

# The Reinforcement of Leather Split by Constructing an Interpenetrating Network via In-situ Recombination of PVA

by

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## Abstract

In order to improve the quality and utilization of leather split, the strength of leather split should be enhanced. The in-situ polymerization of some monomers has proven to be an effective approach in constructing an interpenetrating network (IPN) in split and increasing its strength. But this method is almost unacceptable in practice because of the use of volatile monomers and organic solvents. In this study, a new method to construct the IPN structure in split, in-situ recombination, was developed. Polyvinyl alcohol (PVA) was used as compositing agent, and its molecular structure and modification conditions were optimized. Scanning electron microscope (SEM), potentiometric analyzer and differential scanning calorimeter (DSC) were used to characterize the mechanism of in-situ recombination. The results suggested that PVA with an average polymerization degree of 500 and an average alcoholysis degree of 88% could enhance the strength of split most effectively through compositing reaction of PVA and split in 5% PVA aqueous solution for 120 min under 80°C and pH 7.0. The IPN structure was successfully constructed between PVA and collagen fibers via in-situ recombination. A method to enhance the strengths of leather split with practical application was established.

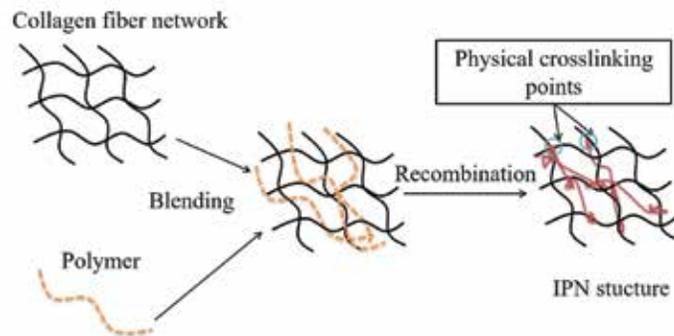
## Introduction

Hides and skins are usually split into several layers during leather manufacture. Compared with grain wet-blue (top-layer), the mechanical properties of wet-blue split are much weaker due to bulky collagen fibers, loose weave and larger texture angle. As a result, wet-blue splits are more easily torn apart during post-tanning processes, which will decrease the value of the leather. So, if the mechanical properties of wet-blue split can be reinforced, the quality and utilization of leather split could be improved.

In our previous studies, the mechanical properties of leather split were successfully improved by constructing an

interpenetrating network (IPN) in collagen fiber network.<sup>1,2</sup> The IPN structure was built by in-situ polymerization of n-butyl methacrylate (nBMA) monomers. Unfortunately, the use of monomers and organic solvents makes this modification method difficult to implement in production. The problem of residual monomers in leather split is a concern as they are hard to fully remove.

On this occasion, we tried to use another method, the “in-situ recombination,” to build the IPN structure in wet-blue split. As is commonly known, the molecular state of polymers can be altered by changing the solvent environment such as pH, concentration and temperature.<sup>3,4</sup> Herein, water-soluble linear macromolecules were added into collagen fiber network of wet-blue split at a relatively high temperature first, and then the combination was induced by cooling. During the recombination, the conformation of molecular chains would change from extended to contracted, and thus molecular chains would twist around collagen fibers and be crosslinked with collagen fiber network. The formation progress of in-situ recombination is shown in Scheme 1. The polymer used in our modification was polyvinyl alcohol (PVA), which is a widely used water-soluble polymer with high strength and high modulus.<sup>5</sup> Related literature show PVA can be used as a reinforcement agent in the



Scheme 1. Composite materials with IPN structure prepared through in-situ recombination.

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preparation of modified polymer, paper and cement.<sup>6-8</sup> Moreover, a large amount of hydroxyl groups on PVA molecular chains can form hydrogen bonds with collagen fibers, which benefits the combination. On the basis of this speculation, the optimized in-situ recombination conditions of PVA in wet-blue split were investigated in this study, and the interaction pattern of collagen fiber and PVA in PVA/split composite were also studied.

## Experimental

### Materials and Equipment

Wet-blue splits of cattle hide with an average thickness of 1.6mm were obtained from a local tannery in China. Sodium bicarbonate ( $\text{NaHCO}_3$ ), sodium formate ( $\text{HCOONa}$ ) and formic acid ( $\text{HCOOH}$ ) were all chemical pure and purchased from Kelong Chemical Reagent Factory, Sichuan, China. Degreasing

**Table I**  
The PVAs used in experiments.

Sample No.	Polymerization degree	Alcoholysis degree (%)	Viscosity (mPa·s)
PVA-A	350	88	3.2 ~ 3.6
PVA-B	500	88	4.0 ~ 5.0
PVA-C	1000	88	10.0 ~ 11.0
PVA-D	1700	88	22.0 ~ 27.0
PVA-E	500	99	5.2 ~ 6.0
PVA-F	500	78	6.0 ~ 6.7
PVA-G	500	70	5.0 ~ 5.8

**Table II**  
Preparation progress of PVA / split composites.

Step	Material	Dosage* (%)	Temperature (°C)	Time (min)	pH
Rewetting	water	400	35	40	
	Degreasing agent	0.4			
Washing	water	400	35	10	
Neutralization	water	200	35	30	6.5~7.0
	HCOONa	2			
	$\text{NaHCO}_3$ (1:10)	0.6×n			
Washing	water	200	35	10	
Compositing**	water	100	80	x***	x***
	PVA	x***			
Fatliquoring	water	40	50	60	
	Fatliquoring agent	10			
Fixing	HCOOH (1:10)	0.5		10×n+30	3.8~4.0
Washing	water	100×3	25	15×3	

Hanging to condition and milling

\*: All the dosages were based on the weight of wet-blue splits.

