

# Effect of Interaction between Hydroxyl Group and High Valence Metal Ion Impurity on the Electrospinnability of Polyvinyl Alcohols

Xinsheng Zhu, Qiang Gao, Detao Xu, Xiaoli Shi

*Division of Nonwoven Materials Engineering, Faculty of Textiles and Clothing Engineering, Suzhou University, Suzhou, Jiangsu 215021, People's Republic of China*

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**ABSTRACT:** The production of superfine polyvinyl alcohol (PVA) fiber is usually much difficult by using the routine spinning, whereas electrospinning is a viable technique as the mechanism of fiber formation is different. In this article, the effects of solution properties in terms of the residual acetyl group and high valence metal ion impurity of PVA on electrospinning were carefully investigated. Both the solution viscosity and the surface tension tendencies with PVA concentration indicated that there existed strong physicochemical interaction besides concentration and molar mass factors. NMR spectra and DSC thermographs indirectly showed that the devoid acetyl group of PVA would

promote the physical gelation and the formation of hydrogen bondings, and the physical cross-linking occurred at high saponification degrees in the presence of high valence metal ion impurity. All the interactions aggravated the electrospinnability. Nevertheless, both removal of high valence metal ion impurity and the selection of PVA with low saponification degrees would be always accessible routes to ensure the PVA electrospinning. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 143–149, 2009

**Key words:** water soluble polymer; solution properties; microstructure; cross-linking; fibers

## INTRODUCTION

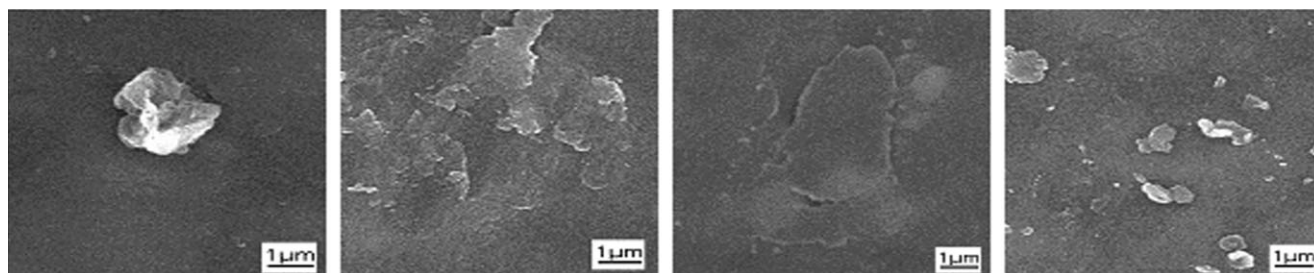
Polyvinyl alcohol is a semicrystalline hydrophilic polymer with excellent biodegradability, physicochemical properties and thermal stability. The prominent properties make it attractive for a variety of applications such as film, fiber and coatings in industry. With nanotechnology and nanostructure materials widely being recognized, the electrospinning of nanofibers or ultrafine fibers from polyvinyl alcohol and its mixtures has received a great deal of attention in the past decade.

The effects of spinning conditions, polymer microstructure, and additives on the PVA electrospinnability have been investigated intensively. Zhang et al. comprehensively studied the effects of electric voltage, tip-target distance, flow rate, and cosolvent ethanol on fiber morphology.<sup>1</sup> Tao and Shivkumar found that, the structural regimes for beads, beaded fibers, complete fibers and flat ribbons were mapped with the product of intrinsic viscosity and polymer concentration from 8.1 to 22.1; the onset of significant polymer chain entanglements accompanied the development of a stable fiber structure.<sup>2</sup> Shenoy et al. thought that chain entanglement numbers in the

nonspecific polymer-polymer interaction solution for both fiber initiation and complete formation should be larger than 2.5 and 3.5, respectively.<sup>3</sup> In their successive work, they further proposed that the entanglement numbers for the two events be much smaller for the polymer solutions with physical gelation occurring.<sup>4</sup> In addition, both Zhang et al.<sup>1</sup> and Yao et al.<sup>5</sup> found that it was very difficult to prepare ultrafine fibers for the fully hydrolyzed PVA with high molar mass. In fact, saponification degree of PVA will also switch electrospinning owing to the variation of physical gelation and hydrogen bonding interaction. Therefore, the polymer chain entanglement, the physical gelation and the hydrogen bonding interaction will strongly dominate the electrospinnability and electrospinning behavior.

