

# Hygienic Property of Microfiber Synthetic Leather Base Modified via a “Two-Step Method”

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## ABSTRACT

A “two-step method” was adopted to improve the hygienic property of polyamide microfiber synthetic leather base. Firstly, the amino-terminal hyperbranched polyamides (NH<sub>2</sub>-HBP) synthesized by N, N'-methylene bisacrylamide (MBA) and diethylene triamine (DETA) was cross-linked to microfiber synthetic leather base pretreated with formic acid, in which glutaraldehyde was the crosslinking agent. Secondly, Gelatin hydrolysate was cross-linked to the preliminary modified microfiber synthetic leather base by using glutaraldehyde as the crosslinking agent. The modified microfiber synthetic leather base was then obtained. Hygienic performances, mechanical properties, and the micro morphology were taken as indexes to optimize the dosages of glutaraldehyde and NH<sub>2</sub>-HBP.

The results show that when the glutaraldehyde dosage was 1.1 times that of the primary amino groups (the primary amino group dosage was about 0.201 mmol/g), the modification effect improved greatly. In this condition, the water vapor permeability, hygroscopicity, tensile strength, and tear strength of the base were 0.7691 g/10 cm<sup>2</sup>·24 h, 3.357 mL/g·24 h, 18.79 N/mm<sup>2</sup>, and 103.18 N/mm, respectively. These values were 86.7%, 48.8%, 19.8%, and 2.69% higher than those of unmodified base, respectively. When NH<sub>2</sub>-HBP dosage was three times that of the primary amino groups, the modification effect also improved. In this case, the water vapor permeability, hygroscopicity, tensile strength, and tear strength of the base were 0.5761 g/10 cm<sup>2</sup>·24 h, 3.274 mL/g·24 h, 18.79 N/mm<sup>2</sup>, and 103.4825 N/mm, respectively. These values were 113%, 42.3%, 3.5%, and 2.98% higher than those of the unmodified base, respectively. Meanwhile, the SEM image of the modified base showed that fiber dispersion was greatly increased in this condition.

**Keywords:** two-step reaction; amino-terminal hyperbranched polyamides; microfiber synthetic leather base; glutaraldehyde

## INTRODUCTION

Natural leather goods are preferred by many customers because of their excellent properties, such as superior hygroscopicity, good water vapor permeability, and wearing comfort. However, leather resources are limited. Therefore, the development of synthetic leather with excellent performance as a supplement of natural leather has gained increasing attention and has become a widely interesting research topic. The microfiber synthetic leather which has emerged in recent years is the most ideal substitute for natural leather. Continuous development in this research area led to an expansion of microfiber synthetic leather applications. Although properties such as the mechanical behavior of microfiber synthetic leather are better than those of natural leather, a relatively deep gap exists between microfiber synthetic leather and natural leather in the terms of several other properties, especially hygienic ones[1]. The water vapor permeability of crust leather is about 800 mg/(10 cm<sup>2</sup>·24 h), whereas that of microfiber synthetic leather is about 400 mg/(10 cm<sup>2</sup>·24 h) [2]. The moisture permeability of microfiber synthetic leather is the most optimal property among all the synthetic leathers. The main reason for the difference between the hygienic property of microfiber synthetic leather and natural leather is that more hydrophilic groups exist in the collagen fibers of natural leather than those in microfiber synthetic leather [3].

Several exploratory studies regarding the modification of microfiber synthetic leather have been carried out to solve this problem. By integrating numerous published reports, it was

found that increasing the internal active groups of microfiber synthetic leather is the most effective modification method. This method can be divided into two directions according to the two components of microfiber synthetic leather. In other words, modified polyamide fiber [4–11] and modified polyurethane [12–17]. However, whether the modification should be based on polyamide fiber or polyurethane has not been ascertained. Therefore, in this paper, a "two-step" modification process was carried out to improve the hygienic property of microfiber synthetic leather base. The "two-step" modification process means that a preliminary modified microfiber synthetic leather base was obtained by crosslinking amino-terminal hyperbranched polyamides (NH<sub>2</sub>-HBP) to a microfiber synthetic leather base pretreated with formic acid. In this process, glutaraldehyde was used as the crosslinking agent. Gelatin hydrolysate with more active groups was cross-linked to the preliminary modified microfiber synthetic leather base by using glutaraldehyde as the crosslinking agent. Thus, the active groups of the microfiber synthetic leather can be greatly increased, and their hygienic property would be effectively enhanced.

## EXPERIMENTAL

### Materials and Instruments

The materials and instruments used in the experiments were as follows: N, N'-methylene double acrylamide (AR, Tianjin Kemiou Chemical Reagent Co., Ltd.), DETA (AR, Tianjin Damao Chemical Reagent Factory), secondary distilled water (self-prepared), acetone (AR, Tianjin Fushen Fine Chemical Co., Ltd.), salicylaldehyde (AR, Sinopharm Chemical Reagent Co., Ltd.), pyridine (AR, Tianjin Kemiou Chemical Reagent Co., Ltd.), thymolphthalein (AR, Wuxi Zhanwang Chemical Co., Ltd.), sodium methoxide (AR, Tianjin Fuchen Chemical Reagent Factory), pancreatin (AR, Tianjin Fuchen Chemical Reagent Factory), gelatin (AR, Tianjin Fuchen Chemical Reagent Factory), glutaraldehyde (AR, Jinan Chemical Reagent Factory), microfiber synthetic leather base for shoes (industrial product, Zhejiang Zhonghui Synthetic Leather Base Co., Ltd.), constant temperature water bath oscillator (SHZ-C, Shanghai Pudong Optical Instrument Factory), and five-cylinder tanning machine (DJDØ350, Dongbei Pond Mining Machinery Factory, Xishan City).