\*\* : PVA was dissolved in water at 80°C before adding into drum. Our determinations showed, in this way, the time for penetration was shorten with better modification effect. Moreover, PVA solution at 80°C has minimum viscosity, and PVA molecule has maximal hydrodynamic radius which favors penetration of PVA in collagen fiber network.

\*\*\*: x meant the dosage, time, pH was changed in different trails.

agent was industrial grade and supplied by Sichuan Dowell Science & Technology Inc, Sichuan, China. Fatliquoring agents were industrial grade provided by Zschimmer & Schwarz, Shanghai, China. All PVAs (shown in Table I) were industrial grade and supplied by KURARAY Co., Ltd. The drum ( $\varnothing$  30 cm) commonly used in leather processing trials was employed to rotate the chemicals and wet-blue split to aid penetration.

### Preparation of PVA / Split Composites

The wet-blue split was somewhat uneven in thickness and tightness. To make the experimental results comparable, all the wet-blue split samples (20 cm  $\times$  20 cm) were cut from butt area following back line. These selected samples were washed and wrung, and then processed as in Table II to obtain PVA / split composites. The crust split (the split only fatliquored) and the composited split (un-fatliquored PVA / split composite) were also prepared as in Table II for comparison.

When optimal compositing time (penetration time) was investigated, 10% PVA-B solution was used at pH 7.0, and penetration time was 60 min, 120 min, 180 min, 240 min and 300 min, respectively.

When the effect of polymerization degree and alcoholysis degree of PVA on compositing performance were investigated, 10% solutions of different PVAs were used at pH 7.0, and penetration time was 120 min.

When the effect of pH on compositing performance was investigated, 10% PVA-B solution was used for penetration of 120 min, and compositing pH was 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0, respectively.

When the effect of PVA concentration on compositing performance was investigated, PVA-B solutions with different concentrations were penetrated for 120min at pH 7.0, and the concentrations of PVA-B solutions were 1%, 3%, 5%, 10% and 15%, respectively.

### Measurements and Instruments

The thickness of PVA / split composites was measured with a dial thickness gauge (MY-3130-A2, MingYu, Dongguan, China). The mechanical properties of composites were tested with a universal testing machine (AI-7000SN, GOTECH, Dongguan, China) according to International standards ISO 3376: 2002 and ISO 3377-2: 2002. The softness of composites was measured with a ball pressure softness tester (GT-303, GOTECH, Dongguan, China). The shrinkage temperature of composites was determined according to International standards ISO 3380: 2002. The isoelectric points of wet-blue split, crust split, composited split and PVA/split composite were measured with a potentiometric analyzer (Mutek™ SZP-10, BTG, Germany) according our former research.<sup>9</sup>

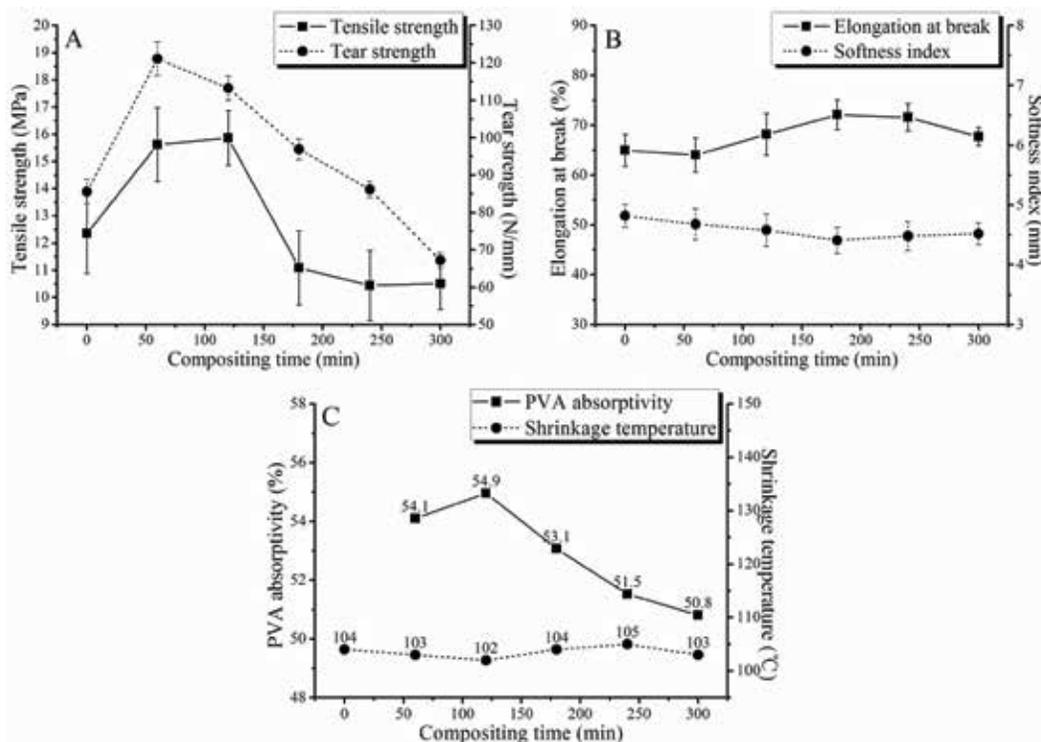


Figure 1. Properties of PVA / split composites prepared with different compositing time.

