Polyurethane Electrospun Fiber Biomimetics Membrane for Constructing the Structure of Grain Layer with Good Breathability for Cattle Split Leather

by

Nan Chen,[1,2] Yanchun Li,[1,2*] Jianbo Qu,[1,2*] Jian-Yong Wang[1,2]

[1]*School of Light Industry and Engineering, Qilu University of Technology (Shandong Academy of Science);*

[2]*Key Laboratory for Green Technology of Leather Manufacture,* China National Light Industry Council

No. 3501 Daxue Rd, Changqing District, 250353, Jinan, Shandong Province, China

Abstract

The traditional thick coating on split leather does not have the ability to breathe like full grain leather. The air and water vapor permeabilities of full grain leather are well known properties due to its fiber woven structure. Simulating the fiber morphology and weaving structure of the dermis or grain layer is very important to construct a top surface layer for split leather. In this paper, a PU (polyurethane) foam layer is put first on the split to enhance the adhesion of a second application of a superfine fibrous PU resin. This foam uses well-known waterborne polyurethane foaming technology. This dried foam has good breathability because of high porosity. A superfine fiber membrane is next put atop of the foam layer by using an electro-spun polyurethane resin. This second resin imitates collagen fibers in the network structure of the leathers' grain layer. Thus, this resultant electrospun fiber biomimetics membrane simulated the grain layer of natural leather. SEM showed the morphology and structure of this electrospun fiber biomimetic membrane to be like that of the grain layer of natural leather. The porosity and apparent density were basically the same as the grain of leather, which were 63.65% and 583.878 kg/m^3 respectively. The air and water vapor permeability of the biomimetics membrane were also as high as 2250 mL·cm^{-2}·h^{-1} and 8753.02 μg·cm^{-2}·h^{-1} respectively. Therefore, the biomimetics membrane largely restored the ability to breathe of split leather. Thus, this method simulates the performance and structure of full grain leather and is a novel method for industrial production.

Introduction

There is no comparison between the flat non-porous coating or finish on split leather with the natural grain layer of leather which has good breathability due to its disorderly and tightly woven fiber network structure. [1-3] In the tanning production process, the cattle leather is usually divided into the valuable top grain leather and the less-valued split leather through the splitting operation.[4] This resultant split leather has a low worth which needs to be recovered. Polyurethane (PU) resin is usually used to coat or finish the surface of split cattle leather.[5] The thick coating or finish on split leather, hides the morphology of the collagen fibers and closes its natural pores. Clearly, the finish seriously affects its ability to breathe and adversely impacts the handle [feels like plastic] of the finished leather.[6, 7] Therefore, the deposition on split of a biomimetics grain layer gives a fiber network woven structure which endows good breathability and can readily replace the traditional PU coating to enable a very broad application prospect.

Electrospinning technology continuously produces nano-scale fibers which were reported by many groups.[8-11] The electrospun fiber membranes prepared by electrospinning technology with good performance are widely used in textiles, packaging, filtration and other fields.[12,13] Electrospinning technology gives a disorderly-arranged and reticular braiding structure fiber membranes with similar structure, high porosity, good air and water vapor permeability compared with natural leather grain surface layer.[14-16] This also provides a guarantee for simulating the grain surface layer of natural leather and the resultant artificial grain surface or [biomimetics finish] imitating natural leather.

In this paper, the PU foam coating was prepared by using water-borne polyurethane foam technology. The topside of the split was thinly coated with this foam resin to get a high porosity structure [after drying] in order to ensure the ability to breathe, and to enhance the adhesion of electrospun fiber to it. The electrospinning technology used another polyurethane resin to deposit its biomimetics electrospun fibers on the foam first or basecoat. The selected biomimetics fibers have a similar structure to collagen fiber and are composed of a special network morphology like the grain layer of the leather. Thus, the electrospun fiber biomimetics-membrane is a topcoat which imitates the grain layer of the leather. The morphology and structure of the electrospun fiber biomimetic membrane was analyzed by SEM. It was similar to the grain layer of leather. The porosity and apparent density of the split coated with a foam basecoat and electrospun fiber biomimetics membrane topcoat were basically the same as the parent split leather. The air and water vapor permeability of the split coated with the biomimetics membrane are also nearly as high as the not coated split leather. By comparing