Son et al., thought that the pH value strongly affected the PVA electrospinnability and fiber morphology possibly due to protonation with saponification degree 99.7%.<sup>6</sup> The average fiber diameter and morphology of the chitosan polyvinyl alcohol blend much depended on the chitosan content and the two polymer concentrations.<sup>7</sup> The bovine serum albumin, manganese acetate and calcium phosphate were blended respectively, with aqueous PVA solution to study electrospinnability and to prepare functional materials.<sup>1,8,9</sup> Copper/PVA nanocables were produced via the electrospinning of mixture solutions of PVA, copper chloride, sodium hydrogen sulfite and

Correspondence to: X. Zhu (xzhu1988@yahoo.com.cn).



**Figure 1** SEM images of electrospayed deposits from HS1799 (Notation for each panel based on the order from left to right: 7, 9, 11, and 13 w/v%).

hydrazine hydrate.<sup>10</sup> It is well-known that high valence metal ions, chitosan and protein in aqueous PVA solutions will interact with hydroxyl group, and the cross-linking structure and hydrogen bondings can thus be formed. This can change the electrospinning behavior simply due to the increase of electrospinning solution viscosity. We were wondering how and to which extent the electrospinnability was affected in the presence of divalent metal ions?

Up to now, the effect of high valence metal ion impurity on the electrospinning of PVA hasn't attracted many interests. We briefly reported electrospinnability of PVA in the presence of high valence metal ion impurity.<sup>11</sup> In this work, the interrelationship between metal ions and high saponification degree on electrospinning were further studied in detail.

## EXPERIMENTAL

### Raw materials

Five commercial PVA products were used, and they were HS1799, GW1999, BY1799, FL1699, and BY1788. The two English letters were the abbreviation of PVA manufacturers. In the four Arabic numerals, the former two numbers indicated polymerization degree, for instance, 17 implied polymerization degree 1700; the latter two saponification degree (SD), 99 meant SD 99%.

### Electrospinning conditions

PVA was firstly dissolved into deionized water at 70°C for 2 h. The spinneret tip-target distance was 130 mm, spinning voltage 16 kV, ambient temperature 20°C, relative humidity about 70%. The spinning spinneret was made in the following way: a glass tube was heated and melt drawn to get a conical tip, and the commercial polyethylene vial sampler (0.5 mL) was fixed tightly on the glass conical tip. The internal diameter of the polyethylene vial was about 0.7 mm, and the flow rate was approximately 0.1 mL/h, measured with syringe pump.

Usually, the electrospinning was performed within 2 h after PVA was dissolved completely, otherwise the spinning solution would be treated with ultrasonic dispersion before electrospinning.

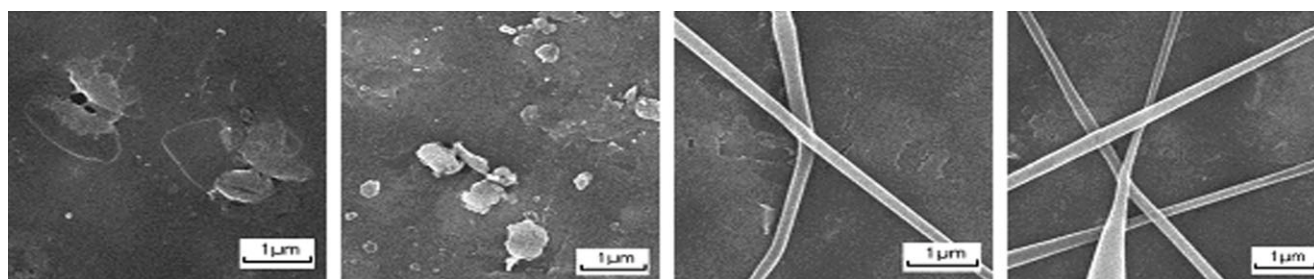
### Characterization of solution properties and fiber morphology