The total organic carbon content in compositing solutions was tested by total organic carbon analyzer (TOC, vario TOC, Elementar, Germany). The absorptivity of PVA was calculated as  $(1-P2/P1) \times 100\%$ , where P1 and P2 were total organic carbon content in compositing solutions before and after compositing, respectively.

The morphologies of fracture cross-sections of crust split and composite were observed by scanning electron microscope (SEM, QUANTA 250, FEI, U.S.A.) with an accelerating voltage of 20 kV. All these samples for SEM were obtained from the samples after mechanical property test.

The thermal properties of composites were measured with a differential scanning calorimeter (DSC, DSC 204 F1, NETZSCH, Germany) at the ramping rate of  $10^\circ\text{C}/\text{min}$  in the range of

$40\text{--}150^\circ\text{C}$  under  $\text{N}_2$  atmosphere. The hydrodynamic radiuses of PVA in 0.1% aqueous solution at different pH were detected by a static laser scattering apparatus (BI-200SM, Brookhaven, U.S.A.) with 532nm laser source in vertical direction.

## Results and Discussion

### Effect of Compositing Time on Mechanical Properties of PVA / Split Composites

In order to maximize the modification effect, the modifier (PVA) should permeate into collagen fiber network thoroughly. But when the compositing time is too long at a high temperature ( $80^\circ\text{C}$ ) the mechanical properties of split may be weakened as partial denaturation of the collagen fibers. So, a reasonable

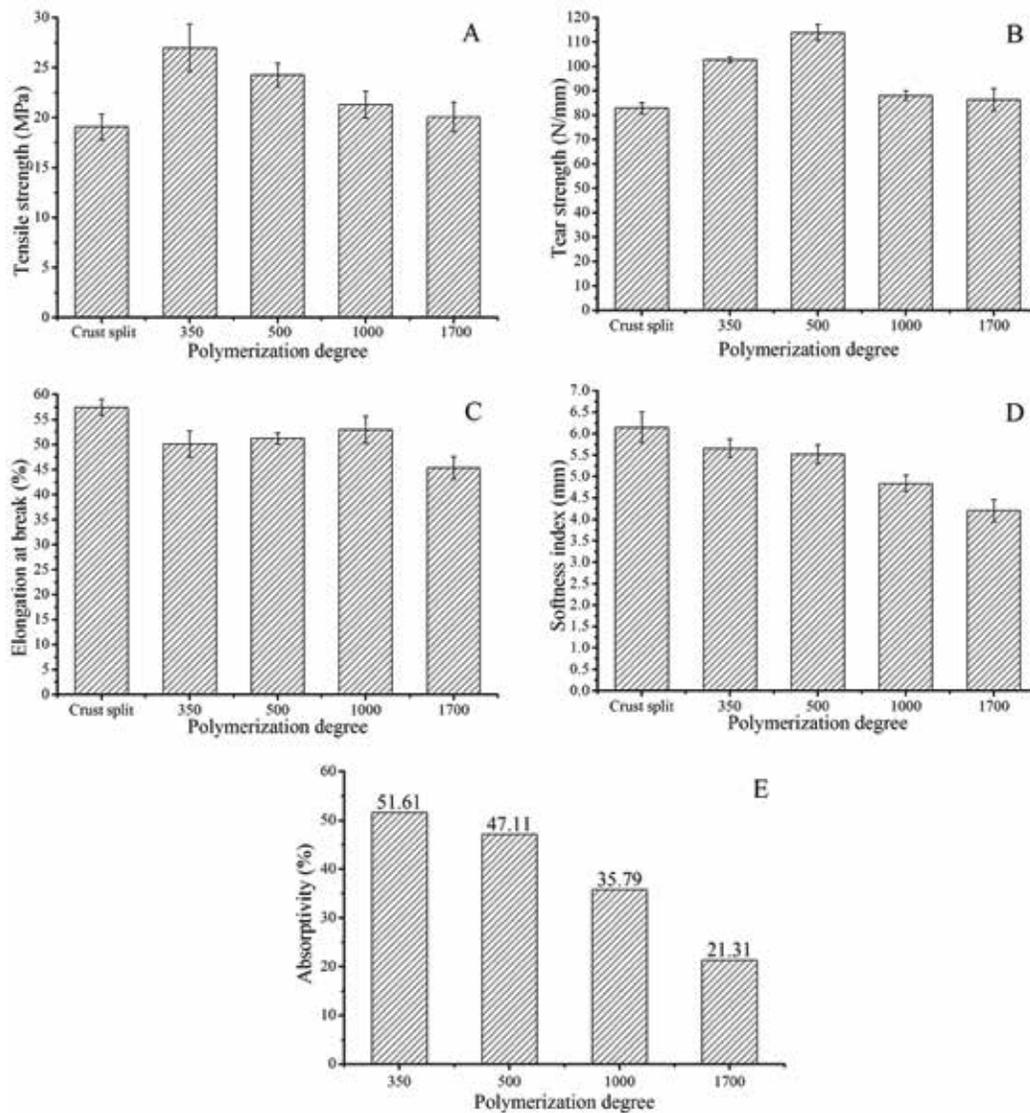


Figure 2. Mechanical properties of PVA / split composites prepared using PVAs with different polymerization degrees and absorptivities of these PVAs.

