

Water states and thermal processability of boric acid modified poly(vinyl alcohol)

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ABSTRACT: To further improve the processability of water plasticized poly(vinyl alcohol) (PVA), boric acid (BA), which can rapidly form reversible crosslinked structure with the hydroxyl groups of PVA, was adopted as a modifier, and the water states, thermal performance, and rheological properties of modified PVA were investigated. The results showed that ascribing to the formation of the crosslinked structure between PVA and BA, the content of nonfreezing water in system increased, indicating that the bondage of PVA matrix on water enhanced, thus retarding the tempestuous evaporation of water in system during melt process and making more water remained in system to play the role of plasticizer. Meanwhile, this crosslinked structure shielded part hydroxyl groups in PVA chains, leading to the further weakening of the self-hydrogen bonding of PVA, and guaranteeing a lower melting point and higher decomposition temperature, thus obtaining a quite wide thermal processing window, i.e., $\geq 179^{\circ}\text{C}$. The melt viscosity of BA modified PVA slightly increased, but still satisfied the requirements for thermal processing, thus reinforcing the flow stability of the melt at high shearing rate. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43246.

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INTRODUCTION

Poly(vinyl alcohol) (PVA), one of the few polymers that can be synthesized via non-petroleum route, has excellent comprehensive properties, such as nontoxic, good mechanical properties, good abrasion resistance, and anti-alkaline resistance, excellent barrier properties, and biodegradability under certain conditions, thus becoming more and more important in the situation of petroleum scaring and being expected to be an ideal material for food packaging, baby products, and biomedicine.^{1–3} All these special properties of PVA are rooted in its particular multi-hydroxyl structure, which endows it with strong intra- and inter- molecular hydrogen bonding as well as high crystallinity,^{4,5} but also results in high melting point, i.e. $220\sim 245^{\circ}\text{C}$, making PVA easily to be decomposed during the melt process.^{6–9} Therefore, the existing applications of PVA are most based on its solution, which has complex process and long production cycle, and is difficult to prepare products with thick wall and complex shape, severely limiting the application of PVA. The realization of the thermal processing of PVA, which is simple, efficient, environmentally friendly, and cost saving, is vital for widening the application fields of PVA and has been seen as a big revolution in PVA industry.

Extending the gap between melting point and decomposition temperature is the key point to realize the thermal processing of PVA, and the most commonly used methods are copolymerization,^{10,11} polymer blending,^{12–15} and plasticization.¹⁶ Copolymerization is carried out by introducing comonomers, such as alkyl, lactic acid, etc., to the backbone or grafting long carbon chains to weaken the hydrogen bonding in PVA and destroy the regular arrangement of PVA molecular chains, hereby improving its extrusion property. Polymer blending is another efficient method to improve the processability of PVA due to the good compatibility of PVA with other polar polymers, including starch,¹⁵ collagen hydrolysate,¹⁴ polyamide 6,¹³ etc. But, the simplest way is adding some small molecules to plasticize PVA. Among a lot of plasticizers, water is the most suitable one for PVA because of its well-known water-solubility. Water, which can form hydrogen bonding with the hydroxyl groups of PVA, can effectively increase the free volume and the chain mobility of PVA, thus depressing its melting point. According to the intermolecular complexation technology developed in our research group, water, and other small molecules having complexation structure with PVA were chosen as a compound plasticizer to control the supramolecular structure of PVA, limit its

crystallization, depress its melting point, and increase its thermal decomposition temperature, thus obtaining 120°C ~ 180°C thermal processing window for PVA.^{17–20} But water, whose boiling point is low ($\leq 100^\circ\text{C}$), is easy to evaporate at the melt processing temperature of PVA, causing foaming and unstable flow. Therefore, how to control water evaporation is quite important for the stable melt process of water plasticized PVA.

