

Improvement of the Sanitary Property of Microfiber Synthetic Leather Base by PAMAM

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ABSTRACT

In this paper, polyamidoamine dendrimers were cross-linked to polyamide microfiber synthetic leather base pretreated with sulfuric acid by using glutaraldehyde and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide as crosslinking agents to improve the hygienic properties of the base. Water vapor permeability and moisture absorption were the main performance indicators in this process. The SEM and AFM images of the modified base show that the microfiber pores moderately opened and the fiber became rougher. Contact angle and energy dispersive spectrometer analyses reveal that the hydrophilicity of the modified microfiber base were enhanced and the active groups increased. In addition, the hygienic property of the modified microfiber base significantly improved, and its physical properties relatively increased.

Keywords: Microfiber synthetic leather base, polyamidoamine, hygienic property, glutaraldehyde, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide.

INTRODUCTION

Microfiber synthetic leather, which is a composite material made from microfiber and polyurethane (PU) elastomer, has many excellent performance characteristics such as no location difference, high cutting rate, superior mechanical properties, and its chemical resistance, waterproof, mildew resistant are better than that of natural leather. However, as the most ideal material of leather imitation, synthetic leather has poor water vapor permeability and moisture permeability because fewer hydrophilic groups exist in the microfiber and it has narrow gaps between microfiber bundles and PU [1-5]. Thus, further research is needed to improve the wearing comfort and hygienic property of the

microfiber synthetic leather [6-10]. Studies have shown that the most effective modification method is to increase the internal active groups of microfiber synthetic leather.

Polyamidoamine (PAMAM) dendrimers are hyperbranched macromolecules which have precise structures, symmetric heights, and numerous active functional groups. In 1978, dendritic macromolecules were synthesized for the first time by Professor Vögtle [11] from University Bonn, Germany. Dendritic macromolecules are widely applied in the field of medicine [12], liquid crystal [13], membrane materials [14,15], and nanocomposite materials [16,17] because of their controllable molecular weight, molecular structure, surface chemistry, and internal cavity. In this paper, PAMAM were cross-linked to polyamide microfiber synthetic leather base by using glutaraldehyde as crosslinking agents, and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC) was used for further combining PAMAM and microfiber synthetic leather base, thereby forming base-PAMAM which have numerous active groups, and their hygienic property would be effectively enhanced. Scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), thermogravimetric analysis (TGA), and atomic force microscopy (AFM) were performed to analyze the change in surface morphology, hygienic properties, and physical properties of the microfiber base before and after modification.

EXPERIMENTAL

Materials and Raw Materials

Polyamide microfiber base for shoe upper leather was purchased from Yantai Wanhua Co., Ltd. (Yantai, China). Amine-terminated G1 PAMAM

was self-prepared by applying the method reported by Dufes et al. [18]. EDC was purchased from Shanghai Dibai Chemical Technology Co., Ltd. (Shanghai, China). Glutaraldehyde (25%) was purchased from Tianjin Fuchen Chemical Regents Factory (Tianjin, China). Formaldehyde scavenger was prepared based on literature [19]. Other reagents were of analytical grade. DY-9606 drum was provided by Xinda Light Industrial Mechanical Factory in Wuxi City (Wuxi, China).

Microfiber Base Modification

All operations were carried out in a drum. First, the microfiber synthetic leather base was hydrolyzed with sulfuric acid to expose some active groups. Glutaraldehyde and EDC were then utilized as cross-linking agents in combining amine-terminated G1 PAMAM and hydrolyzed bases, respectively. Before the experiment, all microfiber synthetic leather bases were boiled for 1 h at 50 °C to remove oil and other filth. The detailed process was shown in *Table I*.

Characterization and Measurements

The surface of the modified base was coated with gold and then examined with a Hitachi S-4800 SEM and EDS with an acceleration voltage of 15 kV. **CSPM3000** contact AFM was used to further analyze the surface morphology of the modified base. TGA was conducted at temperatures ranging from 50 °C to 600 °C by using 2960 SDT 290 TA with a heating rate of 10 °C/min in a nitrogen atmosphere and an air flux of 100 mL/min. The weight of each sample was controlled from 4 mg to 5 mg. The contact angle was measured using OCA 20.

