

# Enhancing Mechanical Properties of Poly(vinyl alcohol) Blown Films by Drawing and Surface Crosslinking

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**ABSTRACT:** Thermal blowing of poly(vinyl alcohol) (PVA) film was successfully realized based on molecular complexation. Ways to enhance the performance of the PVA blown films (drawing and surface crosslinking) were studied. The experimental results showed that water exists in PVA films in different states through hydrogen bonds with PVA and other modifiers and influences the drawability of PVA films, as well as the structure and properties of the stretched films. When the initial water content of the film was higher than 35.0%, the draw ratio of the PVA film was quite large because of the effects of the bound water with PVA, as well as the plasticization of free water. With the

increase of the initial water content in PVA, the free water content and draw ratio of the films increased but the strength of the films decreased because of the higher residual water in the films. Surface crosslinking can improve the stretchability of PVA films because more water remains in the films and disrupts the hydrogen bonding of PVA. In addition, crosslinking enhances the mechanical properties of stretched PVA films. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 774–779, 2005

**Key words:** poly(vinyl alcohol) blown film; water states; drawing; crosslinking

## INTRODUCTION

Poly(vinyl alcohol) (PVA) film has numerous potential applications because of its excellent characteristics, such as good barrier properties to oxygen and oil, antistatic properties, high strength, and solubility and biodegradability under certain conditions. However, the application of PVA film is limited by its difficult processing. PVA films have been processed mainly from an aqueous solution<sup>1,2</sup> because of their simultaneous thermal degradation during melting. Thus, they have some shortcomings, such as a long production cycle, low production efficiency, and high operating cost.

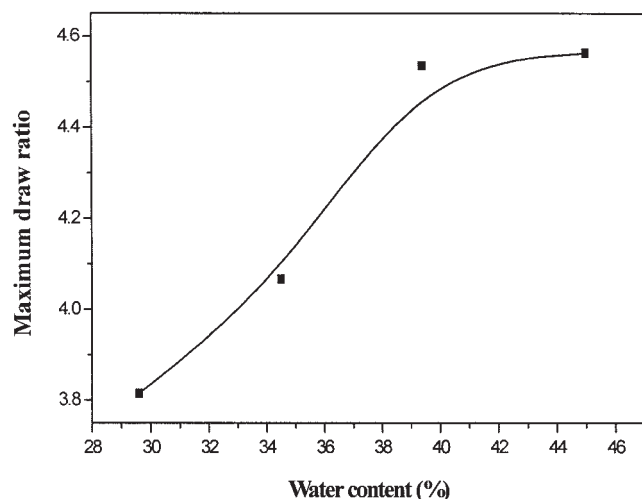
Numerous studies have been devoted to realizing the thermal processing of PVA by copolymerization, blending, and plasticization.<sup>3–13</sup> Plasticization is the most frequently used method and water, glycerol, and glycol are also widely utilized. However, complicated posttreatment is still a big challenge for this process and limits its industrialization. In order to reduce the complicated manufacturing process of PVA films, we adopted molecular complexation in former work.<sup>14,15</sup>

The thermal blowing of PVA film was successfully realized by adding small-molecule compounds, which have a complementary structure to PVA, together with water. PVA films were obtained with a Haake extrusion-blowing machine. A complex modifier efficiently reduced the amount of required water and simplified the posttreatment of the film. In addition, the rheological properties of modified PVA and the mechanical properties of the blown film were studied.<sup>16,17</sup> This is a big breakthrough in the manufacture of PVA film.

To further enhance the mechanical properties of the products, drawing and crosslinking are important methods. However, the drawing of PVA is compromised by the presence of inter- and intramolecular hydrogen bonds between the adjacent hydroxyl groups. For our blown films, the existence of water and other small-molecule compounds disrupts the intra- and intermolecular hydrogen bonds of PVA, restrains its crystallization, and thus improves the drawability of PVA. In addition, the newly formed interactions between water and PVA or water and small-molecule compounds makes water exist in PVA in different states and retards its evaporation,<sup>18</sup> which is beneficial to the realization of the melt processing of a modified PVA system and endows the films with good thermal drawability. Furthermore, crosslinking can also disrupt the intra- and intermolecular hydrogen bonds of PVA, further inhibit the evaporation of water, and improve the drawability and mechanical

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**Figure 1** The relationship between the maximum draw ratio and the initial water content in PVA blown films.

properties of the film. The thermal-plasticizing mechanism of water in PVA blown films, the effect of the water content on the drawability of the films, the effect of crosslinking on the water content, the drawability of the films, and the structure and properties of stretched films were studied.