Generally, based on the different association of water with PVA, water in PVA is usually divided into three states, i.e. free water, freezable bound water, and nonfreezing water.^{4,5,16,21} Compared with nonfreezing water which has strong interactions with the hydroxyl groups of PVA, free water with no interactions with PVA, and freezable bound water with weak interactions with PVA, both of which were also named as freezable water, are easier to escape from the bondage of PVA matrix during the melt process. Accordingly, if the content of nonfreezing water in PVA can be increased, stable melt process should certainly be realized. In this article, the environmentally friendly boric acid (BA) which could fast form reversible crosslinked structure with the hydroxyl groups of PVA,²² was selected as another modifier except water to further control the water states in system, and consequently solved the foaming problem caused by the rapidly evaporation of water and achieved the stable extrusion.²⁶ The effects of BA content on water states, melting behavior, and rheological properties of modified PVA were systematically studied.

EXPERIMENTAL

Materials and Sample Preparation

PVA 1799 (GB12010-89, degree of polymerization: 1750, degree of hydrolysis: 99%) was purchased from Sichuan Vinylon Works, SINOPEC (China). Before being used, PVA was washed several times with deionized water until the pH was 7 and then dried at 60°C in a vacuum oven to constant weight. BA was analytical reagent. Deionized water was used throughout the experiment.

The BA modified PVA was obtained by adding a certain amount of dried PVA to the prepared BA aqueous solution, and then letting the solution completely seep into PVA at 60°C for 5 hours in a sealed vessel. The swelled samples were extruded using a single screw extruder (Jin Hu Plastics Machinery, Zhejiang, China) with an $\phi 30$ mm annular die, to prepare BA modified PVA pellets.

CHARACTERIZATIONS

Fourier Transform Infrared Spectroscopy (FT-IR)

The Fourier transform infrared (FT-IR) spectrum of modified PVA was recorded by Nicolet 6700 IR spectrometer (Thermo Nicolet, Vernon Hills, IL). The BA modified PVA pellets were first cut into quite small slices and then tested in the attenuated total reflection (ATR) model at a revolution of 4 cm^{-1} from 650 cm^{-1} to 4000 cm^{-1} . The absorbency A of hydroxyl stretching peak was calculated by the following equation according to Beer-Lambert law²³:

$$A = \log \left(\frac{I_0}{I} \right)$$

where I_0 and I are the strength of incident infrared radiation and transmitted infrared radiation, respectively.

Differential Scanning Calorimetry (DSC)

The states and evaporation behavior of water in modified PVA were tested on a TA Q20 thermal analyzer (TA Instruments Co., New Castle, DE) under nitrogen atmosphere with a flow rate of 50 mL/min in an aluminum pan. The sample weight was about 5~7 mg. The samples were first heated from -50°C to 20°C at a rate of 5°C min^{-1} to obtain the melt curves of ice, then were held for 2 minutes and continued to be heated from 20°C to 200°C at a rate of $10^\circ\text{C min}^{-1}$ to obtain the evaporation curves of water.

The melting and crystallization behavior of modified PVA with different BA content were also recorded using TA Q20 under a flowing N_2 by first heating the samples from ambient temperature to 240°C , then holding for 1 minute and cooling the samples from 240°C to 100°C at a rate of $10^\circ\text{C/min}^{-1}$. The crystallinity of PVA was calculated by using the following equation:

$$X(\%) = \Delta H_f / (\Delta H_f^0 \times R) \times 100\%$$

Here, ΔH_f^0 is the heat enthalpy of pure PVA, 168 J g^{-1} ,²² ΔH_f is the enthalpy of modified PVA; and R is the proportion of PVA in the tested sample.

In order to simulate the hermetic seal circumstance during melting extrusion, high-pressure pans were used to observe the melting behavior of modified PVA from ambient temperature to 250°C at a heating rate of $10^\circ\text{C/min}^{-1}$.

Thermogravimetric Analysis (TGA)

The thermal degradation behavior of modified PVA was tested on TA Q50 (TA Instruments Co., New Castle, DE) under a nitrogen atmosphere with the flowing rate of 50 mL/min from 40°C to 500°C at a heating rate of 10°C/min .