In addition, the tensile strength and breaking elongation of the modified base were measured in standard conditions by using a desktop tension tester according to ISO 3376-1976. This paper used YG (B) 216-II to test water vapor permeability according to GB/T 12704-91. The water absorption of the base were tested referring to QB-T 1811-1993

RESULTS AND DISCUSSION

Preparation of Base-PAMAM

Base-PAMAM preparation was carried out in three steps. First, base-aldehyde was synthesized through the Mannich reaction between amino groups and aldehyde groups of the microfiber synthetic leather

base and glutaraldehyde. Then, the amino groups of G1 PAMAM continue to react with aldehyde groups of microfiber synthetic leather base to improve the amino groups of the latter. A new dehydrant, EDC, was added in the last step to activate the carboxyl group of the microfiber synthetic leather base and then through the amidation with PAMAM prepare base-PAMAM. The synthetic pathway is shown in Scheme 1.

Surface Morphology

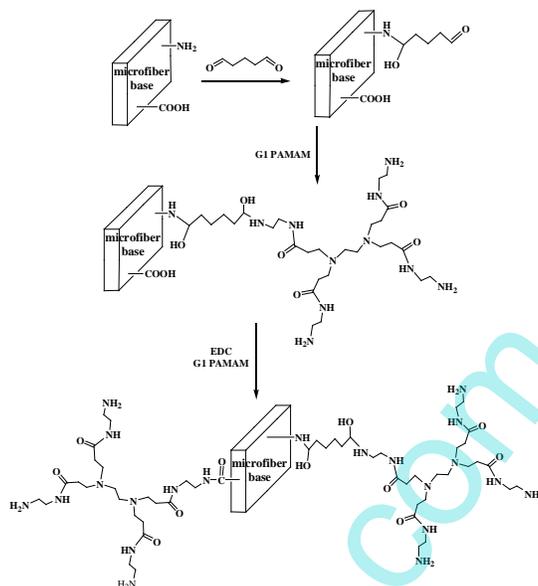
The SEM images of the surface morphology of the microfiber base before and after modification are shown in *Figure 1*. As shown in *Figure 1*, the microfiber base exhibited better dispersion after modification that due to the base was hydrolyzed in acid condition to cleavage its amide bond. Microfiber surface morphology was further analyzed by using AFM. The AFM images (*Figure 2*) indicating that the average roughness of the microfiber base improved by hydrolysis and crosslinking modification, and the surface of the base-PAMAM was coarse. These observed changes resulted from the exposure of the right amount of active groups after hydrolysis and the crosslinking of PAMAM to the microfiber base. However, the combination between PAMAM and microfiber base was limited because the content of the active groups of the hydrolyzed base was restricted, given that the physical properties of the base must not be damaged.

Thermal Properties

The thermal stability of the microfiber base before and after modification was measured using TGA (*Figure 3*). As shown in *Figure 3*, the untreated base, hydrolyzed base, and base-PAMAM have similar weight loss behaviors. The weight loss of the materials was minimal at low temperatures (50 °C to 280 °C), which was caused by the loss of absorbed moisture in the microfiber. The weight loss of base-PAMAM was greater compared with that of the untreated base, which confirms the increase in hygroscopicity of the modified microfiber. The greatest weight loss of the materials was observed in temperatures ranging from 280 °C to 465 °C, which was caused by the decomposition of the microfiber into small molecules, such as CO₂, H₂O, and other substances. At 600 °C, microfiber decomposition was nearly completed, and the remaining substances were char residue. The final

char residue was the most important difference in the TGA curves. The final char residue decreased at 600 °C and reached up to 14.01% and 9.1% for the hydrolyzed base and base-PAMAM samples, respectively. By contrast, the final char residue of

the untreated base sample was 20.71%, which could be explained by the dispersion of microfiber and the change of the microfiber composition mainly include the increase of functional active groups.



SCHEME 1 Synthetic pathway of the multi-amino base.

TABLE I. Techniques in microfiber base modification.

Process	Chemicals	Dosage (%)	t (min)	T (°C)	Remarks
		Water		5000% (according to base weight)	
Hydrolyzing	H ₂ SO ₄	15	240	50	Draining
Washing	Water	2000	3*30	room temperature	Draining
Cross-linking modification	Water	2000		room temperature	pH: 8.0
	Glutaraldehyde	15	120	35	Draining
	Water	2000	3*30	room temperature	Draining
	Water	2000		room temperature	pH: 8.0
	PAMAM-1G	24	120	35	
	c	1.5	60	40	Draining
	Water	2000	3*30		Draining
	PAMAM-1G	20	30	room temperature	
	EDC	20	180		pH: 4.5
Washing	Water	2000	3*30		Draining
Airing					Fully dried before proofing
Proofing and measuring the physical properties of the modified base					

Annotations:

(A) Amino content and physical mechanical properties are considered indexes when the microfiber base is hydrolyzed. Active groups must be exposed without affecting the physical mechanical properties of the microfiber base, which preserves the base for the next modification research. The optimum conditions for the process above are shown.