## EXPERIMENTAL

### Materials

PVA 1799 (GB12010-89, degree of polymerization = 1750, degree of hydrolysis = 99%), which was provided by Sichuan Vinylon Factory, was used in this study. CL, the plasticizer of PVA, is a kind of high boiling water-soluble compound with an amido group. The amount of CL is unchanged in every system.

### Preparations of modified PVA and PVA blown film

Modified PVA was obtained by adding a certain amount of PVA into the prepared aqueous solutions with a calculated CL concentration and then letting the solution completely seep into PVA at an ambient temperature in sealed equipment. PVA blown films were prepared from modified PVA by using a Haake extrusion-blowing machine with a  $\phi$  25-mm annular die.

### Drawing of PVA blown film

Drawing of the film was conducted with a tensile testing machine (4302) at a rate of 10 mm min<sup>-1</sup> at 373 K.

### Crosslinking of PVA blown film

PVA crosslinked films were obtained by coating a layer of 2 wt % borax solution on the surface of PVA blown films, and the redundant water was absorbed by filter paper.

### Characterization of PVA film

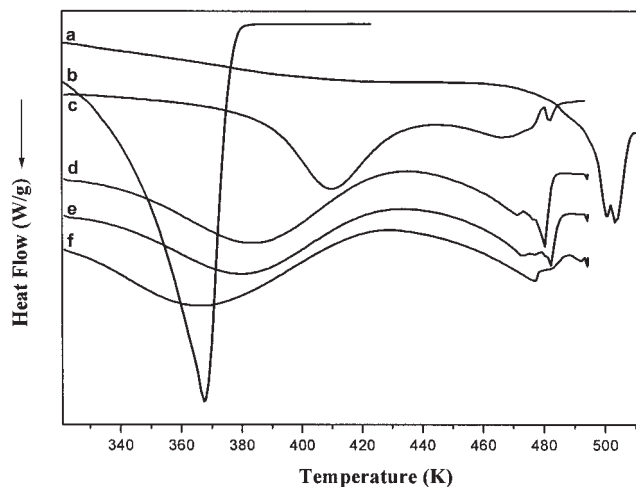
Differential scanning calorimetry (DSC) curves were recorded on a Netsch 204DSC differential scanning calorimeter. Approximately 6 mg of sample was used and the measurements of the samples were performed by heating from 313 to 513 K at an increasing temperature rate of 10 K/min under a nitrogen atmosphere.

The tensile strength, Young's modulus, and elongation of PVA films were tested by extension measurements at room temperature using a tensile tester (4302). The crosshead speed was 100 mm min<sup>-1</sup>. The initial gauge length of the specimen was 75 mm, and the widths and thicknesses of the films were measured with a micrometer.

## RESULTS AND DISCUSSION

### Drawing of PVA blown film

Water, which can form strong intermolecular hydrogen bonds with PVA, is the key plasticizer in realizing the melt processing of PVA and the drawability of PVA blown film. Figure 1 shows the relationship between the maximum draw ratio and the initial water content in PVA blown films. The maximum attainable draw ratio of the films increases with increasing initial water content. When the initial water content of the films increases from 29.6 to 45.0%, the maximum draw ratio is enhanced from 3.8 to 4.6. This is the result of the complicated plastic effects of water on PVA films.