compositing time should first be established. Figure 1 shows properties of PVA / split composites prepared with different compositing time, including tensile and tear strengths (Figure 1A), elongation at break and softness index (Figure 1B), absorptivity of PVA and shrinkage temperature of composites (Figure 1C). The sample with compositing time of 0 stands for crust split. It is obvious that the tensile and tear strength increased first and then decreased with extending compositing time, which showed the in-situ recombination was effective for the enhancement of leather split strengths at the initial stage (< 120min). A longer compositing time would act against the modification performance, which might be due to the structure damage of collagen fiber network caused by high temperature. The differences in elongation at break, softness index and shrinkage temperature of composite were not significant in all the range of compositing time. The highest absorptivity of PVA in wet-blue split (54.9%) was achieved when compositing time

was 120 min. The decrease of PVA absorptivity with further extending compositing time might be due to the fact that the damaged collagen fiber network structure failed to absorb more PVA. Taken together, 120 min is considered as the most suitable compositing time for the in-situ recombination. A shorter time caused insufficient permeation, and a longer time leads to no significant improvement or even poorer properties of the composites.

#### Effect of Polymerization Degree and Alcoholysis Degree of PVA on Mechanical Properties of PVA / Split Composites

PVA is a water-soluble polymer obtained by free radical polymerization of vinyl acetate and partial hydrolysis of acetate groups. The water solubility of this macromolecule is affected both by its polymerization degree and alcoholysis degree.<sup>10</sup> When the alcoholysis degree is too low, the content of hydrophobic ester groups will make the macromolecule water-