(B) Water vapor permeability and moisture absorption are considered indexes when the microfiber base is modified. Additive sequences, action time, temperature, and pH are optimized. The optimum conditions for the process above are also shown.

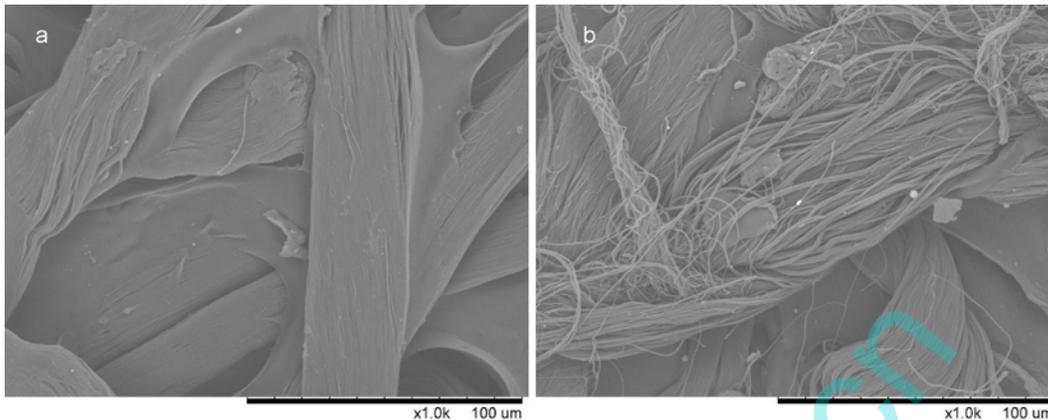


FIGURE 1. SEM images of (a) untreated base and (b) modified base.

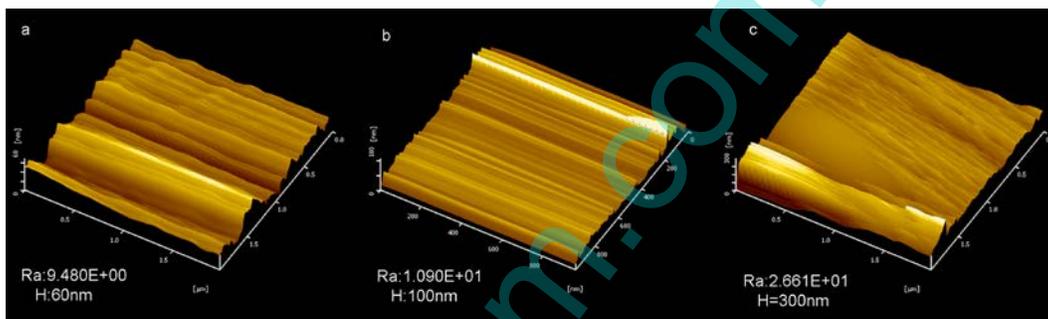


FIGURE 2. AFM images of (a) untreated base, (b) hydrolyzed base, and (c) base-PAMAM.

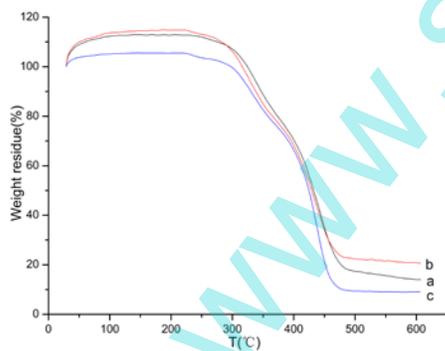


FIGURE 3. TGA curves of (a) the hydrolyzed base, (b) the untreated base, and (c) the base-PAMAM.

Active Groups

The behavior of moisture absorption can be determined by observing the change in the active groups of the microfiber base before and after modification. The contact angle images (Figure 4) show the hydrophility of the microfiber base before and after modification. Base-PAMAM has good

Hydrophilicity, because the number of its active groups increased. Moreover, EDS (Figure 5) analyses results reveal that the weight and atomic percents of nitrogen on the modified base improved, which may be caused by the crosslinking of PAMAM to the appropriate hydrolyzed base.

Performance Comparison of Bases

Table II lists the water vapor permeability, moisture absorption, tear strength, tensile strength, breaking elongation, and amino content of untreated, hydrolyzed, and modified bases. Compared with the untreated base, these values respectively increased by 96.72 %, 349.59 %, 27.95 %, 23.95 %, 57.21 % and 330.61 %. This phenomenon may be caused by the followings: 1) According to the appropriate hydrolyzed base, some amide linkages of the microfiber synthetic leather base were broken after hydrolysis that lead to irregular wind of microfiber. To a certain extent, this curling effect of microfibers improved the physical and mechanical properties of the microfiber synthetic leather base. By the way,

the crosslinked action and filling effect of PAMAM with the microfiber synthetic leather base also improved its tenacity and strength. 2) After modification, the active groups of the microfiber base increased, and the water channels among the fibers broadened. Therefore, water vapor permeability and moisture absorption improved to some extent.