Rheological Properties

The rheological properties of modified PVA were measured on a high-pressure capillary rheometer (Rosand RH7D, Malvern Instruments. Co., Britain), whose length to diameter ratio (L/D) was 16 and diameter was 1.2 mm.

RESULTS AND DISCUSSION

Interactions in BA Modified PVA System

The FTIR-ATR spectra of modified PVA with varying BA content were given in Figure 1. Obviously, only one wide absorption peak appeared in each FTIR curve in the region of 3000 cm^{-1} to 3600 cm^{-1} , corresponding to the overlapping stretching vibration peaks of O-H in PVA, water as well as BA. Compared with pure PVA (curve e), the hydroxyl stretching peak of PVA/water (curve a) shifted to higher wavenumbers, showing that the addition of water weakened the original inter- or intra-molecular hydrogen bonding among the hydroxyl groups of PVA and the newly formed hydrogen bonding between PVA and water was weaker. With the increase of BA content, the position of this peak changed little, while its intensity gradually weakened, indicating that the addition of BA did

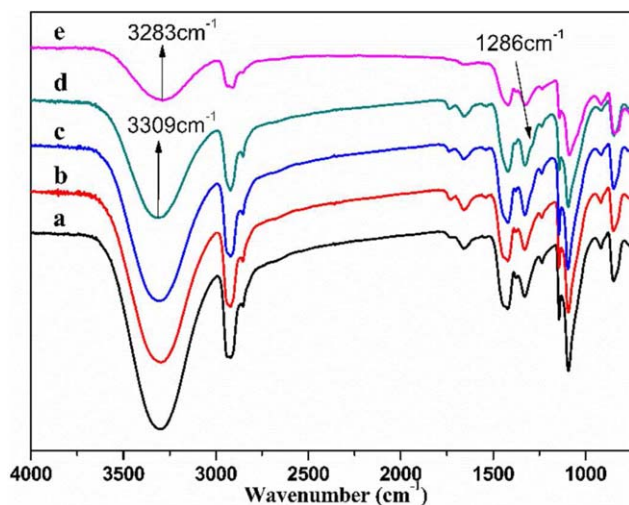


Figure 1. FTIR spectra of PVA/water with different BA content ((a) 0 wt % BA; (b) 1 wt % BA; (c) 3 wt % BA; (d) 5 wt % BA; and (e) pure PVA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

not change the hydrogen bonding types in system, but decreased its numbers. Boron (B) in BA possesses one unoccupied molecular orbital, which endows it with strong ability to accept electrons to react with the hydroxyl groups of PVA. The reactive mechanism between PVA and BA had been suggested to be a didiol type, i.e., two diol units of PVA and one borate ion formed a crosslink (Figure 2).²⁵ In this way, the available hydroxyls to establish hydrogen bonding in system gradually reduced, leading to the decrease of the intensity of the O–H absorption peak. However, the rest hydroxyls still kept the state of highly association, resulting in no change of the O–H absorption peak in position. To further identify the intensity changes of the hydroxyl groups, the unchanged C–H flexural vibration peak of PVA set at 1450 cm^{-1} ²⁴ was chosen as the criterion to calculate $A_{\text{OH}}/A_{\text{CH}}$ values, as shown in Figure 3. The obvious reduction of $A_{\text{OH}}/A_{\text{CH}}$ value with the increase of BA content further confirmed the reduction of the hydroxyl groups in system.

