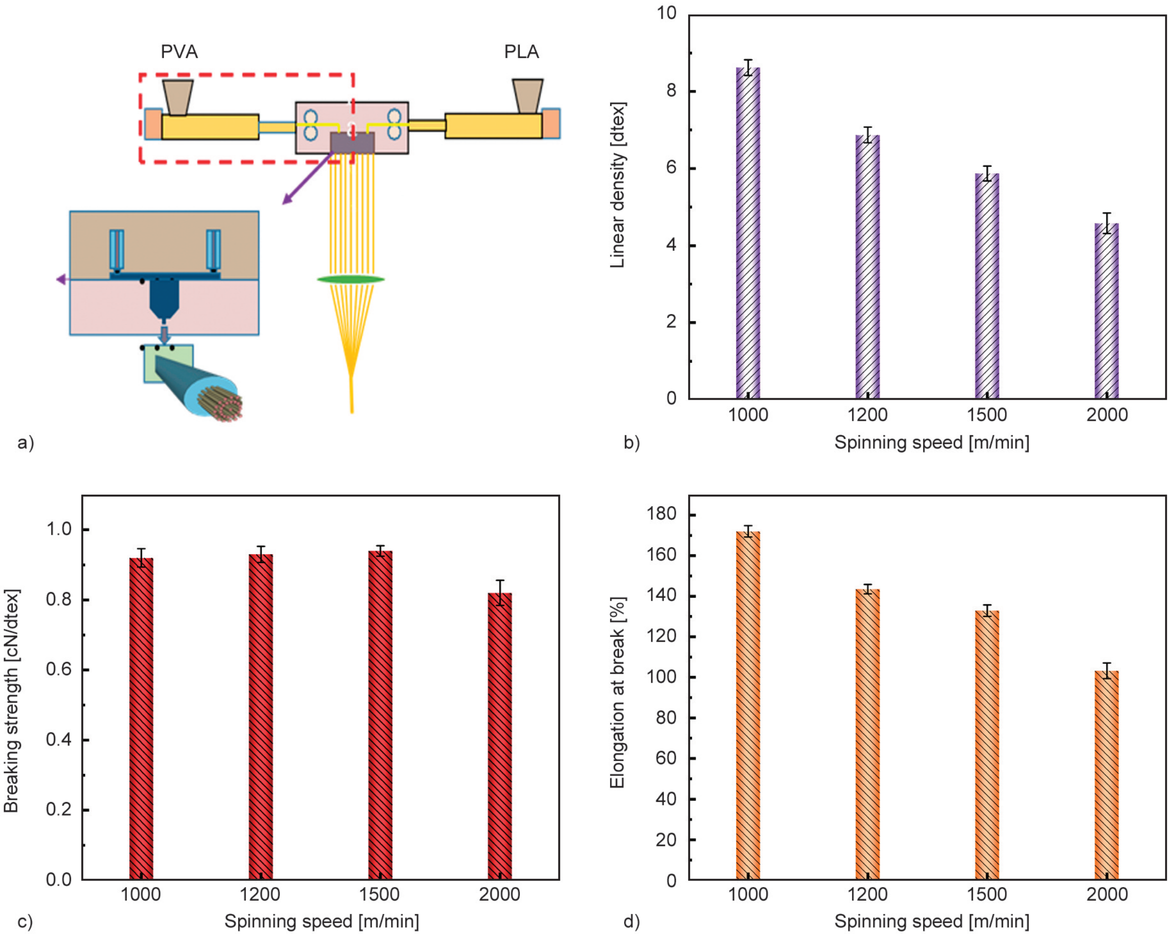

Figure 5. a) PVA-PLA sea island fiber processing diagram; PVA-PLA fibers: tensile properties b) linear density, c) breaking strength, d) breaking elongation vs. spinning speed, respectively.

The morphology of the prepared PVA-PLA island fiber, as well as the corresponding PLA superfine fibers, are shown in Figure 6. A distinct interfacial phase of PVA-PLA fibers was observed. This was due to the prominent difference in melt properties between PVA and PLA. Increasing the spinning speed the diameter of sea-island fiber reduced. However, SEM photos showed that the cross-section of fiber began to deform when the speed was higher than 1200 m/min. This is because the TPVA melt breaks under a high stretching speed. The superfine PLA microfiber was obtained after water splitting in hot water at 95 °C for 3 min. PLA microfibers with a uniform diameter of about 6.5 µm (0.42 dtex) were obtained, as shown in Figure 6e. Compared to the traditional benzene or alkali reduction for the splitting of sea-island fiber, the use of water-soluble TPVA could effectively reduce splitting time during the preparation of superfine fibers.