The electric conductivity and surface tension of PVA aqueous solutions were measured by using a conductivity meter (DDB-303A, Shanghai Leici Instruments) and a surface tension meter (DW-P503-4AC), respectively, at 20°C. The viscosity of PVA aqueous solutions was measured on a coaxial cylinder viscometer (NDJ-79, Shanghai Changji Geological Instruments) at 20°C. The morphology of electrospun fibers was observed on a scanning electron microscope (SEM) (HITACHI S-570) after gold coating. A weighted PVA sample was burned in a Muffle furnace at 600°C for 2 h, and the residue was dissolved in dilute nitric acid. The acidic solution was used for measuring the concentrations of metal ions with Plasma Emission Spectrometry (PLA-SPECI). The <sup>1</sup>H NMR spectra were acquired with Bruker AV-400 NMR spectrometer, D<sub>2</sub>O as a solvent. The measurement was performed at ambient temperature. The thermograph of PVA raw materials was acquired with Perkin-Elmer (DSC-7) under nitrogen flow with the flow rate 40 mL/min and the heating rate 10°C/min.

## RESULTS AND DISCUSSION

### Electrospinnability

The electrospinnability can be judged in the light of three different features, the stability of liquid drop hanged at the spinneret tip, the continuity of spinning process and the defects free fibers. As shown in Figure 1, there were only particles produced at four different PVA concentrations, and no fibers but particles appeared for the sample HS1799. In fact, during spinning process, no stable liquid drops hanged at the spinneret tip. Similar result was obtained for



**Figure 2** SEM images of electrospun particles and fibers from BY1799 (Notation for each panel based on the order from left to right: 7, 9, 11, and 13 w/v%).

GW1999. Electrospinning happened again at low PVA concentrations whereas a few filaments really appeared for the sample BY1799 at high PVA concentrations as indicated in Figure 2.

As shown in Figures 3 and 4, at all four PVA concentrations, really ultrafine fibers are presented. The diameters of the fibers for the low concentration PVA solutions were generally small in comparison to those at high concentrations. There existed adhesions at the fiber junction points for the sample BY1788, whereas not for the sample FL1699. The reason was that, the sample BY1788 had low saponification degree, and the PVA came up with a rather good cold water solubility and namely the water retention ability was strong for BY1788. Conclusively, FL1699 displayed excellent electrospinnability, and so did BY1788. GW1999 and HS1799 really gave us disappointed results. Can we only attribute the good electrospinnability to a low polymer molar mass and a low saponification degree?

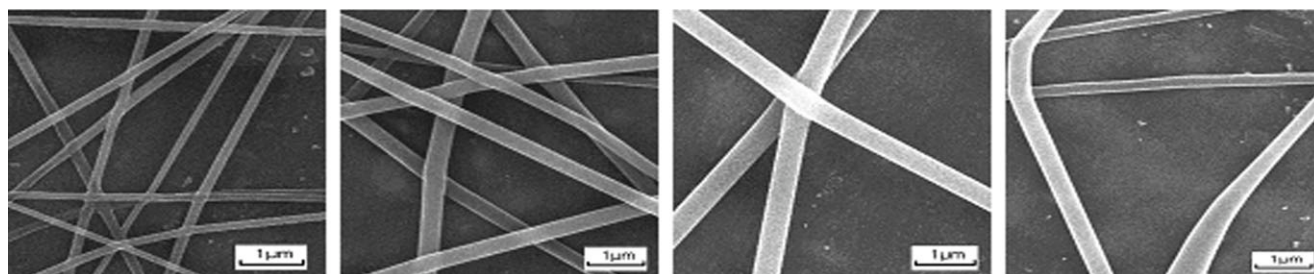
### Solution properties

Essentially, the electrospinning process was controlled by mutually balancing the three forces, electric field force, cohesive force, and surface tension. In reality, the electrospinnability of polymers could be indicated by the solution properties including electric conductivity, viscosity and surface tension. The electric conductivity of five kinds of PVA products is given in Figure 5. The conductivity almost