### Preparation Experimentation

#### *Synthesis of NH<sub>2</sub>-HBP*

Amino-terminal hyperbranched polymers (NH<sub>2</sub>-HBP) were synthesized via a one-step method, in which N, N'-methylene bisacrylamide (MBA) and diethylene triamine (DETA) were raw materials. The procedure was as follows:

A specific amount of DETA was weighed and diluted by secondary distilled water [m(DETA):m (secondary distilled water) = 1:30] in ice-water bath. A specific amount of MBA [m(MBA):m (DETA) = 1:1.1] was weighed and added into a three-neck flask equipped with a thermometer and a refrigeration plant. Then diluted DETA was added, and the mixture reacted for 24 h at 60 °C after stirring and dissolution. After the reaction, the mixture was rotated in a rotary evaporator (the vacuum was -0.09 MPa) for 30 min at 80 °C to remove residual solvent, unreacted monomer and residual moisture. Acetone, the volume is five times of that the mixture was used to precipitate the product repeatedly for three times, and this process was conducted in a pear-shaped funnel. Finally, bright yellow viscous products (the primary amino group content was about 2.83 mmol/g) were obtained after the acetone was removed by the rotary evaporator (the vacuum was -0.09 MPa, rotated for 30 min at 50 °C).

#### *Preparation of Gelatin Hydrolysate*

The 30% gelatin solution was placed in a constant temperature water bath oscillator and oscillated until the gelatin completely swelled. The temperature of the water bath was adjusted to 45 °C, while the pH of the gelatin solution was 7.5. About 0.8% (based on the dry weight of gelatin) pancreatin was added, and the oscillation was continued for 6 h in this reaction conditions. The reaction was kept for 10 min after the temperature was increased to 90 °C to inactivate the enzyme before cooling. The formaldehyde method [18] was used to measure the prepared gelatin hydrolysate. The amine content was about 0.78 mmol/g.

#### *Modification of Microfiber Synthetic Leather Base with a "Two-Step Method"*

The modification method of the microfiber synthetic leather base with the "two-step method" and the dyeing process of the base are shown in Table I.

TABLE I. Dyeing process of NH<sub>2</sub>-HBP applied in the microfiber synthetic leather base.

Process	Dosage (%)	Material	Temperature (°C)	Time /min	Remarks
Formic acid pretreatment	3000	Water	40		
	3	Formic acid	40	60	Determination of the primary amino group content (N <sub>1</sub> / mmol/g)
	3000	Water		2×20	
“First-step” modification	3000	Water			
	1.1 N <sub>1</sub>	Glutaraldehyde	55	30+60	pH adjust to 5.5 after rotating for 30 min.
	3000	Water		3×20	pH adjust to 5.5 after rotating for 30 min.
	3 N <sub>1</sub>	Amino-terminal hyperbranched polymers	55	30+60	
	3000	Water		3×20	Determination of the primary amino group content (N <sub>2</sub> / mmol/g)
“Second-step” modification	3000	Water			
	1.1 N <sub>2</sub>	Glutaraldehyde	55	30+60	pH adjust to 5.5 after rotating for 30 min.
	3000	Water		3×20	pH adjust to 5.5 after rotating for 30 min.
	3 N <sub>2</sub>	Gelatin hydrolysate	55	30+60	
	3000	Water		3×20	
Final step					Extraction and drying.

Summary of the experiment:

- Polyamide microfiber synthetic leather base was used as the raw material in this experiment.
- All bases were boiled for 30 min at 70 °C to remove the oil and other filth before the experiment.
- The dosage percentage related to this experimental process was calculated by the quality of the base, excluding glutaraldehyde, amino-terminal hyperbranched polymers, and gelatin hydrolysate.
- N<sub>1</sub>/N<sub>2</sub> in this process represents the primary amino group content of the base treated with acid, which was measured according to the salicylaldehyde method.
- The glutaraldehyde dosage was calculated according to the formula  $1.1 \times M \times N_1 (N_2) \times 100.12$ , where M is the quality of the base, N<sub>1</sub>/N<sub>2</sub> is the primary amino group content of the base, and 100.12 is the molecular weight of glutaraldehyde.
- The amino-terminal hyperbranched polymer dosage was calculated according to the formula  $3 \times M \times N_1 / 2.83$ , where M is the quality of the base, N<sub>1</sub> is the content of the primary amino group in the base, and 2.83 is the primary amino group content of the amino-terminal hyperbranched polymers.
- The gelatin hydrolysate dosage was calculated according to formula  $3 \times M \times N_2 / 0.078$ , where M is the quality of the base, N<sub>2</sub> is the content of the primary amino group in the base, and 0.078 is the primary amino group content of gelatin hydrolysate.

### **Optimization of Glutaraldehyde Dosage**

According to "the first-step" modification process shown in *Table I*, the glutaraldehyde dosage was optimized. Other conditions had no change. The hygienic and mechanical properties of the microfiber synthetic leather base were taken as indexes, the glutaraldehyde dosage was kept as 0.5, 0.8, 0.9, 1.0, 1.1, 1.2, and 1.5 times higher than those of the primary amino group of the base treated by acid. The glutaraldehyde dosage was optimized.

### **Optimization of amino-terminal hyperbranched polymer dosage**

According to the "first-step" modification process shown in *Table I*, the amino-terminal hyperbranched polymer dosage was optimized. Other conditions were kept the same. The and mechanical properties, as well as the change of fiber dispersion in the microfiber synthetic leather base were investigated. The amino-terminal hyperbranched polymer dosage was 0, 1, 2, 3, 4, 5, and 6 times higher than those of the primary amino group of the acid-treated base. The amino-terminal hyperbranched polymer dosage was optimized.

### **Characterization**

- (1) The water absorption of the base were tested according to GB/T 4689.21-1996 [19], The water vapor permeability of the base was tested according to QB/T 1811-1993 [20], The tensile strength and elongation at break of the base were tested according to QB/T 2710-2005 [21] via Tensile Tester (PT-1171, Dongguan Baoda International co., LTD.), The tear strength of the base was tested according to QB-T 3812.6-1999 [22] via Tensile Tester (PT-1171, Dongguan Baoda International co., LTD.).
- (2) The microstructure of the modified base was observed using a TM-1000 electron microscope (Hitachi Limited).
- (3) The thermal weight loss of the modified base was determined by a TGA Q500 thermogravimetric analyzer (America TA Company).
- (4) The contact angle of the modified base was determined by an OCA20 contact angle measurement instrument (Germany Dataphysics Company).
- (5) The primary amino group content of the base was measured by the salicylaldehyde method [23].
- (6) The carboxyl groups' content of the base was measured with phenolphthalein indicator and hydroxide standard solution [23].