It could also be seen from Figure 1 that a weak peak set at about 1286 cm^{-1} gradually appeared by increasing BA content. This is the stretching vibration peak of B–O–C bond. The

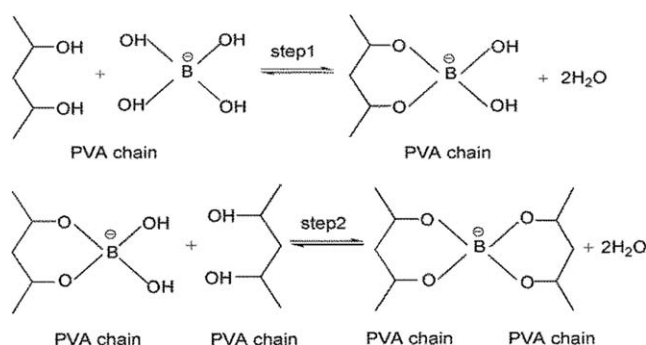


Figure 2. Reaction diagram between BA and PVA in water solution.²⁵

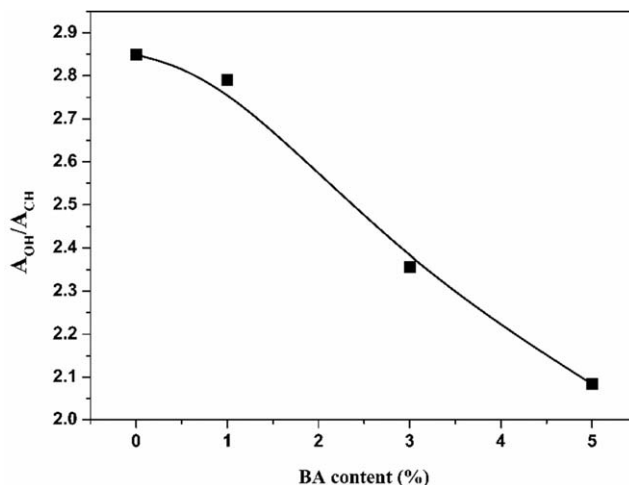


Figure 3. Relationship between $A_{\text{OH}}/A_{\text{CH}}$ value and BA content.

appearance of this peak fully confirmed the reaction occurred between BA and PVA.

Water States in BA Modified PVA System

The states of water could be differentiated by low temperature differential scanning calorimetric (DSC) measurements, as shown in Figure 4. Apparently, two peaks appeared in each DSC curve, respectively representing the ice-melting peak of freezable bound water at lower temperature and the sharp peak of free water at about 0°C . With the increase of BA content, the shapes of these two peaks had no obvious change, but their intensities decreased, indicating that the addition of BA did not change the three basic states of water, but changed their proportion. By using the following equations,^{27,28} the content of nonfreezing water (W_{nf}) and freezable water (freezable bound water and free water, W_{f}) were calculated.

$$W_{\text{f}} = \frac{\Delta H_{\text{m}}}{\Delta H_0 \times W_{\text{c}}} \times 100\%$$

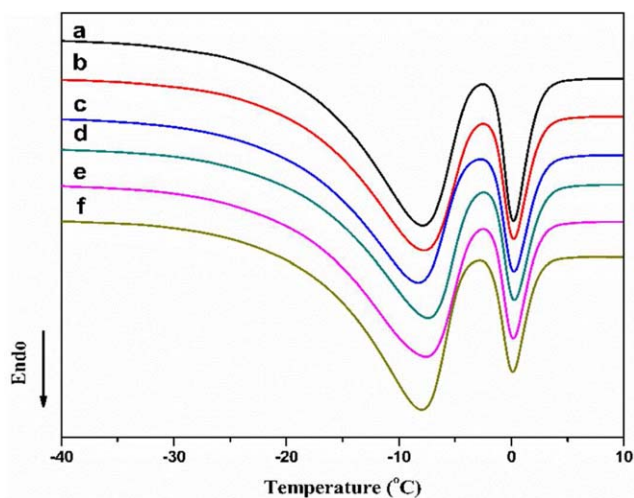


Figure 4. Low-temperature DSC curves of modified PVA with different BA content [(a) 0 wt % BA; (b) 1 wt % BA; (c) 2 wt % BA; (d) 3 wt % BA; (e) 4 wt % BA; and (f) 5 wt % BA]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Ice-Melting Enthalpies and Content of Different States of Water in BA Modified PVA