*Corresponding authors emails: qlulyc@126.com ; qujianbo396@sohu.com

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the fiber denier, horizontal weaving angle and morphology of the biomimetic membrane, the split leather coated with the biomimetics membrane has good air permeability and water vapor permeability. The biomimetics finish has a structure and a performance similar to the dermis grain surface layer. This novel biomimetics finish on split leather gave good breathability and has broad application prospects.

Experimental

Materials and Instruments

Polyurethane (6008D) was purchased from Xuchuan Chemical (Suzhou) Co., Ltd. Waterborne polyurethanes (2040 and 3485) were purchased from Wanhua Chemical Group Co., Ltd.

Electrostatic spinning machine (ET-2535H) purchased from Beijing Ucalery Co., Ltd. China. Desktop scanning electron microscope (Pure) made by Phenom Co.,Ltd., Netherlands and Hot field-emission scanning electron microscope (G500) made by Zeiss Co., Ltd. Germany. Fully automatic mercury porosimeter (PoreMaster-60GT) made by Quantachrome Co., Ltd. America. Screw micrometer (0-25mm 0.001mm) was purchased from Schut Co., Ltd. China. Leather air permeability tester (GT-7007-0) and Low-temperature penetration tester (GT-7045-EV) made by High-speed Railway Testing Instrument Co., Ltd. China.

Preparation of the biomimetics electrospun fiber coating

There are many fluff and fiber protrusions on the surface of the spilt cattle leather, which affect the adhesion of the material and need to be treated. The foaming liquid was prepared by waterborne PU (2040, 3458) through polyurethane foaming technology.[17-19] The foaming liquid was evenly and thin coated on the surface of split cattle leather after high-temperature ironing treatment, and dried and pressed flat at 60°C as the receiver of electrostatic spinning electrospun fiber.[20-22]

Using polyurethane resin (6008D) as the spinning dope, spinning for 3-4 hours was done under the condition of ventilation, positive electric high voltage of 25kV, negative electric high voltage of 5kV, liquid output speed 0.06mm/min, ambient temperature 30°C, humidity 40%. By adjusting the electrospinning angle, the electrospun fiber were evenly covered on the split cattle leather with foam coating, the preparation of PU electrospun fiber biomimetics membrane split cattle leather was finished. The preparation diagram is as follows:

Characterization

Morphology observation

The surface and longitudinal section morphology of full grain cattle crust leather (FGL), split cattle leather with traditional PU coating (PUSL) and PU electrospun fiber biomimetics membrane split cattle leather (NBSL) were analyzed by desktop scanning electron microscope and a hot field-emission scanning electron microscope.[23]

Porosity and apparent density analyses

The porosity of FGL, PUSL, NBSL were measured by fully automatic mercury porosimeter.[24] The apparent density of the fibers of FGL, PU foam coating split cattle leather (PUFSL), NBSL were measured by a screw micrometer through the size method.[25, 26]