- (7) The atomic force microscopy (AFM) images of the microfiber synthetic leather base were obtained by using a CSPM3000 atomic force microscope (Chinese Benyuan Company).

## **RESULTS AND DISCUSSION**

The microfiber synthetic leather base was modified using the "two-step method" as described above, in which glutaraldehyde was the crosslinking agent, and its combination schematic diagram is shown in *Figure 1* and *Figure 2*.

*Figure 3* illustrates the contrastive figure of the contact angle of the modified base via the "two-step method", the unmodified base, as well as the base treated with formic acid. *Figure 3* shows that the contact angle of the modified base via the "two-step method" was greatly reduced, which means that the wettability of the modified base via the "two-step method" was greatly improved compared with that of the unmodified base. That is because  $\text{NH}_2$ -HBP and gelatin hydrolysate were successfully cross-linked to the base via the "two-step method." The water absorption ability of the base also significantly increased. The thermal weight loss of the three kinds of base were compared and analyzed to further confirm the experimental results. As shown in *Figure 4*, the base began to gradually disappear at 230 °C. The treatment with formic acid had no effect on the thermal weight loss of the base; however, the thermal weight loss rate of the modified base via the "two-step method" relatively increased, because when the thermal weight loss was 5 wt%, the temperature of unmodified base,  $\text{NH}_2$ -HBP, and gelatin hydrolysate was about 330 °C, 230 °C, and 240 °C [24], respectively. Therefore, the initial temperature for their decomposition was different. After modification via the "two-step method", a specific amount of gelatin hydrolysate and  $\text{NH}_2$ -HBP were cross-linked with the inner part of the microfiber base. Thus, the thermal weight loss of the modified base was three times that of the thermogravimetric result of the bases, namely,  $\text{NH}_2$ -HBP and gelatin hydrolysate.

*Figure 4* shows that gelatin hydrolysate and  $\text{NH}_2$ -HBP were successfully cross-linked with the base after modification via the "two-step method". *Figure 5* illustrates the AFM contrast figure of the modified base via the "two-step method," the unmodified base and the base treated with formic acid. As is shown in *Figure 5*, the surface roughness of the base treated with formic acid slightly

increased compared with that of the unmodified base. This indicates that the base was corroded by formic acid, and this corrosion increased surface roughness of the base. The base surface roughness increased after it was modified via the "two-step method" because a large amount of gelatin hydrolysate and  $\text{NH}_2\text{-HBP}$  was cross-linked to the microfibrillar base. *Figure 5* also shows that gelatin hydrolysate and  $\text{NH}_2\text{-HBP}$  were successfully cross-linked to the base after modification via the "two-step method". *Figure 6* shows the content of carboxyl groups under different treatment conditions. As shown in *Figure 6*, the content of carboxyl groups of base "modified by the two-step method" could reach to 0.426mmol/g, which was 1.54 times higher than that of the base treated with

formic acid. This might be due to the import of  $\text{NH}_2\text{-HBP}$ , which increased the amino group content of the modified microfibrillar base greatly, and also increased the number of the binding points between gelatin hydrolysate and the microfibrillar base. So the binding capacity between gelatin hydrolysate and the microfibrillar base modified with "two-step method" increased. The content of carboxyl groups increased as well. *Figure 6* establishes that the "two-step method" modification was successful.

From the results presented in *Figures 3, 4, 5 and 6*, it is noted that several active substances were combined with the base. Thus, the modification methods used in these studies were effective.

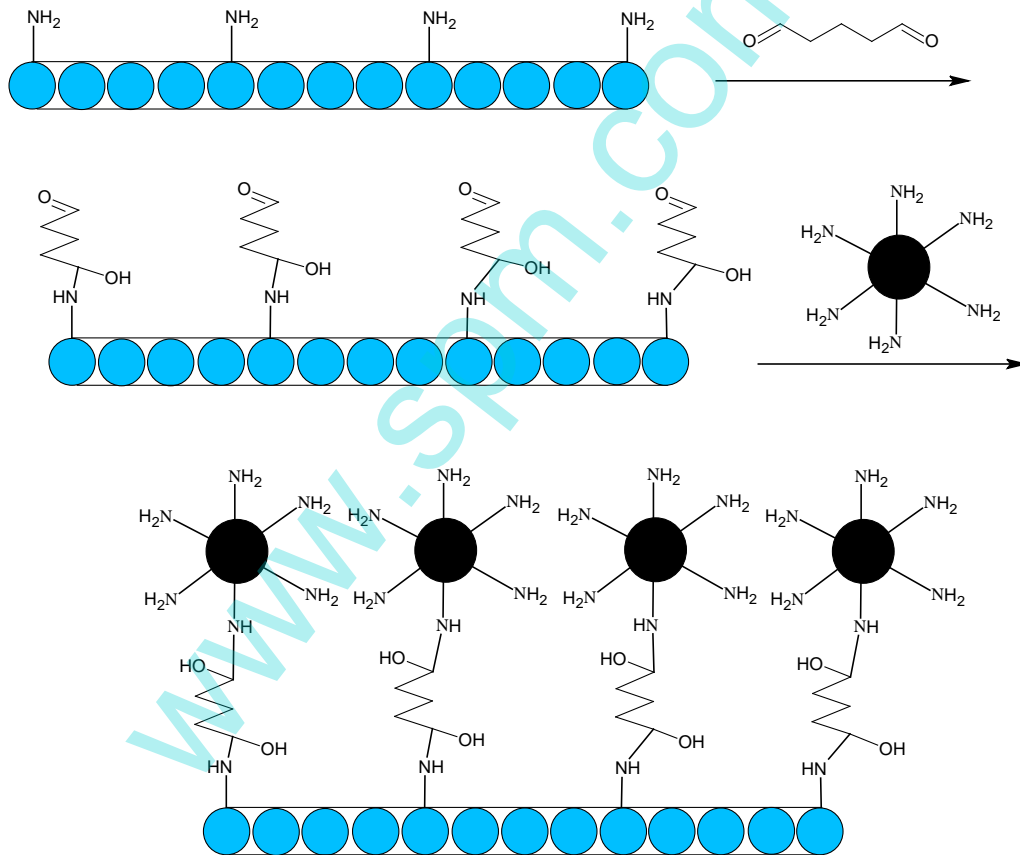


FIGURE 1. First step combination schematic diagram of the microfibrillar synthetic leather base modification by using the "two-step method."