BA content /wt %	ΔH_m for W_{fb} /(J/g)	ΔH_m for W_{ff} /(J/g)	W_f /%	W_{nf} /%
0	48.2	12.5	42.5	57.5
1	45.3	11.6	39.8	60.2
2	43.9	11.7	38.8	61.2
3	44.8	11.5	39.3	60.7
4	48.0	10.9	41.2	58.8
5	49.4	11.6	42.6	57.4

$$W_{nf} = 100\% - W_f = 100\% - (W_{ff} + W_{fb})$$

Here ΔH_m is the tested phase transition enthalpy of water and ΔH_o is the ice melting enthalpy. W_c is the total water content, W_f is the content of freezable water, W_{ff} is the content of free water, and W_{fb} is the content of freezable bound water. It had been reported that the error of enthalpy changes caused by ice structure was less than 1 wt %, so the difference of melting enthalpy between freezable bound water and free water could be ignored, i.e., $\Delta H_o = 333.5 \text{ J g}^{-1}$.⁵ Phase transition enthalpy and the content of different water were listed in Table I. The relative curves of different water vs. BA content were shown in Figure 5. It could be intuitively seen from Figure 5 that with the increase of BA content, the proportion of nonfreezing water increased firstly and then decreased after 3 wt % BA content. This could be ascribed to the weak crosslinking between BA and PVA at low BA content, which had little effect on the reduction of the hydroxyl groups in system, but could still enhance the constraint of the system on water, resulting in the increase of nonfreezing water. When BA content was over 3 wt %, more hydroxyl groups were consumed to form crosslinked structure with BA, hereby largely reducing the number of hydroxyls that could interact with water and making the content of nonfreezing water quickly dropped.

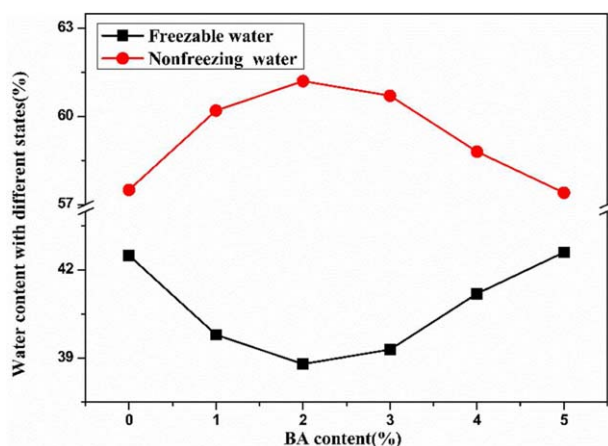
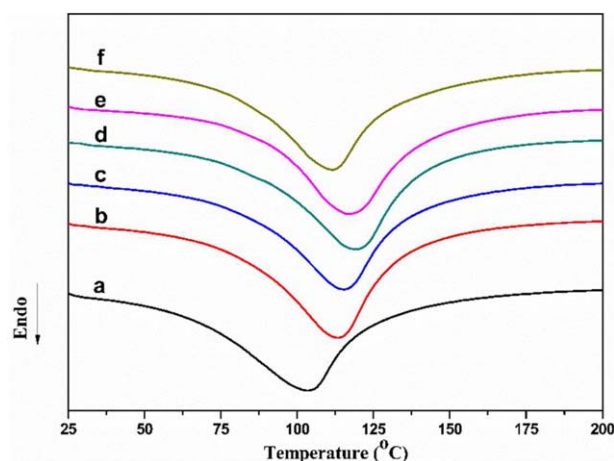
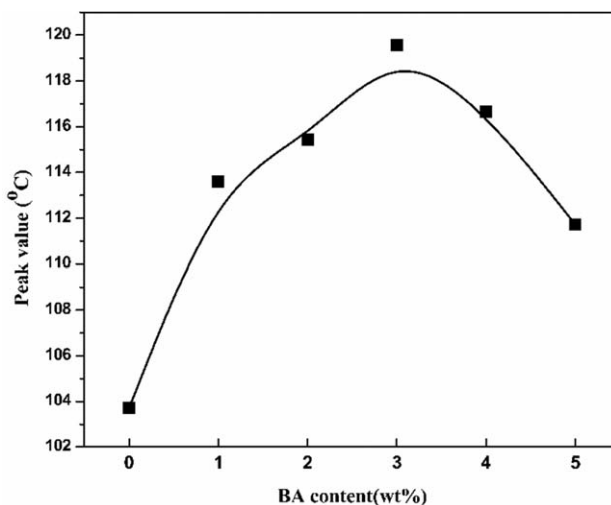
**Figure 5.** Effect of BA content on the content of different water in system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Figure 6.** Evaporation curves of water in modified PVA with various BA content [(a) 0 wt % BA; (b) 1 wt % BA; (c) 2 wt % BA; (d) 3 wt % BA; (e) 4 wt % BA; and (f) 5 wt % BA]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 showed the evaporation curves of water in modified PVA tested by DSC and Figure 7 was the relationship between evaporating temperature of water in system and BA content. It could be seen that with the increase of BA content, the water evaporation peak firstly moved to higher temperature and then decreased. The rise of the evaporation temperature confirmed the enhancing constraint of system on water, which increased the work function of water and made water taken more energy to get rid of the matrix, thus inhibiting its rapid evaporation.