**Figure 2** DSC curves of bulk water, PVA granules, and PVA blown films with different initial water content.

**TABLE I**  
**Results of DSC Curves of Water, PVA Granules, and PVA Blown Films with Different Initial Water Content**

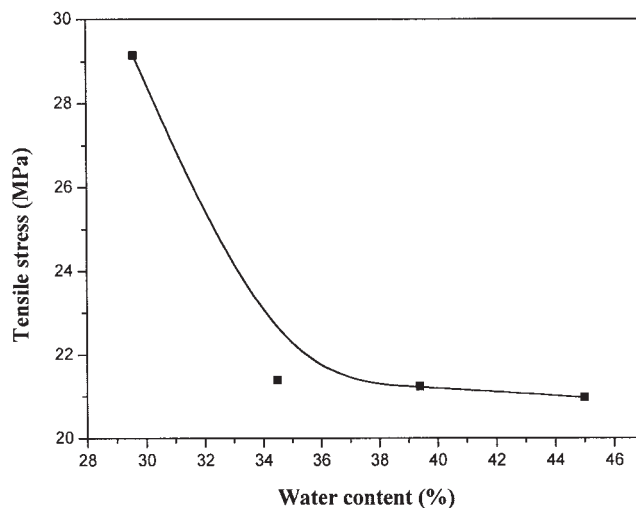
	Bulk water	PVA granules	PVA blown film with			
			45.0% Water	39.4% Water	34.5% Water	29.6% Water
Evaporation peak (K)	369.0	—	366.4	380.6	383.6	408.9
$W_f/W_t$ (wt %)	—	—	60.30	45.70	40.42	3.33

$W_f$ , the content of free water;  $W_t$ , the total water content.

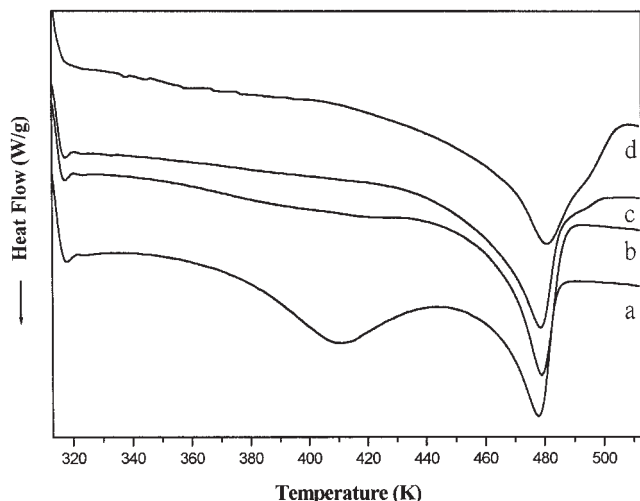
To clarify the thermal-plasticizing mechanism of water in PVA blown films, the evaporation characteristics of bulk water and water in PVA blown films with different initial water content and the thermal properties of PVA granules were investigated by DSC, as shown in Figure 2. There is no obvious water-evaporation endothermic peak in the DSC curve of PVA granules (Fig. 2, curve a). However, for PVA blown films, the water-evaporation endothermic peak is observed below 443 K because of adding water as a modifier (Fig. 2, curves c–f). The water-evaporation endothermic peaks of PVA blown films are completely different from that of bulk water: the evaporation endothermic peak of bulk water is observed at 369 K, which terminates suddenly below 377 K (Fig. 2, curve b), whereas the water-evaporation endothermic peaks of PVA blown films are observed above 369 K, which does not terminate, even when the temperature is over 443 K. The increasing evaporation temperature and the widening evaporation peak of water in PVA films can be attributed to the different interactions between water and the hydroxyl groups of PVA or with the amido groups of CL. Water usually exists in a hydrophilic polymer in three states: free water, freezable bound water, and nonfreezing water.<sup>19–26</sup> The evaporation behavior of free water is similar to bulk water, whereas freezable bound water and nonfreezing water have different interactions with hydrophilic polymers. Different water states show different evaporation behavior; therefore, the wide evaporation peaks found in the DSC curves of PVA blown films actually contain two or more peaks, corresponding to the different states of water. Comparing the DSC curves of PVA blown films with bulk water, the water that evaporates below 377 K for PVA blown films can be defined as free water, whereas water evaporating above this temperature can be defined as bound water, which is affected by both CL and PVA, probably forming strong intermolecular interactions with PVA and CL. The water content also affects the state of water in the films, which can be seen from DSC curves c–f in Figure 2; with the decrease of the initial water content (curves f–c), the water-evaporation endothermic peak of the films shifts to higher temperature and becomes narrower. Some researchers have proved that the

higher the content of water in the system, the higher the ratio of free water.<sup>27–30</sup> When the initial water content is lower than 35%, all of the water in the PVA film is nonfreezing water, whereas when the initial water content is higher than 35%, the nonfreezing water is only 50–65% of the water. According to the above assumption and ignoring the resistance coming from the film, the content of free water in our blown films with different initial water content are calculated and the results are listed in Table I. The ratio of free water to total water ( $W_f/W_t$ ) is reduced with the decrease of water content of the film; and it is only 3.33% when the water content of the film is below 35%, which is in accordance with the research mentioned above.