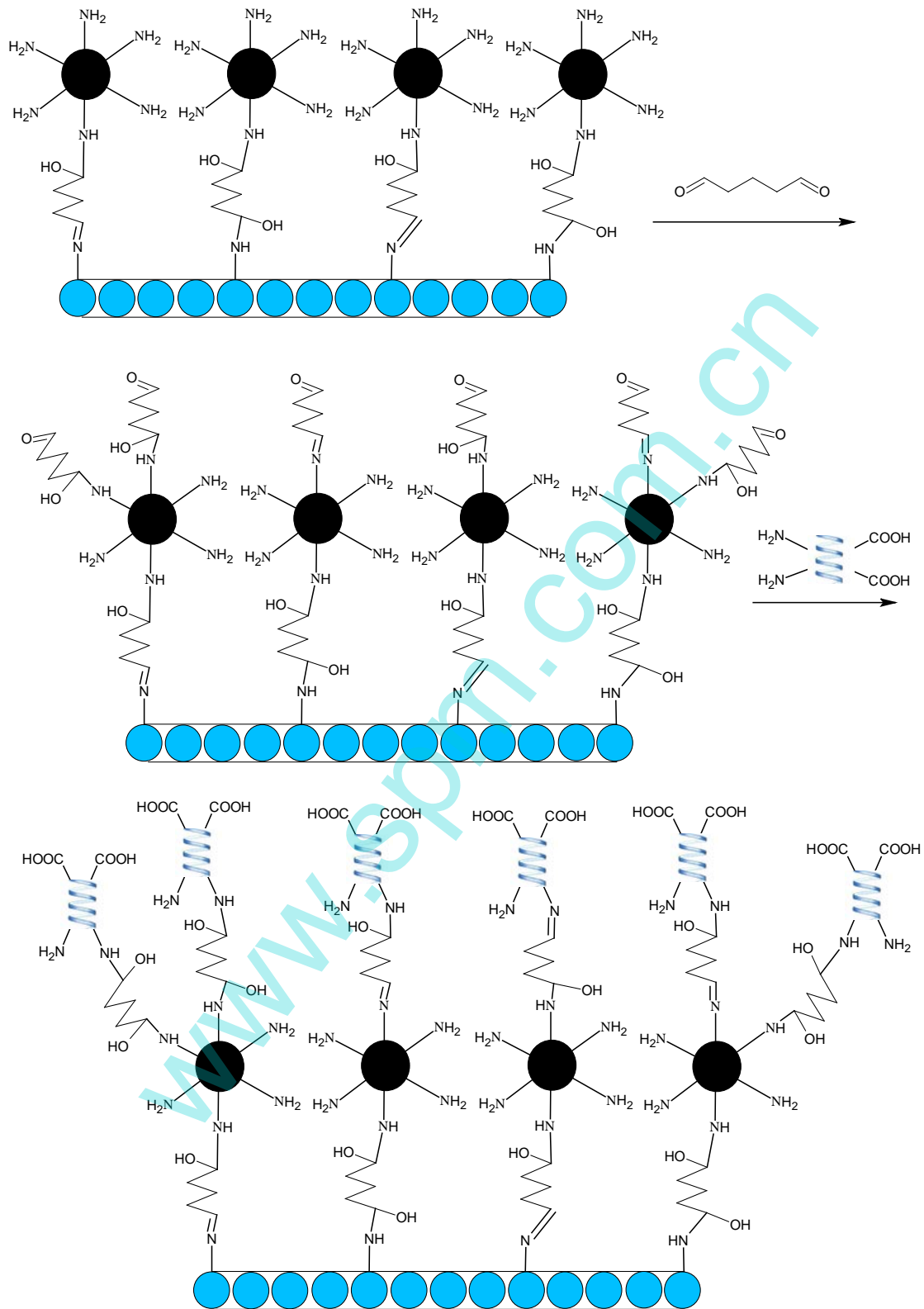


FIGURE 2. Second step combination schematic diagram of the microfiber synthetic leather base modification by using the "two-step method."



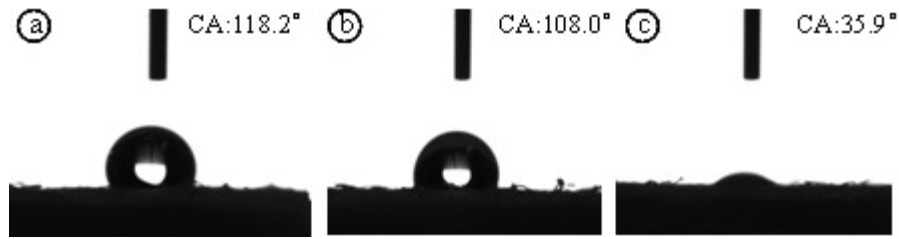


FIGURE 3. Contact angle contrast figure of the unmodified base, the modified base treated with formic acid, and the base modified via the "two-step method." Figures a, b, and c represent the unmodified base, the modified base treated with formic acid, and the base modified via the "two-step method."

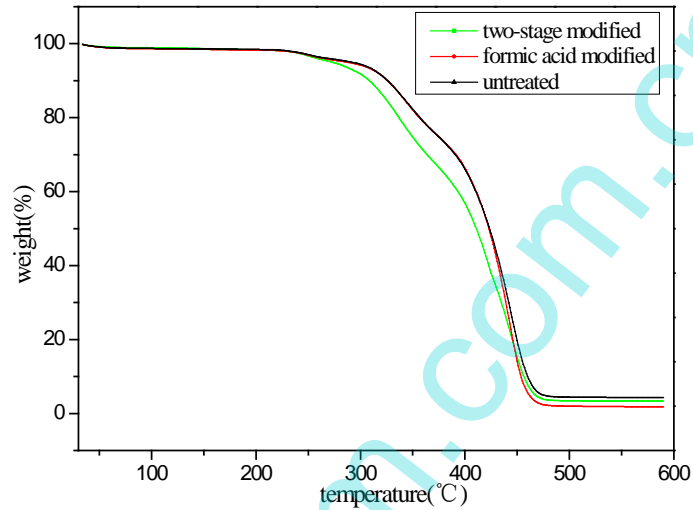


FIGURE 4. TGA contrast figure of the unmodified base, the base treated with formic acid, and the base modified via the "two-step method."