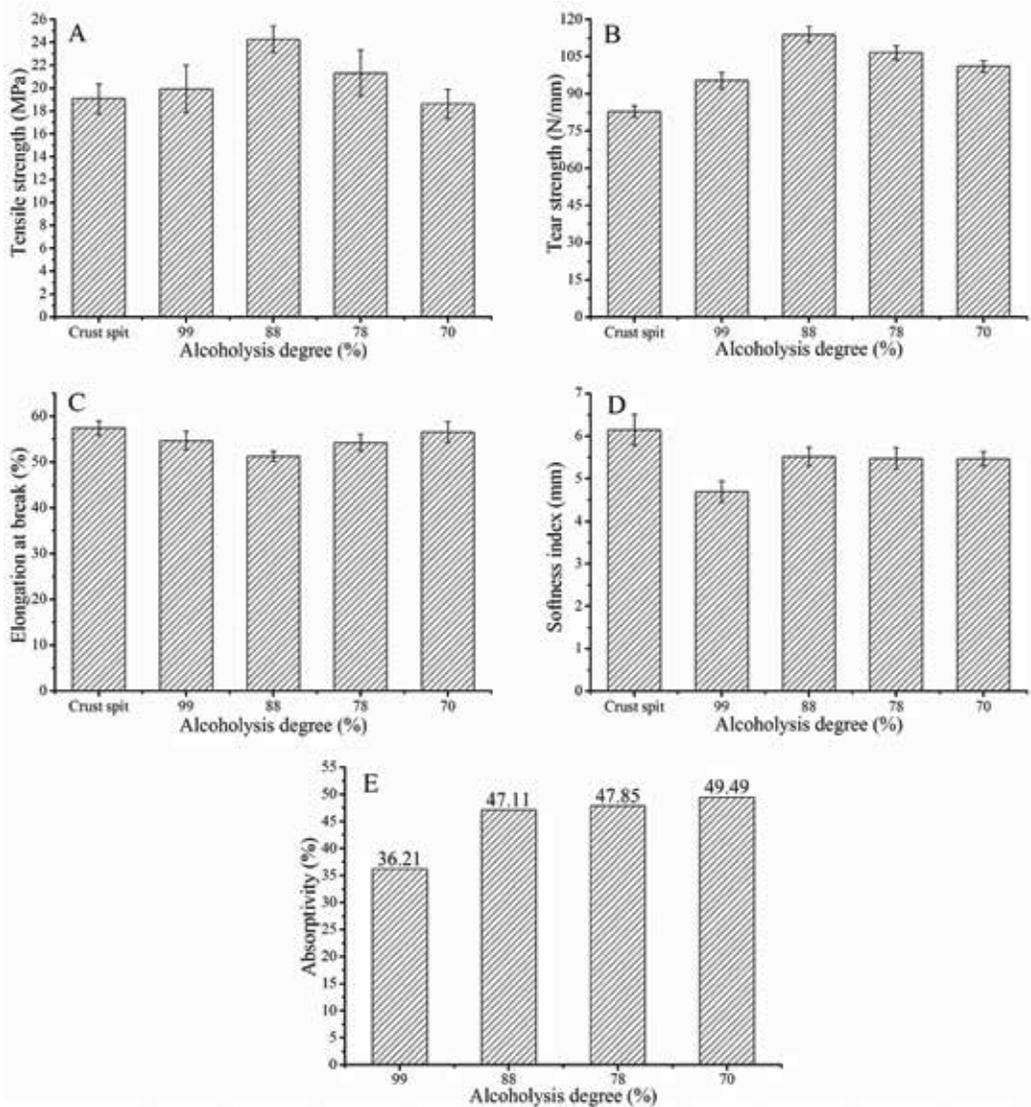


Figure 3. Mechanical properties of PVA / split composites prepared using PVAs with different alcoholysis degrees and absorptivities of these PVAs.

insoluble. When the alcoholysis degree is too high, the strong hydrogen bonding between hydroxyls will also weaken its water-solubility. As compositing agent, the polymerization degree and alcoholysis degree of PVA should be controlled in a proper range so that it has good water-solubility and the ability to form enough physical crosslinks between the collagen fibers.

Figure 2 shows mechanical properties of PVA / split composites prepared using PVAs with different polymerization degrees, and the absorptivities of these PVAs. All these PVAs have the same average alcoholysis degree of 88% (PVA-A, PVA-B, PVA-C, PVA-D). The results show that all these PVAs can enhance the tensile and tear strengths of leather split (Figure 2A, 2B) and decrease the elongation at break and softness index (Figure 2C, 2D). Moreover, collagen fiber network absorbs more PVA (Figure 2E) and presents a better tensile strength (Figure 2A) when the polymerization degree is smaller. Nonetheless, the composite made from PVA-A (average polymerization degree: 350) had a relatively weaker tear strength than that made from PVA-B (average polymerization degree: 500), probably because the short molecular chain of PVA-A failed to form enough physical crosslinks with the collagen fibers. Considering that the improvement of tear strength gets more attention than tensile strength for leather split, the PVA-B with a polymerization degree of 500 is considered as the most suitable compositing agent.

Figure 3 shows mechanical properties of PVA / split composites prepared using PVAs with different alcoholysis degrees and the absorptivities of these PVAs. All these PVAs have the same average polymerization degree of 500 (PVA-B, PVA-E, PVA-F, PVA-G). The results show that all these PVAs can also enhance the tensile and tear strengths of leather split (Figure 3A, 3B) and decrease the elongation at break and softness index (Figure 3C, 3D). The split modified by PVA-B had the best tensile and tear strengths. Moreover, PVA-E (alcoholysis degree: 99%) failed to infiltrate well into the collagen fiber network under experimental

conditions (Figure 3E), probably because of its extremely strong hydrogen-bond interaction with the split surface. The absorptivities of the other PVAs were at the same level. Overall, PVA-B, which has an appropriate chain length and hydroxy content is the most suitable for the in-situ recombination and can best modify split.

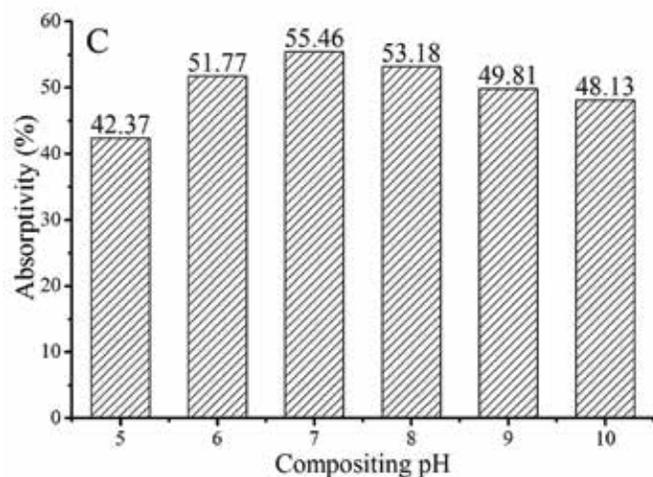
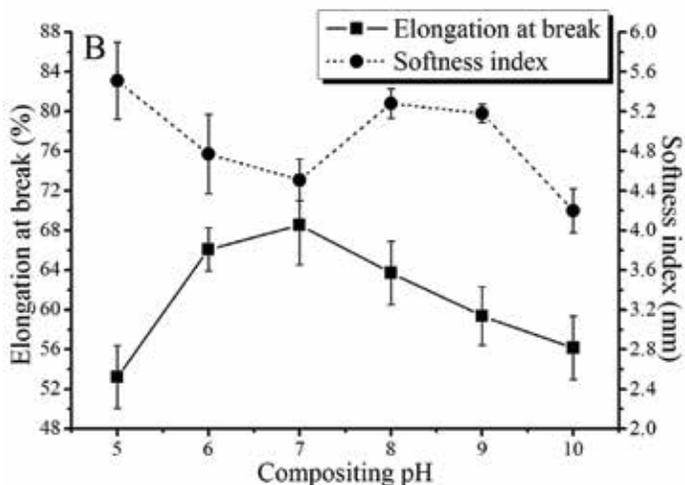
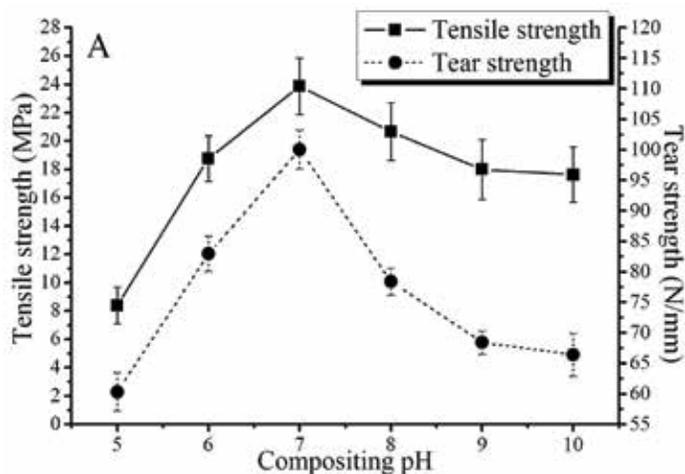