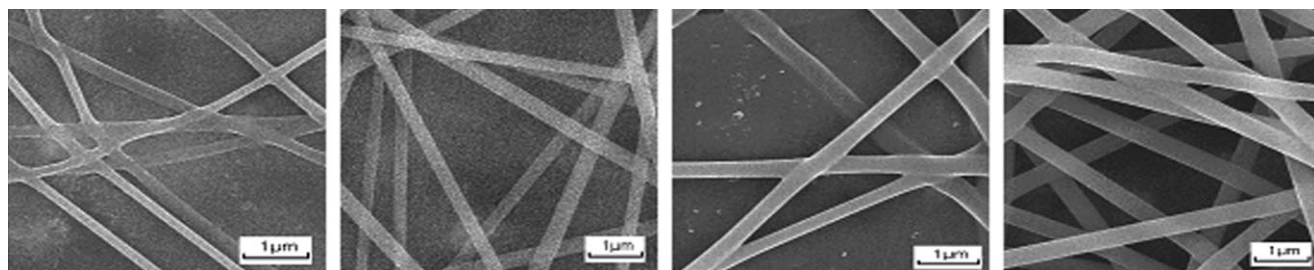
linearly increased with PVA concentration, and this feature might imply that electric conductive components came from the solute PVA. Main electric conductive components should be sodium acetate, the byproduct in the hydrolysis of polyvinyl acetate. The contents of conductive components for FL1699 and BY1788 were less than those of the other three. A high conductivity caused the increase of the electric field force and thus positive charge repulsion was strengthened and the electrospun jets would be torn intensively, at worst only PVA spots were deposited on the target collector and finally a poor electrospinnability occurred.

As indicated in Figure 6, BY1788 and FL1699 presented almost linear relationship of viscosity in the whole PVA concentration range. Both low polymerization degree and low saponification degree favored solubility in water. The linear relationship might be interpreted as the solutions stayed in dilute solution regime, namely, there were no polymer chain overlaps happened for the two samples. Theoretically, this kind of polymer solution can't expect to give any trace of filaments.<sup>3</sup> Nevertheless, as PVA possesses plenty of hydroxyl groups and they will form strong hydrogen bondings, which was explained well by Shenoy et al.,<sup>4</sup> this interaction exceptionally acted as polymer chain entanglements and then promoted fiber initiation.

HS1799, GW1999, and BY1799 all showed linear relationship at the concentrations lower than 10 w/v%, and the nonlinear and upturn tendency



**Figure 3** SEM images of electrospun fibers from FL1699 (Notation for each panel based on the order from left to right: 7, 9, 11, and 13 w/v%).

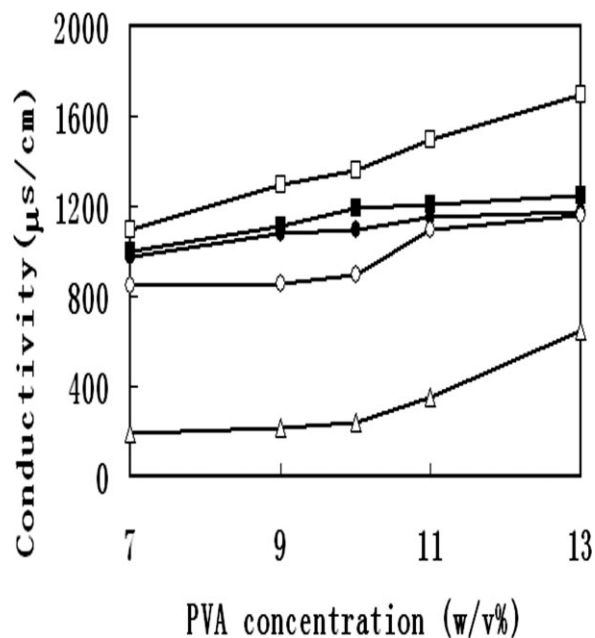


**Figure 4** SEM images of electrospun fibers from BY1788 (Notation for each panel based on the order from left to right: 7, 9, 11, and 13 w/v%).

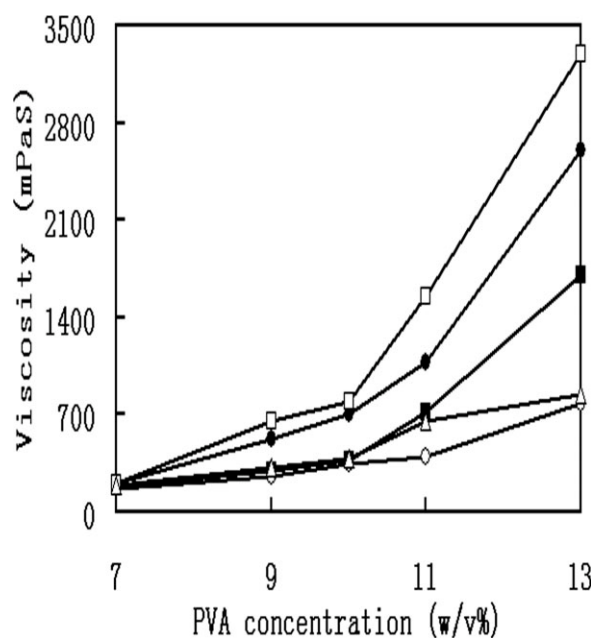
appeared at the concentrations over 10 w/v%. The viscosity upturn behavior implied that the polymer solution experienced transition from the dilute region to semidilute region, and polymer chains started to overlap, and finally polymer chain entanglements would naturally be produced. Fortunately, the sample BY1799 did verify the idea while GW1999 and HS1799 didn't. It seemed that too much chemical and physical interaction violently elevated solution viscosity and caused the solutions not to be electrospun. The differences in the upturn tendencies would be caused by hydrogen bondings, physical gelation and cross-linking besides the concentration and molar mass factors.