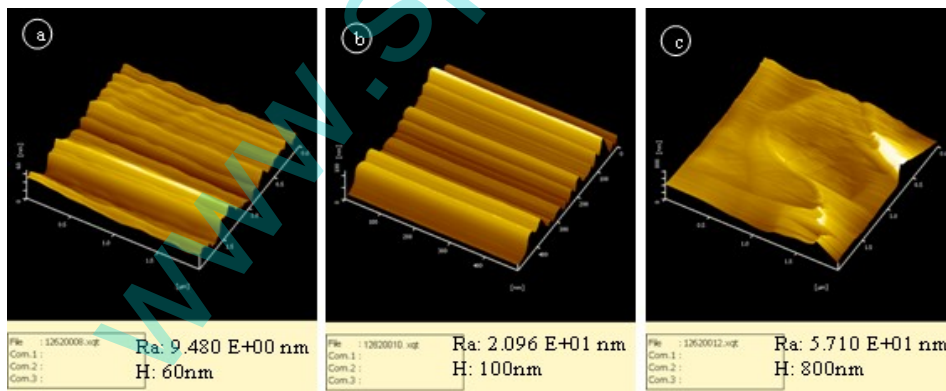


FIGURE 5. AMF contrast figure of the unmodified base, the base treated with formic acid, and the base modified via the "two-step method." Figures a, b, and c represent the unmodified base, the modified base treated with formic acid, and the base modified via the "two-step method."

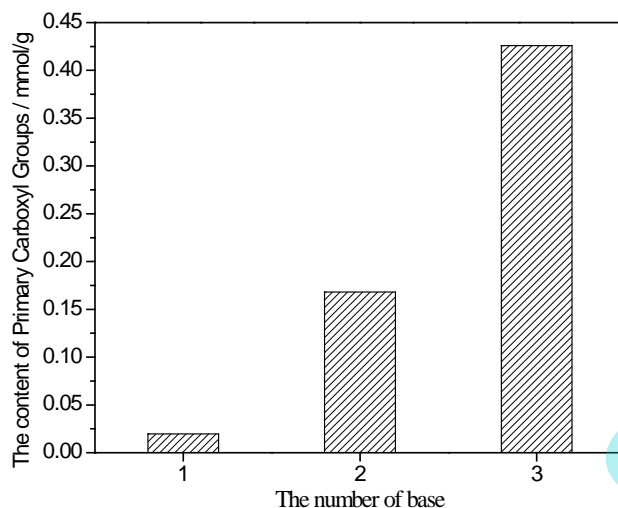


FIGURE 6. The content of carboxyl groups comparison picture in different treatment conditions. The 1, 2 and 3 represent the unmodified base, the modified base treated with formic acid, and the base modified via the "two-step method."

### Optimization of Glutaraldehyde Dosage

The glutaraldehyde dosage was determined according to the operating procedure discussed previously. The hygienic and mechanical properties of the microfiber synthetic leather base were investigated when the glutaraldehyde dosages were 0, 0.5, 0.8, 0.9, 1.0, 1.1, 1.2, and 1.5 times higher than those of the primary amino group of the acid-treated base. The glutaraldehyde dosage was also optimized.

Figure 7 shows that when the glutaraldehyde dosage was more than 1.1 times higher than that of the primary amino group base, the water vapor permeability of the base gradually improved with the increase of the glutaraldehyde dosage. The water vapor permeability gradually became constant. As shown in Figures 1 and 2, the glutaraldehyde might cross-linked with the primary amino group of base and was significantly consumed when the glutaraldehyde dosage was low. Thus, the amount of combination points of NH<sub>2</sub>-HBP with base, as well as the combination quantity of gelatin hydrolysate with base decreased. With the increase of glutaraldehyde dosage, the activity groups which could combine with NH<sub>2</sub>-HBP also increased, as a result, the combination of gelatin hydrolysate with base increased. The water vapor permeability of the base gradually improved as the activity groups increased. When the glutaraldehyde dosage was 1.1 times higher than that of the primary amino group, single point combination of glutaraldehyde and base

was predominate. Therefore, the combination quantities of NH<sub>2</sub>-HBP and gelatin hydrolysate were maximum, which improved the water vapor permeability of the base was the best. Excess glutaraldehyde could be observed as the glutaraldehyde dosage was continuously increased, but the excess glutaraldehyde could be washed out. Thus, the application effect was not better than that when the glutaraldehyde dosage was 1.1 times higher than that of the primary amino group. Figure 7 shows that the water vapor permeability gradually became smooth when the glutaraldehyde dosage was more than 1.1 times higher than that of the primary amino group of the base. Thus, when the glutaraldehyde dosage was 1.1 times higher than that of the primary amino group of the base, the effect was preferable in improving the water vapor permeability of the base.

Figure 8 illustrates the hygroscopicity of the base modified under different glutaraldehyde dosages. As can be seen in Figure 8, the hygroscopicity of the base improved and then gradually became smooth as the glutaraldehyde dosage increased. The same trend was exhibited by the change in the water vapor permeability of the base for the same reason. Thus, the glutaraldehyde dosage at 1.1 times higher than that of the primary amino group of the base was preferable in improving the hygroscopicity of the base.



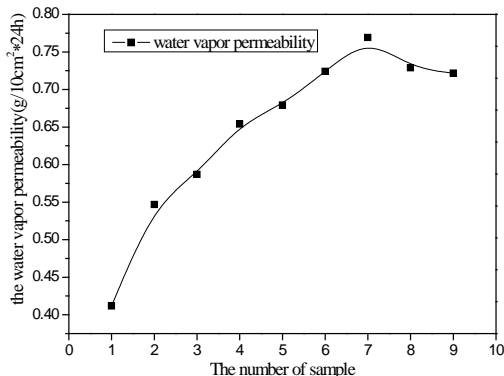


FIGURE 7. Water vapor permeability of the modified base. The Number 1 represents the unmodified base. Numbers 2, 3, 4, 5, 6, 7, 8, and 9 represent the modified bases with glutaraldehyde dosage at 0, 0.5, 0.8, 0.9, 1.0, 1.1, 1.2, and 1.5 times higher than those of the primary amino group of the base, respectively.