Thermal Performance of BA Modified PVA System

The key issue to realize the thermal processing of PVA is obtaining its thermal processing window, i.e., enlarging the gap between melting temperature and decomposition temperature. In order to imitate the sealed circumstance during extrusion, DSC curves tested in high-pressure pans were also conducted, as shown in Figure 8. Obviously, the more the BA content, the lower the melting temperature of modified PVA.

**Figure 7.** Relationship between evaporating temperature of water in system and BA content.

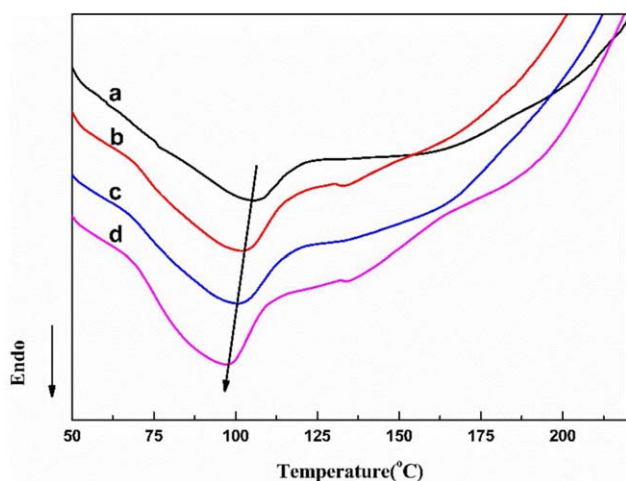


Figure 8. Melting behaviors of modified PVA with various BA content tested in high-pressure pans [(a) 0 wt % BA; (b) 1 wt % BA; (c) 3 wt % BA; and (d) 5 wt % BA]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Ascribing to the special interactions formed among BA, PVA, and water, the influence of BA on melting behaviors of modified PVA was quite complex. Usually, B atom in BA could fast crosslink with the hydroxyl groups of PVA, thus limiting the motility of PVA molecular chains and increasing its melting temperature. However, this crosslinked structure could also weaken the self intra- and inter- molecular hydrogen bonding of PVA to a certain extent as well as constrain more water in system, thus enhancing the plasticizing effect of the remained water, further inhibiting the crystallization of PVA, and contrarily decreasing its melting point. These were two competitive phenomena. But, it could be clearly seen from the DSC results that the later factor played more important role, so consequently resulted in the decrease of the melting temperature of modified PVA.