The relationship between surface tension and PVA concentration appears in Figure 7, which didn't show similar trends as in Figures 5 and 6. The surface tensions of the samples FL1699, HS1788, and

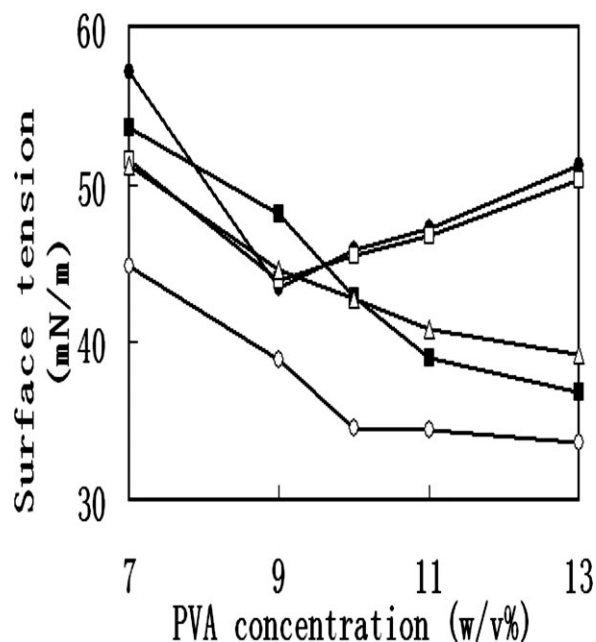
BY1799 were expectedly decreased with the increase of PVA concentration. In this case, PVA behaved itself as a surfactant, the increase of surfactant resulted in the decrease of surface tension of the solution, possibly the dissolution of PVA in water reduced the enrichment of water molecule on the solution surface due to the physical replacement of polyvinyl alcohol macromolecule. The diminution tendency of surface tension seemed an accurate signpost of PVA electropinnability. However, why the surface tension was increased when the PVA concentrations were over 9 w/v% for the samples HS1799 and GW1999? When the viscosity behavior as shown in Figure 6 was taken into consideration, we could confirm that PVA chain did form strong interchain interaction, such as hydrogen bonding. This inversely lowered the phenomenological solubility of PVA and finally the surface tension was



**Figure 5** Electric conductivities of PVA aqueous solutions (● HS1799, □ GW1999, ■ BY1799, △ FL1699, ○ BY1788).



**Figure 6** Viscosity behaviors of PVA aqueous solutions (● HS1799, □ GW1999, ■ BY1799, △ FL1699, ○ BY1788).

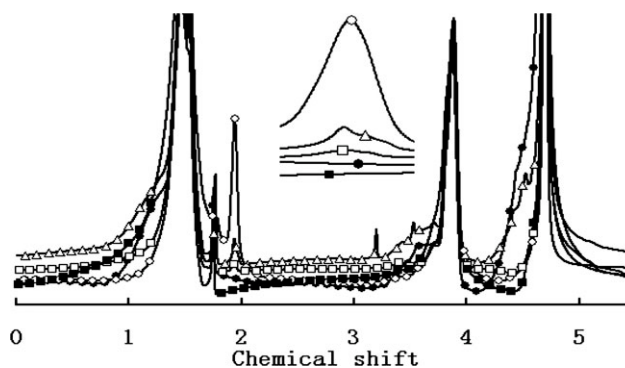


**Figure 7** Surface tensions of PVA aqueous solutions (● HS1799, □ GW1999, ■ BY1799, △ FL1699, ○ BY1788).

increased with PVA concentration. We may imagine that, at high PVA concentrations, the formation of physical gel due to hydrogen bondings gradually spread over the whole vessel, and the surface tensions of PVA aqueous solution were sampled only by breaking the PVA gel and then the surface tension close to the value of pure water was acquired. The formation of PVA gel may mutually comply with the high viscosity for the samples HS1799 and GW1999.