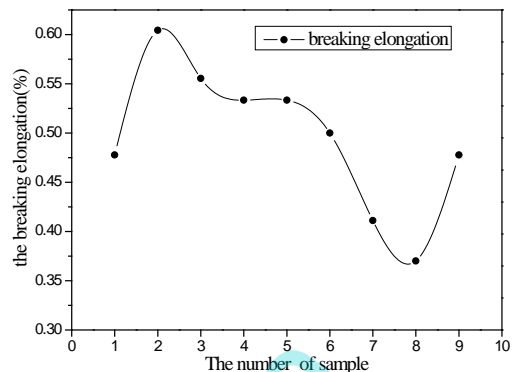


FIGURE 10. Breaking elongation of the modified base. The Numbers of sample are the same as in Figure 7.

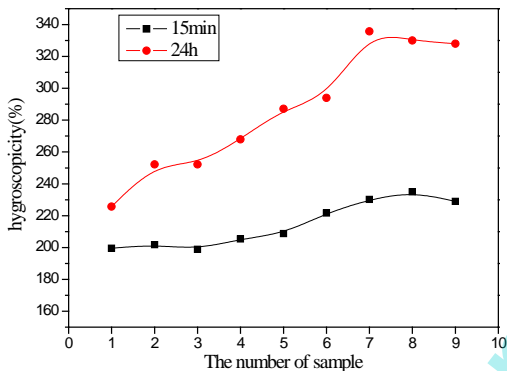


FIGURE 8. Hygroscopicity of the modified base. The Numbers of sample are the same as in Figure 7.

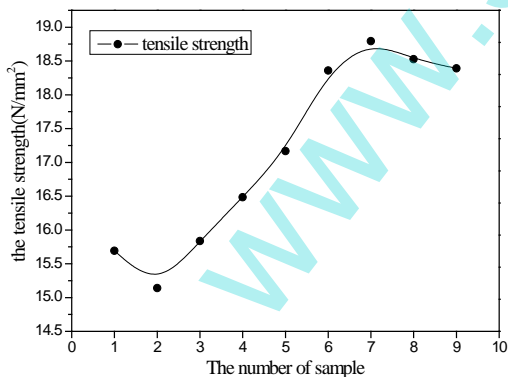


FIGURE 9. Tensile strength of the modified base. The Numbers of sample are the same as in Figure 7.

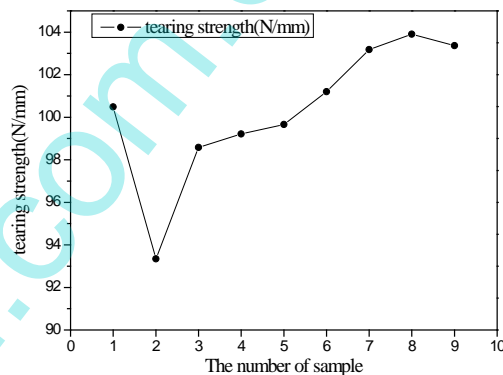


FIGURE 11. Tear strength of the modified base. The Numbers of sample are the same as in Figure 7.

Figures 9, 10, and 11 show the change of the mechanical properties of the base modified with different dosages of glutaraldehyde. Based on the figures, the mechanical properties of the base slightly decreased when the glutaraldehyde dosage was zero, because of the acid hydrolysis effect on the base. However, the crosslinking of glutaraldehyde and base increased the mechanical properties of the base when glutaraldehyde was added. Meanwhile, the crosslinking of NH<sub>2</sub>-HBP and gelatin hydrolysate with base carried out in the inner part of the base also yielded an improvement of the mechanical properties of the base, because of the greater number of active groups in NH<sub>2</sub>-HBP and gelatin hydrolysate. A large number of active groups in NH<sub>2</sub>-HBP and gelatin hydrolysate could increase the hydrogen bonding forces of the base, which had an effect on the mechanical properties of the base.

### Optimization of Amino-Terminal Hyperbranched Polymer Dosage

The NH<sub>2</sub>-HBP dosage was determined according to the procedure discussed previously. The hygienic and mechanical properties of the microfiber synthetic leather base were investigated with NH<sub>2</sub>-HBP dosages of 0, 1, 2, 3, 4, 5, and 6 times higher than that of the primary amino group of the acid-treated base. The NH<sub>2</sub>-HBP dosage was also optimized.

Figure 12 shows the change of the water vapor permeability of the base with different NH<sub>2</sub>-HBP dosages. As can be seen from Figure 12, the water vapor permeability of the base gradually improved with the increase of the NH<sub>2</sub>-HBP dosage. The water vapor permeability of the base slightly decreased when the NH<sub>2</sub>-HBP dosage was more than three times higher than that of the primary amino group of the acid-treated base. Taking the results of Figures 1 and 2 into consideration, the amino active groups in the inner part of the base also increased when the NH<sub>2</sub>-HBP dosages gradually increased. Thus, the combination quantity of gelatin hydrolysate in the second step also gradually increased. The hydrophilic groups increased; as a result, the water vapor permeability of the base was improved. However, when the NH<sub>2</sub>-HBP dosage was excessive, the combination quantity of NH<sub>2</sub>-HBP and gelatin hydrolysate on the surface of the base were also excessive. Moreover, the pores of the base were jammed to an extent; thus, the passage of water vapor through the base was difficult, and in this case, the water vapor permeability reduced. Therefore, the NH<sub>2</sub>-HBP dosage that was three times higher than that of the primary amino group of the base was optimum for improving the water vapor permeability of the base.

Figure 13 shows the change of the hygroscopicity of the base with different NH<sub>2</sub>-HBP dosages. From Figure 13, the hygroscopicity of the base improved as the NH<sub>2</sub>-HBP dosage increased. When the NH<sub>2</sub>-HBP dosage was more than three times higher than that of the primary amino group of the acid-treated base, there was nearly no change in hygroscopicity, because the increase of NH<sub>2</sub>-HBP dosage increased the quantity of the hydrophilic groups and improved the hygroscopicity of the base. However, when the NH<sub>2</sub>-HBP dosage was excessive, the combination quantity of NH<sub>2</sub>-HBP cross-linked on the surface of the base was also excessive, which led to the combination of more gelatin hydrolysate to the surface of the base. Penetration and combination became more difficult in the inner part of the base; consequently, the activity groups of the base did not increase as the NH<sub>2</sub>-HBP dosage increased. The change in hygroscopicity of the base gradually became smooth. Therefore, considering the contribution of NH<sub>2</sub>-HBP dosage to the hygroscopicity of the base, the NH<sub>2</sub>-HBP dosage that was three times higher than that of the primary amino group of the base was optimum.