Different water states show different plasticizing effects; free water lubricates PVA molecular chains (i.e., increases the volume), disrupting the regular structure and decreasing the crystallinity of PVA, thus improving the movement of PVA chains. Bound water can disrupt the original intra- and intermolecular hydrogen bonding of PVA and form new stronger hydrogen bonding with it, thus reducing the entanglement of PVA chains and promoting the orientation of PVA chains along the direction of the tensile strength. When the initial water content



**Figure 3** The tensile strength of PVA blown films with different initial water content.



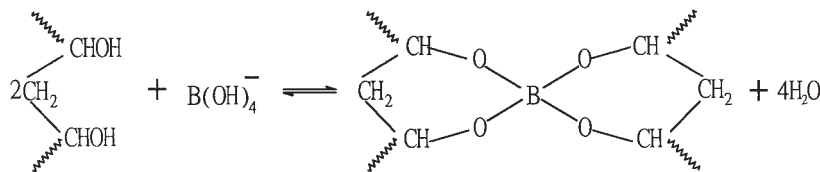
**Figure 4** DSC curves of PVA blown films with different initial water content after drawing 4 times at 373 K.

is below 35%, most of water in the films is bound water and the drawability of the films is mainly influenced by the complexation between water and PVA. When increasing the initial water content, water in the film is not only bound water but also free water; the maximum draw ratio of the films increases because of the overlapping effect of hydrogen bonding complexation and plasticization. It can be concluded that free water produces more effects on the drawability of PVA blown films than bound water. However, too much water will lead to poor mechanical properties of PVA films, as shown in Figure 3; when the initial water content increases from 29.6 to 45.0%, the tensile strength of PVA blown films decreases from 29 to 9 MPa.

To increase the mechanical properties of PVA blown films, thermal drawing, which can make some water evaporate at the proper temperature during drawing, is an optional method. After drawing at 373 K, the water-evaporation endothermic peaks of PVA films become weak, indicating the decrease of water content in the films (Fig. 4); with decreasing initial water in the films, there is less water in the films and its evaporation peak is weaker. Less water content in the films reduces the plasticization of water and improves the crystallinity of the films, which can be seen from the enhanced strength of the melt peaks of the films, and thus endows the films with better mechanical properties. Table II lists the mechanical properties of PVA blown films with different initial water content and drawn 1, 2, and 4 times under 373 K. It can be seen that the tensile strength and the modulus of the films largely increase after drawing and the larger the draw ratio, the higher the mechanical properties of the films. However, more initial water content also leads to lower mechanical properties of the films after being drawn to the same ratio.

**Surface crosslinking of PVA blown film**

Surface crosslinking is another efficient treatment method because it can further break the intra- and intermolecular interactions of PVA and improve the mechanical properties of the films, as well as affect the states of water in the films. Borax is the commonly used crosslinking reagent of PVA, and it can crosslink PVA in several seconds.<sup>1,31-33</sup> The crosslinking reaction is as follows:



After being coated by a 2 wt % borax solution, a layer of net structures forms on the surface of the

films, which will inhibit the evaporation of water; therefore, it needs more energy for water to evapo-

**TABLE II**  
Mechanical Properties of PVA Stretched Films with Different Initial Water Content and Drawn at 373 K

	Water content (%)											
	45.0	39.4	34.5	29.6	45.0	39.4	34.5	29.6	45.0	39.4	34.5	29.6
	Tensile strength (MPa)				Elongation (%)				Young's modulus (MPa)			
Drawing												
1 Time	38	40	56	57	178	160	119	120	111	117	128	174
2 Times	64	73	78	85	82	77	44	40	204	231	358	466
4 Times	123	142	147	177	18	14	13	12	1510	1551	2971	2204