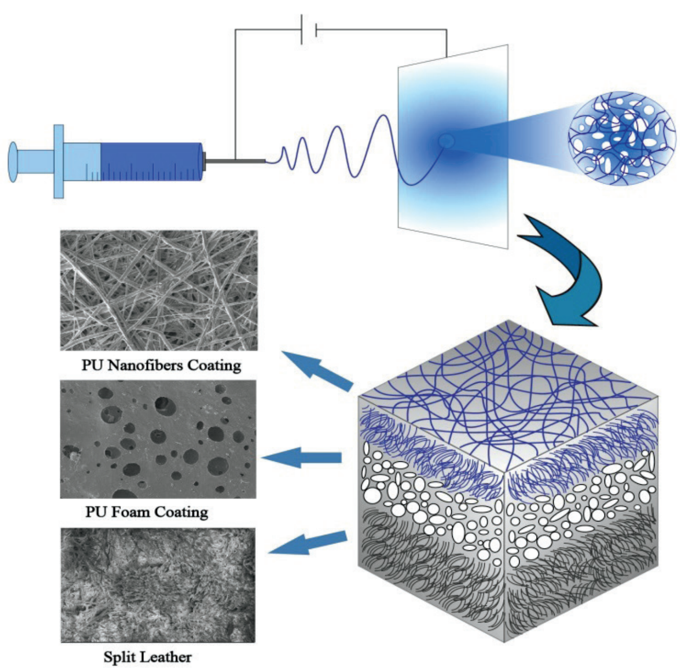

Figure 1. Schematic diagram of preparation of PU electrospun fiber biomimetics membrane split leather

The calculation formula of the size method is as follows:

$$\rho = \frac{m \cdot 10^6}{L \cdot W \cdot H} \quad (1)$$

Where: ρ — Apparent density, (Kg/m^3)

m — Sample quality (g)

L — Sample length (mm)

W — Sample width (mm)

H — Sample height (mm)

Air permeability and water vapor permeability analyses

The air permeability and water vapor permeability of split cattle leather (SL), PUSL, PUFSL, NBSL were tested by the leather air permeability tester and low-temperature penetration tester.[27] The air permeability and water vapor permeability of different materials were calculated by the following formula:

Air permeability calculation formula:

$$K = \frac{100 \times 3600}{10(t - t_0)} = \frac{36000}{t - t_0} \quad (2)$$

Where: K — Sample air permeability ($ml/(cm^2 \cdot h)$)

t — The time required for the specified area of the sample to penetrate 100mL of air (s)

t_0 — Time required for blank experiment (s)

10 — Sample area through air (cm^2)

Water vapor permeability calculation formula:

$$P = \frac{7639 \times m}{d^2 \times t} \quad (3)$$

Where: P — Water vapor permeability ($mg/(cm^2 \cdot h)$)

m — Increased mass of the test bottle twice (mg)

d — Inner diameter of test bottle (mm)

t — Time between two sample weighing (min)

Results and discussion

SEM observation of the surface and longitudinal of the sample

Figure 2a, 2b and 2c respectively are the surface morphology of FGL, PUSL, NBSL. We can see from the SEM pictures, the grain layer of FGL is horizontally woven by many fibers of different deniers (Figure 2a). The fiber diameter was about 300~800nm, inter-fiber porosity is obvious. The porosity was 65.55% tested by mercury porosimeter. This high pore fiber structure provides a good breathability of the leather.[28,29]

PU coating method is widely used in the production of split leather.[30,31] We can see from Figure 2b, the PU coating completely covered the surface of the split cattle leather, the coating has a flat, non-porous structure and lacks open pores communicating with the outside, which was quite different from the three-dimensional network structure of the grain layer fiber of leather. The closed structure greatly affects the ability of the split leather to breathe.

In order to solve the problem of poor breathability performance of the thick PU coating on the split leather,[32,33] PU electrospun fibers were prepared by electrospinning technology, and the derma grain layer was simulated from aspects of the size, structure and weaving mode (Figure 2c). The PU electrospun fiber diameter was 400~900nm, and the NBSL porosity was 63.65%, which all are very close to the fiber fineness and porosity of dermis grain layer. The PU electrospun fiber membrane was composed of two kinds of different denier fibers. The fibers with larger denier imitate the supporting effect of the thicker collagen fibers in the grain layer of leather, while the fibers with smaller denier imitate the network structure formed by the finer fibers in the grain layer of leather. Compared with the traditional PU coating, the electrospun fiber membrane was closer to the natural leather grain layer in morphology, while ensuring the fiber weaving, it retains more pores and has a weaving angle similar to that of dermis grain layer fibers.[34] In addition, by calculating the apparent density of the biomimetics electrospun fiber membrane, it is found that the biomimetics membrane has a fiber weave density similar to that of leather (Figure 3), which achieves a high degree of simulation in structure.