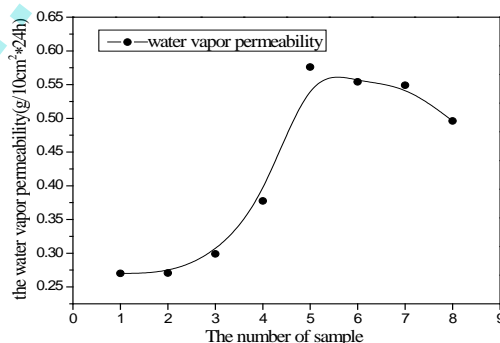


FIGURE 12. Water vapor permeability of the modified base. Number 1 represents the unmodified base. Numbers 2, 3, 4, 5, 6, 7, and 8 represent the modified base with amino-terminal hyperbranched polyamide dosage at 0, 1, 2, 3, 4, 5, and 6 times higher than that of the primary amino group of the base.

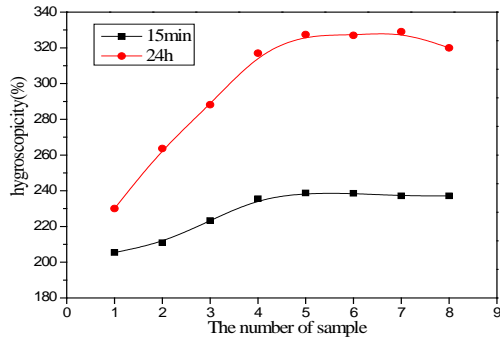


FIGURE 13. Hygroscopicity of the modified base. The Numbers of sample are the same as in Figure 12.

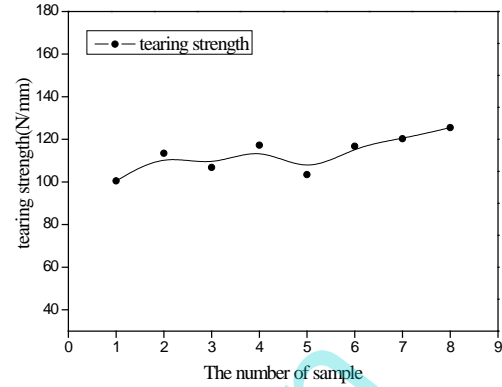


FIGURE 16. Tear strength of the modified base. The Numbers of sample are the same as in Figure 12.

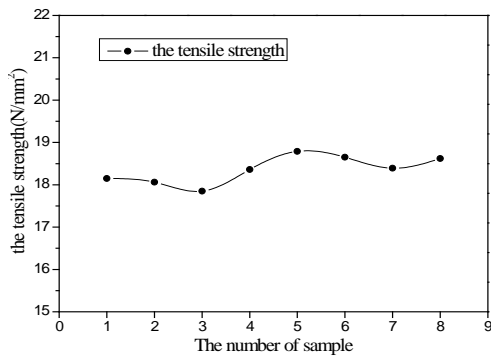


FIGURE 14. Tensile strength of the modified base. The Numbers of sample are the same as in Figure 12.

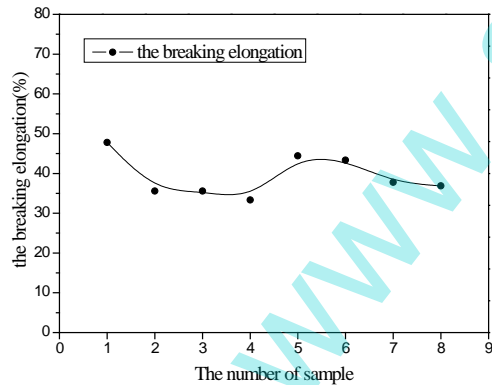


FIGURE 15. Breaking elongation of the modified base. The Numbers of sample are the same as in Figure 12.

Figures 14, 15, and 16 show the change in tensile strength, elongation at break, and tear strength. The mechanical properties of the base were not greatly affected by the  $\text{NH}_2\text{-HBP}$  dosage, because the mechanical properties of the base were mainly affected by the crosslinking effect of glutaraldehyde with base. Therefore, the  $\text{NH}_2\text{-HBP}$  dosage had minimal effect on the mechanical properties of the base when the same glutaraldehyde dosage was used. Overall, the mechanical properties of the base were not greatly reduced when the modification method was used. This result confirms that the effect of this modification method was good.