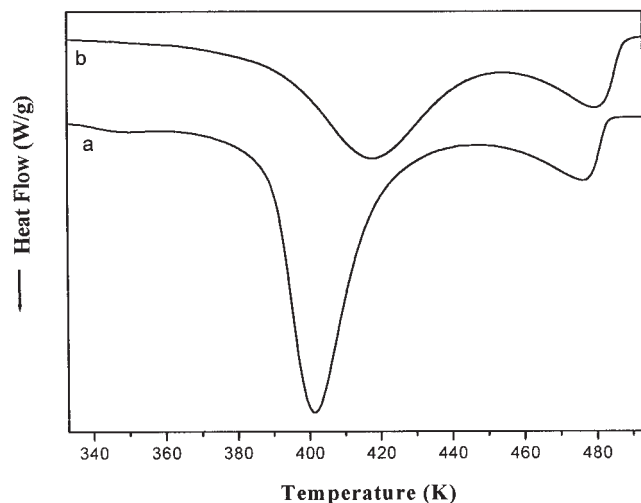


Figure 5 DSC curves of uncrosslinked and crosslinked PVA films.

rate. The changes of the evaporation behavior of water in crosslinked PVA film can be seen from Figure 5. The water-evaporation endothermic peak of crosslinked PVA film (curve b) shifts to a higher temperature and its width widens compared with the uncrosslinked PVA film. Similar results can be obtained by observing the process of water loss at 373 K (Fig. 6). When heated at 373 K, the amount of water loss in the crosslinked film is obviously reduced and the water evaporation rate slows down. Under the influence of crosslinking and water, PVA blown films have better drawability and the maximum attainable draw ratio increases. (Table III). The existence of crosslinking points also improves the tensile strength, yield strength, and Young's modulus of PVA blown films after drawing (Table IV), even though more water remained in the films.

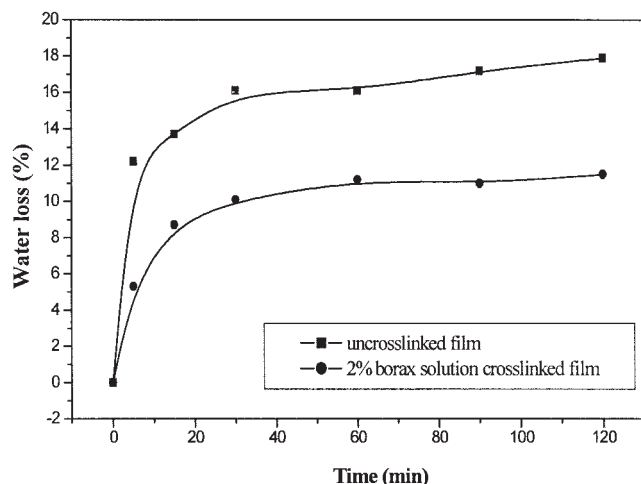


Figure 6 A comparison of the water loss of uncrosslinked and crosslinked PVA films at 373 K.

TABLE III  
Comparison of Mechanical Properties of Uncrosslinked and Crosslinked PVA Films

	Tensile strength (MPa)	Yield strength (MPa)	Young's modulus (MPa)	Elongation (%)
Uncrosslinked film	27.0	10.7	52.4	329.6
Crosslinked film	32.4	11.8	50.6	376.7

## CONCLUSIONS

Water existed in PVA blown films in different states through hydrogen bonding with PVA and small-molecule compounds, so it influenced the drawability of the blown films and the structure and properties of the stretched films. The states of water in PVA films could be controlled by adjusting the initial water content in the films or adopting crosslinking on the surface of the films. With the increase of the initial water content in the films, the free water increased and the maximum attainable draw ratio of PVA blown films increased because of the effects of bond water with PVA or with a small-molecule compound, as well as the plasticization of free water. However, the mechanical properties of the films decreased because of the higher residual water in the films. Drawing and crosslinking are two important ways to enhance the performance of the films. After being drawn at 373 K, the water content of the films was reduced and the mechanical properties of the films improved. Surface crosslinking improved the drawability of PVA films by further breaking the inter- and intramolecular hydrogen bonding of PVA and more water remained in the films, thus enhancing the mechanical properties of PVA films for the existence of crosslinking points.

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TABLE IV  
Comparison of Mechanical Properties of Uncrosslinked and Crosslinked PVA Films After Drawn at 373K

Draw ratio	Tensile strength (MPa)	Young's modulus (MPa)	Elongation (%)
1 Time			
Uncrosslinked film	64.40	139.33	147.72
Crosslinked film	64.46	146.71	129.62
2 Times			
Uncrosslinked film	94.13	177.47	93.65
Crosslinked film	97.18	336.05	76.37
4 Times			
Uncrosslinked film	165.1	1180.00	24.58
Crosslinked film	202.7	1413.00	22.17

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