Figure 5 .Mechanical properties of PVA-B / split composites prepared with different compositing pH and absorptivities of PVA-B.

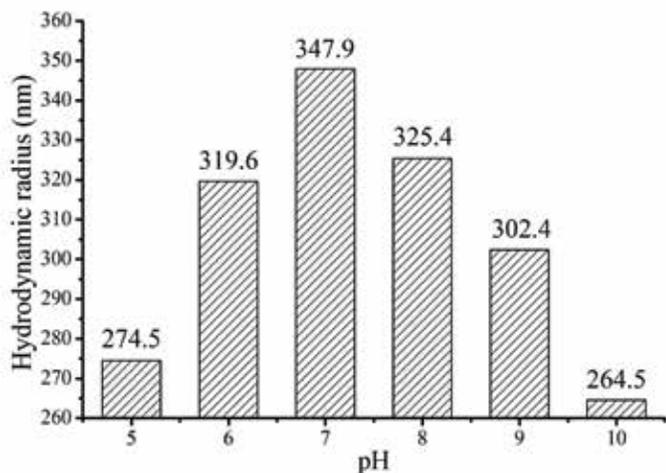


Figure 4. Hydrodynamic radius of PVA-B in 0.1% aqueous solution at different pH.

**Effect of pH of Compositing Progress on Mechanical Properties of PVA / Split Composites**

For most of the water-soluble polymers, there exists a suitable pH for achieving a stretched conformation.<sup>11</sup> A stretched conformation of PVA is very important to the in-situ recombination in this study, since it benefits the penetration of