PU electrospun fiber membrane was prepared by electrospinning technology to simulate the reticular braiding structure of pellet surface fiber. Its fibers are very close to collagen fibers in fiber morphology, size, fiber weaving angle and density. The disordered fibers produced by electrospinning technology due to the interaction of charges also provide sufficient pores for the biomimetic PU electrospun fiber membrane.[35,36] From the structure point of view, the PU electrospun fiber-biomimetics membrane can greatly retain the ability to breathe of the split leather.

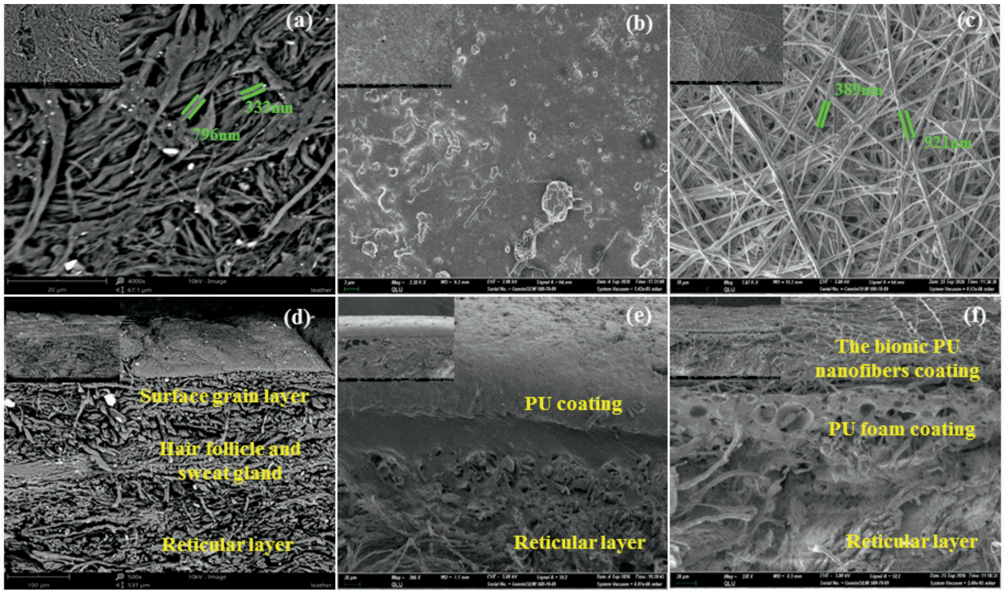

Figure 2. **(a)** SEM of the surface of FGL. **(b)** SEM of the surface of PUSL. **(c)** SEM of the surface of NBSL. **(d)** SEM of longitudinal section of FGL. **(e)** SEM of longitudinal section of PUSL. **(f)** SEM of longitudinal section of t NBSL.

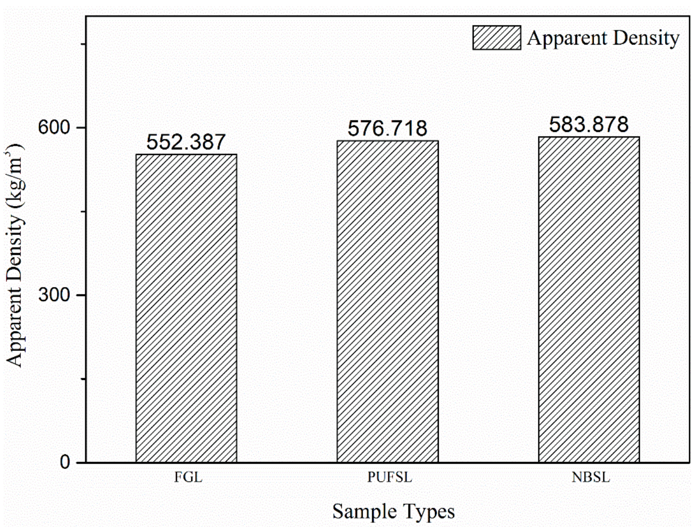

Figure 3. The apparent density was compared by the size method.

The longitudinal sections of FGL, PUSL, NBSL were analyzed by SEM (Figure 2d, e, f), we can see the changes in the fiber structure of three different types of leather more intuitively.