Figures 9 and 10 were the thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) curves of BA modified

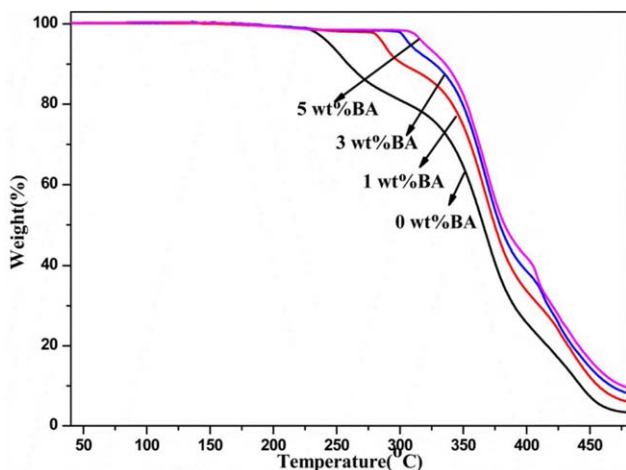


Figure 9. TG curves of modified PVA with different BA content (Dry state). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

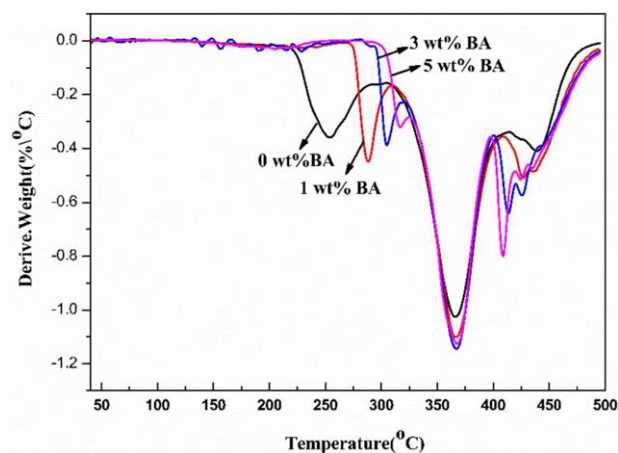


Figure 10. DTG curves of modified PVA with different BA content (Dry state). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PVA, and the corresponding data were listed in Table II. The thermal degradation of PVA could be divided into two steps,⁹ i.e., the elimination of hydroxyl groups, and the chain-scission and cyclization reactions. It was the elimination reactions that affected more on the thermal processability of PVA. Obviously, the initial decomposition temperature of PVA increased and the relative DTG peak (first peak) shifted to higher temperature with the increase of BA content, attributing to the formation of B–O–C bridges between PVA and BA, which consumed part hydroxyl groups, thus effectively inhibiting the dehydration of hydroxyl groups and increased the thermal stability of PVA.

The decrease of the melting temperature and the increase of the initial decomposition temperature of BA modified PVA endowed it with a wide thermal processing window (179–210°C), much wider than that of other plasticized PVA with no BA (120–180°C),^{17–20} thus providing a good basis for realizing the stable thermal processing of modified PVA.

Rheological Properties of BA Modified PVA System

Flow behavior of polymer, which can directly instruct practical processing, is quite important and necessary to be studied. Figure 11 showed the rheological properties of BA modified PVA at 125°C. Apparently, PVA melts with different BA content were pseudoplastic fluids exhibiting a shear thinning phenomenon, and the more the BA content, the higher the melt viscosity of the modified system. But, when BA \geq 3 wt %, the melt viscosity of modified PVA just had a slight increase due to the formed

Table II. Parameters Obtained from the DSC and TG Curves of BA Modified PVA

BA content/wt %	$T_m/^\circ\text{C}$	$T_d/^\circ\text{C}$
0	105.9	234.7
1	103.4	282.3
3	101.9	299.3
5	98.2	308.9

T_m : melting point tested by using high-pressure pan; T_d : initial decomposition temperature.