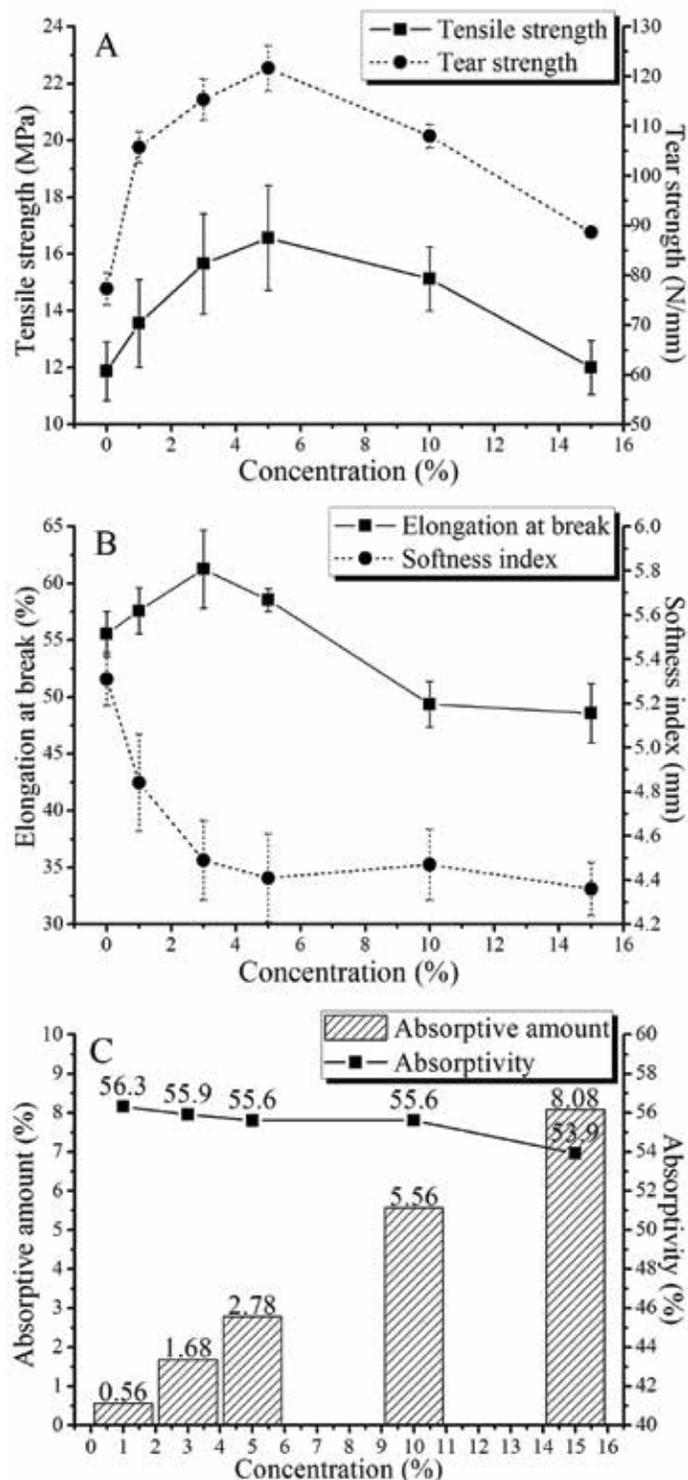


Figure 6. Mechanical properties of PVA / split composites prepared with different concentrations of PVA-B solutions and absorptions of PVA-B in split.

PVA, and makes molecular chains grasp collagen fibers more easily to form the IPN structure. Our determinations found that the hydrodynamic radius of PVA-B in 0.1% aqueous solution was the biggest (most stretched conformation) at pH 7.0, as shown in Figure 4. This implies that the suitable pH for compositing reaction of PVA and split would be 7.0. The results of mechanical property tests and absorptivity tests proved this point as shown in Figure 5. The split modified at pH 7.0 presented the highest absorptivity of PVA-B and the best tensile and tear strengths. Hence, pH 7.0 is considered as the most favorable solvent environment for the in-situ recombination modification.

**Effect of PVA Concentration on Mechanical Properties of PVA / Split Composites**

Apart from coulombic interaction, the collision between molecules and entanglement of molecular chains also affect molecular conformation, molecule-size and deformation resistance of PVA, and thus may influence the permeation in collagen fiber network and the crosslinking with collagen fibers.<sup>12,13</sup> Figure 6 shows mechanical properties of PVA-B / split composites prepared with different concentrations of PVA-B solutions and the absorptions of PVA-B in split. The sample with

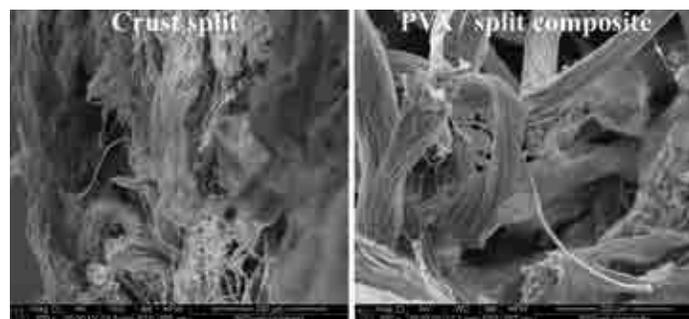


Figure 7. SEM photos of fracture cross-section of crust split and PVA / split composite (x500).

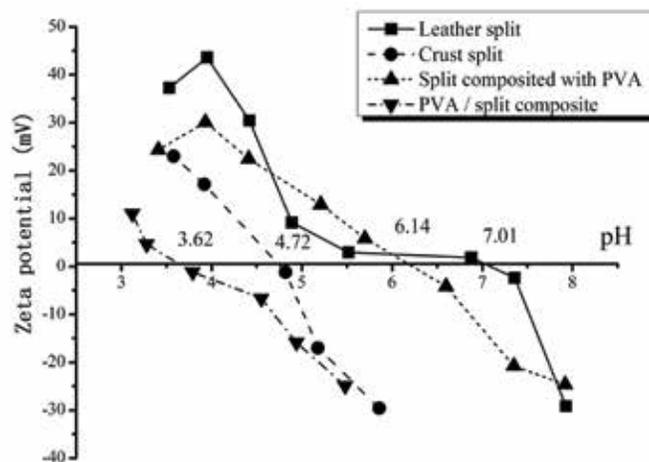


Figure 8. Zeta potential of wet-blue split, composited split, crust split and PVA / split composite.

a concentration of 0 stands for crust split. The results showed that tensile strength, tear strength and elongation at break of PVA / split composites had similar tendency (Figure 6A, 6B), i.e., these properties rose at the beginning with increasing concentration of PVA-B, peaked at the concentration of 5%, and then reduced. The softness index declined almost continually (Figure 6B). What's more, the increase of PVA-B concentration improved the absorptive amount, but mostly had no influence on the absorptivity (Figure 6C), which indicated PVA-B could penetrate into collagen fiber network well under experimental conditions. As we know, it is a general rule that the more polymer is contained in a material, the higher strength and lower elongation at break the material will have.<sup>14-16</sup> The strange-seeming regularities in this study might be caused by the different states of PVA-B blended in collagen fiber network. When the concentration of PVA-B was relatively low, PVA molecule chains could extend and transfer freely,<sup>13</sup> which was beneficial for the establishment of IPN structure in split, and thus the strengths of composites increased. When the concentration of PVA-B was relatively high, instead of forming physical crosslinks, PVA-B permeated into collagen fiber

network and became stress concentration points, and thus the composites could be undermined easily (both strengths and elongation at break decreased).<sup>17,18</sup> Besides, the increase of elongation at break in the low concentration range of PVA-B might be caused by a looser braided structure due to the high temperature. Meanwhile, the observed formation of PVA film on the surface of composite was reflected as a stiffer hand feel of the composite. In general, PVA-B solution with the concentration of 5% can enhance the strengths of leather split most significantly.