#### Microstructure of macromolecular chains

The proton NMR spectra of five PVA aqueous solutions are given in Figure 8, and the peak assignments are listed in Table I. The resonance peak for residual acetyl group was magnified in the center part in Figure 8. As named, BY1788 really contained most amount of acetyl groups and FL1699 medium, whereas there were almost no acetyl groups presented in the samples of GW1999, HS1799, and BY1799. Naturally, BY1788 and FL1699 would produce less chemical and physical interaction, and



**Figure 8**  $^1\text{H}$  NMR spectra of PVA in  $\text{D}_2\text{O}$  (● HS1799, □ GW1999, ■ BY1799, △ FL1699, ○ BY1788).

their viscosity and surface tension were consequently small, and vice versa for the other three. This may also symbolize the electrospinnability of PVA.

Figure 9 shows the thermographs of five PVA raw materials. As expected, BY1788 and FL1699 possessed the low melting temperatures approximately 197 and 218°C respectively, whereas BY1799, GW1999, and HS1799 gave the high melting temperatures about 222, 228, and 231°C, respectively. The residual acetyl groups in PVA chain damaged its regularity and crystallization process was hindered, and thus small crystals were resulted, and the melting temperatures of the crystals were reduced. The reduction of melting temperature complied with the analysis of content of residual acetyl group in Figure 8. In addition, as indicated with black arrows in Figure 9, HS1799, and GW1999 gave extra shoulder peak at low temperatures and were expected to form some paracrystallites in aqueous solution, and thus the existence of the crystalline states as physical gels may deteriorate electrospinnability. Conclusively, the tiny discrepancy in saponification degree induced remarkable change in crystallinity and electrospinnability.

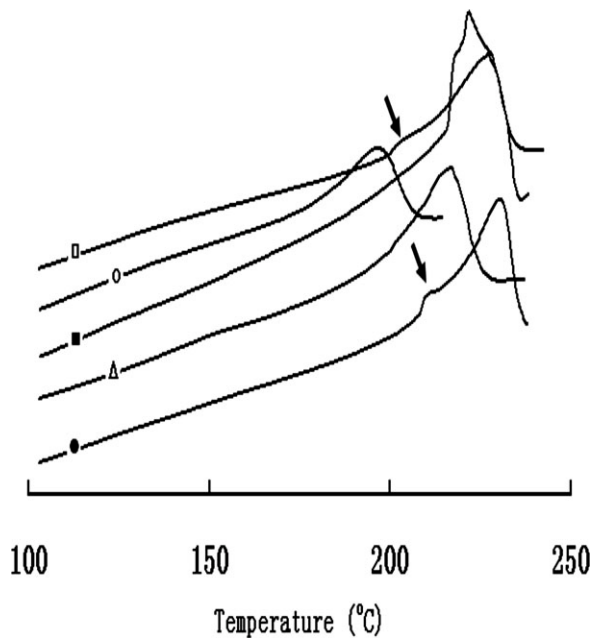
We were wondering whether the GW1999 and HS1799 couldn't be electrospun for ever and whether hydrogen bonding and physical gelation were the only two reasons to jeopardize the electrospinnability.

**TABLE I**  
The Peak Assignments From  $^1\text{H}$  NMR Spectra

H source	OH from water and PVA	Methine —CH—	Methyl from methanol <sup>a</sup>	Residual acetyl groups (CH <sub>3</sub> CO—)	Sodium acetate <sup>b</sup> (CH <sub>3</sub> COONa)	Methylene from chain (—CH <sub>2</sub> —)
Position	4.702	3.888	3.205	1.905–1.991	1.775	1.457–1.560

<sup>a</sup> Methyl group came from residual solvent methanol in PVA particles.

<sup>b</sup> Sodium acetate was a byproduct during saponification.