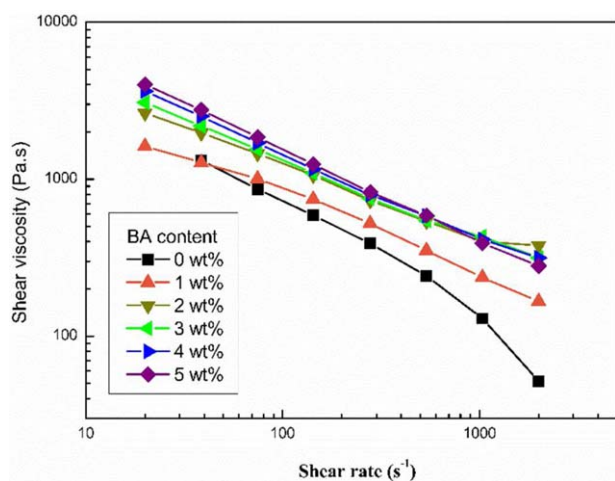


Figure 11. Relationship between shear viscosity and shear rate of modified PVA with various BA content (125°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crosslinked structure between BA and PVA, which increased the entanglement of PVA molecular chains and restricted their movement. Comparing with the curve of system with no BA, BA modified PVA melts showed a linear decreasing trend rather than the sharp decrease of PVA melt at high screw rotation speed, indicating that BA improved the flow stability of the system and reduced the shear sensitivity of the melt.

Figure 12 showed the rheological properties of modified PVA with 3 wt % BA at different temperature. It could be seen that the shear viscosity of BA modified PVA melts changed little with the increase of temperature, indicating that the melts were not sensitive to temperature and were mainly the shear sensitive fluid. It was worth noting that although the addition of BA increased the melt viscosity of the modified system, it still met the requirements of extrusion and injection, and effectively increased the processing stability.

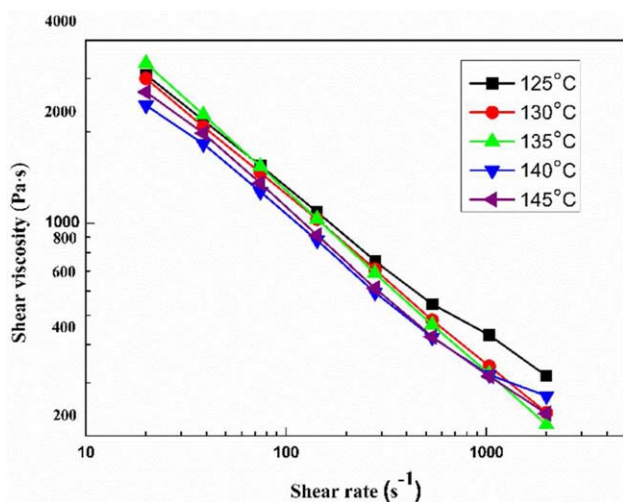


Figure 12. Relationship between shear viscosity and shear rate of 3 wt % BA modified PVA at different temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

Based on the novel thermal processing technology of PVA developed in our research group, BA, which could rapidly react with the hydroxyl groups of PVA and form reversible crosslinked network, was selected as the second modifier for PVA to solve the foaming problem of water at the thermoplastic processing temperature. Ascribing to the crosslinked structure formed between BA and PVA, the content of nonfreezing water in system increased, making water evaporation peak shifted to higher temperature, thus inhibiting the intense water evaporation during the melting process and improving the processing stability of modified PVA. The retarded water evaporation made more water remained in system at processing temperature and played the role of plasticizer, leading to the decrease of the melting point of PVA. Moreover, this crosslinked network decreased the movability of PVA molecular chains and shielded some PVA hydroxyl groups, largely increasing the thermal decomposition temperature of the system. In this way, a wider thermal processing window for modified PVA was obtained. Although the addition of BA slightly increased the melt viscosity of modified PVA, it still satisfied the requirements for extrusion, injection molding, compression molding, and other conventional thermoplastic processing.

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