CONCLUSION

In conclusion, we have successfully prepared a multi-amino base by using glutaraldehyde and EDC as crosslinking agents to combine amine-terminated G1 PAMAM appropriate hydrolyzed bases, respectively. The water vapor permeability, moisture absorption, tear strength, tensile strength, breaking elongation, and amino content of the

modified base were 796.3 mg/(m²·24h), 5.53 %, 127.6 N/mm, 17.96 MPa, 90.32 %, and 0.422 mol/kg. These values respectively increased by 96.72 %, 349.59 %, 27.95 %, 23.95 %, 57.21 % and 330.61 % compared with that of unmodified base. EDS analysis and contact angle images indicate an increase in the number of active groups in the modified base which greatly affects the hygienic property of the microfiber synthetic leather. The SEM and AFM images of the modified base show that the microfiber pores moderately opened and the fiber became rougher which was helpful for improving hygienic property of the base. The crosslinking of PAMAM and the microfiber base improved the mechanical properties of the base when glutaraldehyde and EDC was added.

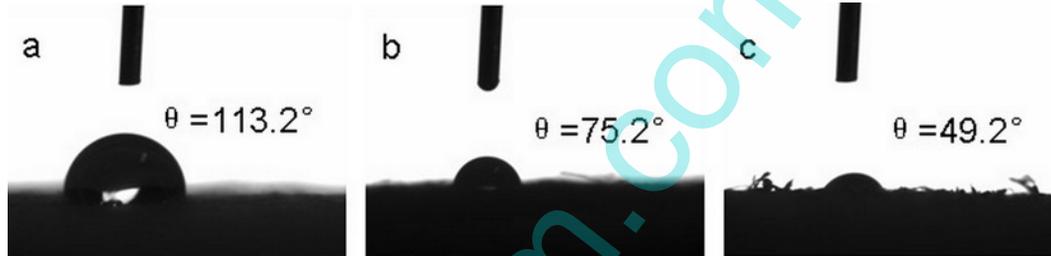


FIGURE 4. Contact angle images of (a) the untreated base, (b) the hydrolyzed base, and (c) the base-PAMAM.

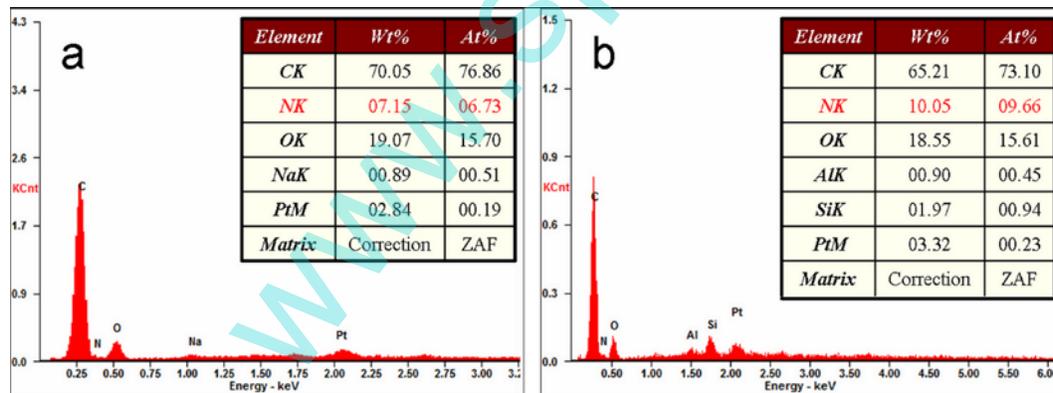


FIGURE 5. EDS analyses of (a) the untreated base and (b) the modified base.

TABLE II. Comparison of the base properties before and after modification.

	Untreated base	Hydrolyzed base	Modified base	Change ratio
Water vapor permeability (mg/(m ² ·24h))	404.78	459.6	796.3	96.72
moisture absorption (%)	1.23	1.78	5.53	349.59
Tear strength (N/mm)	99.73	114.39	127.6	27.95
Tensile strength (MPa)	14.49	16.62	17.96	23.95
Breaking elongation (%)	57.45	97.59	90.32	57.21
Amino content (mol/kg)	0.098	0.201	0.422	330.61

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