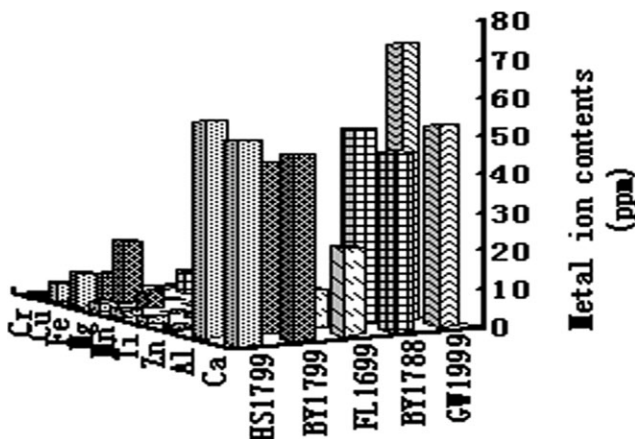


**Figure 9** Thermographs of PVA in nitrogen (● HS1799, □ GW1999, ■ BY1799, △ FL1699, ○ BY1788).

### High valence metal ion impurity

Figure 10 depicts the major divalent and trivalent metal ion contaminants in five PVA raw materials. As we can see that, calcium, aluminum and iron ions were main impurities. The sample FL1699 contained least and GW1999 most abundant whereas the other three showed more or less similar situations. As shown in Figures 1–4, the presence of high valence metal ions affected the electrospinnability possibly by forming physical cross-linking between high valence metal ion and hydroxyl group via switching viscosity and surface tension behaviors.

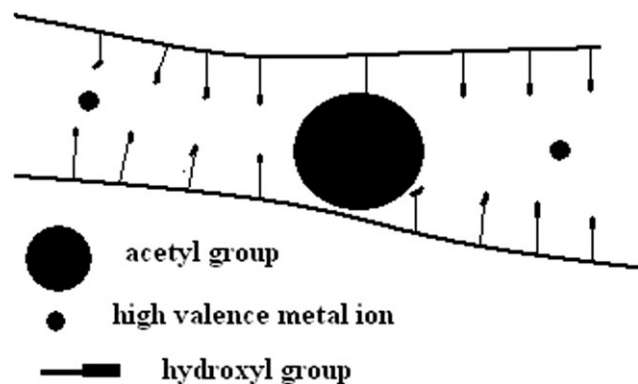
The complexation process between high valence metal ion and hydroxyl group would be concentra-



**Figure 10** Contents of higher metal ion impurity.

tion dependent. At low PVA concentrations or in the dilute solution region, polymer chains dispersed in solution at the molecular level and no polymer chain contact event happened, and thus the complexation took place via intrachain mode. At high PVA concentrations or in the semidilute or even concentrated solution region, polymer chains would be crowded into the whole vessel, and thus the complexation occurred via interchain mode. The two interaction modes produced physical cross-linkings with opposite viscosity behavior, namely, the lower solution viscosity was produced at low PVA concentration, and vice versa. This would deteriorate the electrospinnability of PVA samples with high saponification degree. In our previous articles,<sup>13,14,15</sup> the sample HS1799 also showed pretty good electrospinnability after its solutions were dialyzed or complexed with ethylene diamine tetraacid or polyvinyl pyrrolidone or added with cosolvent acetic acid. Conclusively, high valence metal ions were thought to fortify the physical cross-linking at high saponification degree as well. Nevertheless, the residual bulky acetyl groups would prevent hydroxyl groups from forming physical cross-linking and hydrogen bonding with high valence metal ions and with other hydroxyl groups. The hindrance manner of the residual acetyl groups is schematically given in Figure 11. That's why the presence of large amount of metal ions didn't disturb the electrospinnability of BY1788.

How can we explain the preparation of some functional materials by electrospinning the blend solution of PVA and divalent metal ion solution? We could understand the experiments in two aspects. Firstly, the divalent metal ions showed much less or even no damage on electrospinnability at the lower saponification degrees. The electrospinning of FL1699 aqueous solution was still possible even though a small amount of calcium chloride was added into the solution.<sup>11</sup> Secondly, the electrospun fibers were often



**Figure 11** Hindrance of physical cross-linking due to the bulky acetyl group between hydroxyl group and metal ions.

precursors other than final products, and whether the presences of spindle and bead defects in electrospun fibers or not weren't major concern.

### CONCLUSIONS

1. The physical gelation and physical cross-linking with high valence metal ions for the fully hydrolyzed PVAs switched the solution viscosity behavior and surface tension behaviors and thus spoiled electrospinnability.
2. Both the removal of high valence metal ions and the selection of PVA with lower saponification degree were always viable routes to ensure electrospinnability.

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