From Figure 2d, we can clearly see the fiber network structure in the grain layer in the longitudinal section of the leather, the fibers are arranged tightly and disorderly, and the pores left after removing the hair follicles and sweat gland tissues by the tanning process can be seen. The coating of PUSL was a flat non-porous PU film with no fiber cross-section structure, which was an indivisible whole (Figure 2e). The coating of NBSL has a clear fiber section and obvious inter-fiber pores, which was very similar to the natural leather grain surface fiber in morphology (Figure 2f). The thin PU foaming layer on the surface of the split leather coated by water-based polyurethane foaming technology form a porous structure. This porous structure is similar in appearance to the cavity left by removing the hair follicles and sweat gland during tanning and also the adhesion of the subsequent electrospun fiber biomimetic membrane to the foaming is improved. From the structural point of view, the breathing ability of leather can be retained.

Test for Air permeability and water vapor permeability

The good air permeability and water vapor permeability of leather are currently difficult to achieve by other materials.[37] While preparing the artificial grain layer for the split leather, the good air and water vapor permeability of the leather should be retained as much as possible. In this research, the air permeability and water vapor permeability of various coatings are compared by experiments and calculations. The results are shown in Figure 4.

It can be clearly seen from Figure 4 that the PU coating (PUSL) greatly decreases the original air permeability and water vapor permeability of the split leather (SL). The water-based PU foaming coating (PUFSL) has little effect on the air permeability and water vapor permeability of the split leather. The NBSL which has a high degree of simulation with the grain layer of leather in structure, has good air permeability and water vapor permeability, it guarantees the ability of the split cattle leather to breathe.

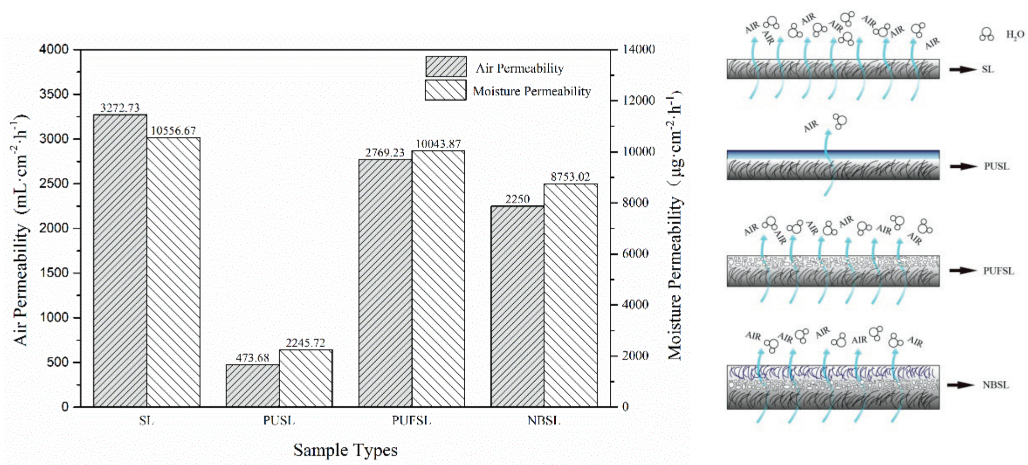

Figure 4. Comparison of air permeability and water vapor permeability of SL, PUSL PUFSL and NBSL.

Conclusions

In summary, a practical method to simulate the structure of the dermal grain layer was proposed. By way of using electrospinning technology, a PU electrospun fiber biomimetics membrane was coated on split cattle leather. It simulated the grain layer of the leather by constructing a three-dimensional woven structure like that of the dermis. Split cattle leather coated by this PU electrospun fiber biomimetics finish has good air and water vapor permeability compared with the traditional thick PU coat on split leather. This novel biomimetic finishing approach is useful to produce split leather of high value, and with the ability to breathe and thus has broad application prospects. There is still a lot of work to be done in the future. We will further research various physical and mechanical properties of the coating, including its adhesion by improving the electrospinning method and other influence factors in order to increase its application properties.

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