So, a satisfactory modification effect of leather split was achieved by using PVA with average polymerization degree of 500 and alcoholysis degree of 88% to composite with split for 120 min in a concentration of 5% at pH 7.0.

### Morphology Analysis of PVA / Split Composite

Figure 7 is SEM photos of fracture cross-sections of crust split and PVA-B / split composite prepared under the most favorable conditions as concluded above. It was shown that the structure of collagen fibers in crust split was not compact and collagen bundles were torn apart, which might mean that most of collagen fiber bore loading alone through the change of stress and strain. The collagen fibers in PVA-B / split composite still adhered firmly together, which meant collagen fibers could bear loading as a whole. These morphologies may be used to explain the enhancement of tensile and tear strengths of PVA / split composite.

### Potentiometric Analysis of PVA / Split Composite

Figure 8 shows the relationship between pH and Zeta potential of wet-blue split, composited split (un-fatliquored PVA / split composite), crust split (only fatliquored) and PVA / split composite (with fatliquoring). It is obvious that PVA compositing will lower the isoelectric point of collagen fibers. This was because the polar groups on collagen fibers were sealed by PVA, which is indirect evidence that the IPN structure was formed via in-situ recombination.

### Thermal Behavior of PVA / Split Composite

To ensure the construction of IPN structure via in-situ recombination, the thermal behaviors of PVA-B, crust split and PVA / split composite were also studied as shown in Figure 9. The DSC test results showed that the glass transition temperature ( $T_g$ ) of PVA-B was about 126.5°C (Fig. 9A), while the  $T_g$  rose to 136.5°C when it blended with collagen fibers (Fig. 9B). This implied that the movement of PVA-B molecular chains was restricted by collagen fiber network, and that the IPN structure existed in the PVA / split composite.

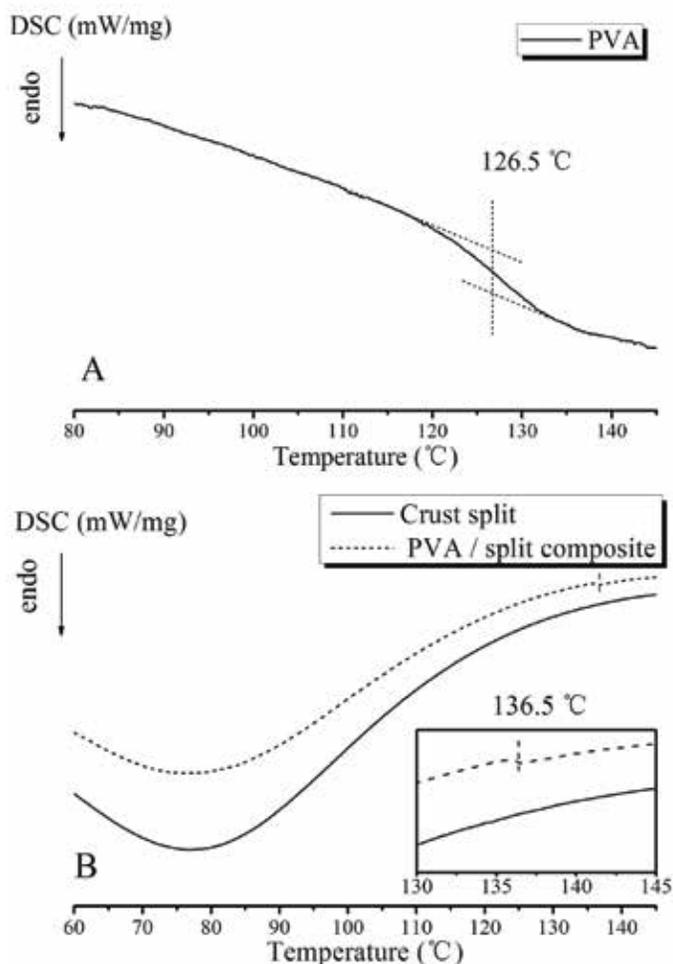


Figure 9. DSC cures of PVA-B crust split and PVA / split composite.

## Conclusions

Tensile and tear strengths of leather split can be improved remarkably by constructing an IPN structure between PVA and collagen fibers via in-situ recombination. The key points of the in-situ recombination include: 1) PVA should have a proper polymerization degree and alcoholysis degree, so that it can permeate well into the collagen fiber network and grasp collagen fibers to form enough physical crosslinks; 2) the appropriate concentration and pH of PVA solution, as well as reaction temperature and time, are required to ensure the PVA molecular chains have ideal stretched conformations during the compositing process. Under the optimized conditions in this research, tensile strength and tear strength of leather split (PVA/split composite) increased by 27% and 49%, respectively, compared to those of crust split. Obviously, the method of in-situ recombination is a cleaner and more acceptable technology for improving the strengths of leather split, since it does not use monomers and organic solvents, and the operations are quite simple.

## Acknowledgement

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