4. Conclusions

This work proposed a novel industrial method to prepare TPVA by physical blending. Two types of polyols were blended and used as a compound plasticizer. The plasticization effect changed with the mass ratio of polyol A and polyol B. Polyol A had a larger molecular volume and contained more hydroxyl, enabling the formation of a stronger H-bonding with PVA macromolecules. As a comparison, polyol B showed a smaller dimension and easily penetrated PVA, breaking the inter-molecular interaction of PVA more effectively. A synergistic effect was found between them. Even though the usage doge of polyols was just 6 wt%, the obtained TPVA showed an MFI as high as 35 g/10 min. This ensured the good spinnability of TPVA. The modified TPVA also had excellent thermal stability and showed an initial decomposition temperature of 273 °C. After plasticization, the window for thermoplastic processing

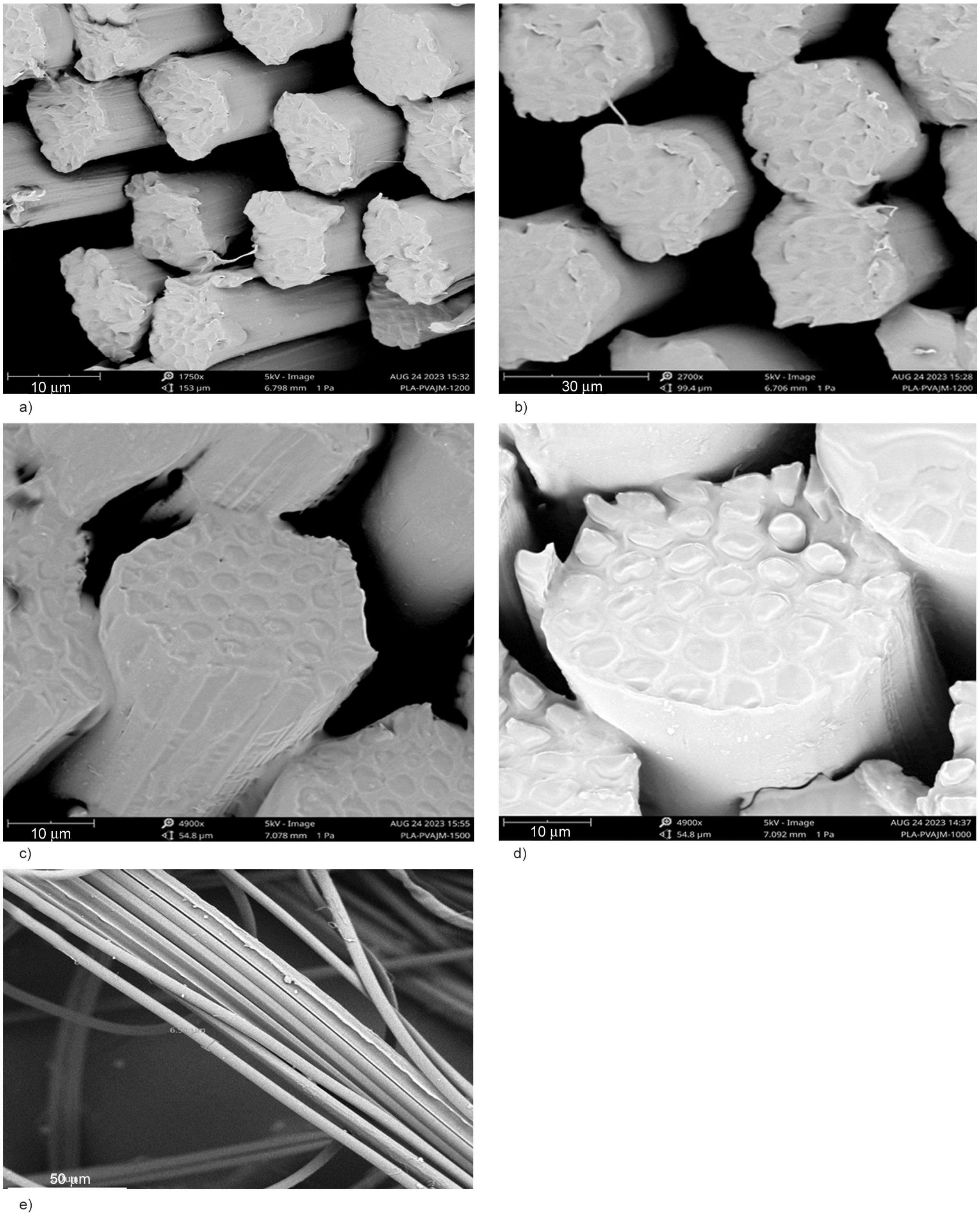

Figure. 6 Cross-section of PVA-PLA sea-island fiber prepared by different rolling speeds a) 2000 m/min; b) 1500 m/min; c) 1200 m/min; d) 1000 m/min and the corresponding PLA superfine fiber e) after PVA removal.

enlarged, and the resistance to oxidation at high temperatures also enhanced greatly. This ensured a conjugated spinning of PVA/PLA blended melts. As-prepared sea-island POY showed a low mechanical strength. The highest tensile strength was 0.94 cN/dtex due to the lack of thermos-fixing treatment. TPVA served as the sacrificial phase. The as-prepared sea-island fibers turned into superfine fibers with a diameter of 6.5 µm in 3 min by water-splitting at 95 °C. This work provided a facile and economical approach to the high throughput fabrication of superfine fibers.

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