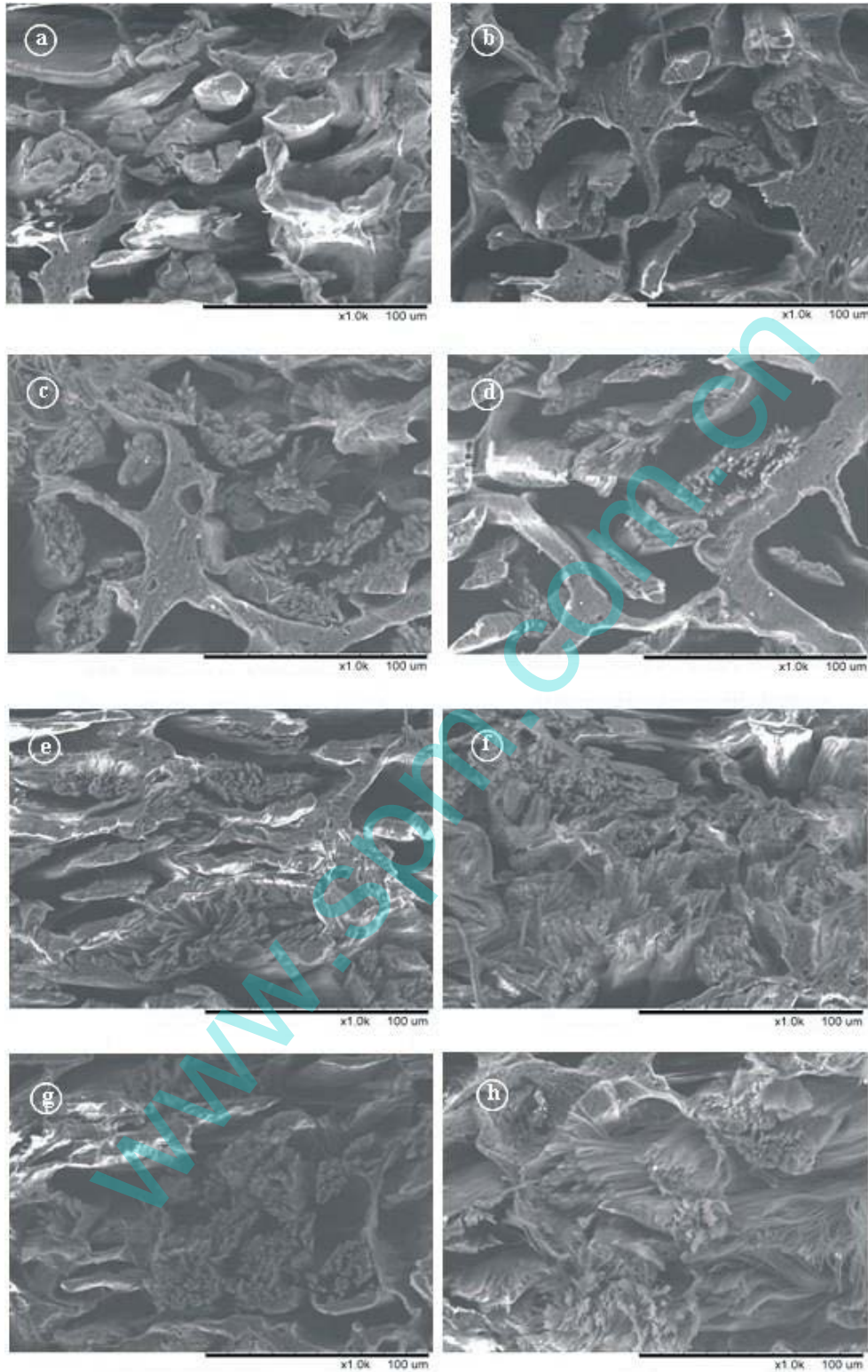


FIGURE 17. SEM contrast diagram of the modified microfiber synthetic leather base with  $\text{NH}_2\text{-HBP}$  at different dosages. Figure a represents the unmodified base. Figures b, c, d, e, f, g, and h represent the modified base with amino-terminal hyperbranched polyamide dosages at 0, 1, 2, 3, 4, 5, and 6 times higher than that of the primary amino group of the base, respectively.

Figure 17 shows the SEM images of the modified base with different NH<sub>2</sub>-HBP dosages. Figure a illustrates that the fibers of the unmodified base adhered to the bundles. Figure b shows that the fiber bundles were loosened to a particular degree by formic acid even if NH<sub>2</sub>-HBP was not added. The degree of looseness of the fiber bundles gradually increased as the NH<sub>2</sub>-HBP dosage increased. When the NH<sub>2</sub>-HBP dosage was more than three times higher than that of the primary amino group of the base, the degree of looseness of the fiber bundles had no significant increase. These groups exhibited positive charge in acid condition because of the hydrolysis of formic acid to the fiber, which made the base expose some groups. Thus, the fiber bundles were slightly scattered. When NH<sub>2</sub>-HBP and gelatin hydrolysate were added to the base, isolation and filling effect among fibers occurred, because of the special space structure, NH<sub>2</sub>-HBP performance, and a greater number of active groups of gelatin hydrolysate. Thus, the fiber bundles in the base were dispersed at a greater degree. The dispersion of the base fibers led to the improvement of the hygienic property of the base, which confirms that the modification effect was excellent from the microcosmic structure.

## CONCLUSION

The “two-step method” was adopted to modify the polyamide microfiber synthetic leather base in this study. Comparative analyses of the contact angle, AFM images, and TGA images of the unmodified and modified bases were performed, and the results show that gelatin hydrolysate and NH<sub>2</sub>-HBP were successfully introduced into the microfiber synthetic leather base. At the same time, the dosages of glutaraldehyde and NH<sub>2</sub>-HBP used in the modification were optimized.

When the “two-step method” was adopted to modify the polyamide microfiber synthetic leather base, the glutaraldehyde dosage was 1.1 times higher than that of the primary amino groups (the primary amino group dosage was about 0.201mmol/g), and the modification effect was good. The water vapor permeability, hygroscopicity, tensile strength, and tear strength of the base were 0.7691 g/10 cm<sup>2</sup>·24 h, 3.357 mL/g·24 h, 18.79 N/mm<sup>2</sup>, and 103.18 N/mm, respectively. These values increased by 86.7%, 48.8%, 19.8%, and 2.69% compared with that of the unmodified base.

The NH<sub>2</sub>-HBP dosage was three times higher than that of the primary amino group of the base. The modification effect was better when the “two-step method” was adopted to modify the polyamide microfiber synthetic leather base. The water vapor permeability, hygroscopicity, tensile strength, and tear strength of the base were 0.5761 g/10 cm<sup>2</sup>·24 h, 3.274 mL/g·24 h, 18.79 N/mm<sup>2</sup>, and 103.4825 N/mm. These values increased by 113%, 42.3%, 3.5%, and 2.98% compared with that of the unmodified base. The SEM images of the modified base show that the fiber dispersed well in this condition.

In summary, the hygienic property of the base can be greatly improved and a favorable effect can be achieved by adopting the “two-step method” to modify the microfiber synthetic leather base.

## ACKNOWLEDGMENTS

This work was supported by the National Science Foundation for Young Scholars of China (No: 51103082), the Doctoral Fund of Ministry of Education of China (No: 20116125120002), Shaanxi Province Science and Technology Foundation for Youths(No: 2013KJxx-78), Key Scientific Research Group of Shaanxi province (No: 2013KCT-08) and Scientific Research Group of Shaanxi University of Science and Technology (No: TD12-04).

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