

Modifications of microfiber synthetic leather base (MSLB) to enhance the sanitary performances: a review

Abstract

Microfiber leather is a type of synthetic leather made up of a high-grade polyurethane resin and microfiber bundles that resemble the microscopic characteristics of natural leather. Microfiber has benefited from its smaller diameter, which is similar to that of real leather fibrils. Microfibers have received a lot of focus and are frequently employed in the synthetic leather basis, which is an important factor in regulating synthetic leather functionality. Microfiber synthetic leather has advantages over natural leather in terms of mechanical behavior, for example. However, there is a significant difference between natural leather and microfiber synthetic leather in terms of other aspects, such as hygiene issues. Microfiber synthetic leather, unlike natural leather, has inferior transmission and absorption qualities, making it feel hotter. As a result, there is a pressing need to improve the sanitary performance of superfine synthetic leather. Several studies have endeavored to improve the hygienic qualities of MSLB by modifying it in various ways. It is attempted to make a review on the different types of modifications in brief.

Keywords: microfiber, modification, sanitary property, synthetic lather base (MSLB)

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Introduction

Natural leather, mainly comprising of collagen fibers, is made from animal skins through physical and chemical treatment. In natural leather, collagen fibers are intertwined to form bundles in three-dimensional structures. Besides, collagen fibers contain several fibrils and have a diameter of 2-8mm, while fibrils have a diameter of 100-150nm.¹ Many customers prefer natural leather products due to their excellent properties, like wearing comfort, good water vapor permeability, and superior hygroscopicity.^{2,3} However, there is a great challenge faced by the current genuine leather industry relating to pressure from several sources, including insufficient raw hides, environmental pollution, and the developing ethical concern over animal rights.^{4,5} Therefore, meeting the rising demand of leather products globally needs an enhanced spring up of artificial leather or other leather substitutes, especially in Southeast Asia.^{6,4} The rapidly developing synthetic leather industry has led to an intense market competition where synthetic leather performance is the key demand requirement. Consequently, an inevitable imitation of natural leather has developed.^{7,8,3} Leather base is the key component of finished synthetic leather and is presently divided into three main categories: knitted leather base, woven leather base, and nonwoven leather base. Like natural leather, nonwoven leather base consists of a three-dimensional net structure. Nonetheless, as the most ideal material for leather base among all, the development of early nonwoven leather base was limited by its larger fiber diameter as compared to collagen fibers.⁹

Microfiber describes a synthetic fiber with a diameter of less than one denier.¹⁰ Besides, it is a hot research material in the fiber field.¹¹ Notably, following the advancement in the spinning technology, the application of microfiber nonwovens as a synthetic leather base has been successful. Such fabricated synthetic leather is called microfiber synthetic leather.⁹ It is third generation of artificial leather in the

marketplace.¹² It is the coating of microfiber non-woven base with a layer of polyurethane or performance PU resins.¹³ The mainly used microfiber nonwovens are of three types: segmented pie spinning microfiber nonwovens (hollow and solid), sea island bicomponent microfiber nonwovens and direct spinning microfiber nonwovens.^{9,14} Undoubtedly, MSLB fiber fineness significantly affects the performance of both morphology and microfiber synthetic leather.¹⁴ Comparatively, hollow segmented pie fibers are more advantageous than islands-in-the-sea fiber, as it is easier to process, non-polluting and has higher mechanical properties.¹⁵

Nonetheless, applications of microfiber synthetic leather have expanded with the continuous advancement in the research area.³ For instance, it has established wide applications in manufacturing of shoes, bags, garments, and upholsteries in the automotive, aviation, and other industries.⁶ For example, over 90% high-end sport shoes are present across the world made from microfiber synthetic leather. Besides, there are several high-grade car seats made from microfiber synthetic leather rather than natural leather.¹¹

In the recent past, microfiber synthetic leather has emerged to be the most ideal natural leather substitute.^{3,16} MSLB properties are the primary factors for the properties microfiber leather, and main cost of microfiber leather is occupied by the base fabric.^{13,17,18,9} Despite microfiber synthetic leather having some better properties than natural leather, such as its mechanical behavior, there are other multiple properties like the hygienic ones, that portray a wide gap between natural leather and microfiber synthetic leather.¹⁸ On contrary, natural leather portrays excellent hygienic performance due to its fiber composition and structure.¹

The significant performance indexes of microfiber synthetic leather are hygienic performance or sanitary properties, mainly including air permeability, moisture absorption, and water vapor permeability

(WVT).^{1,14} This results from performance of the base in eliminating the wearer's sweat vapor and make them feel comfortable.¹⁸ Water vapor permeability describes the ability to allow water vapor to penetrate a large humidity air to that of the smaller one. Based on the water vapor permeability, there is elimination of the water vapor and gas of the wearer.¹⁷ WVT is a crucial indicator to materials' sanitary properties and also acts as a significant factor that impacts the application properties of microfiber synthetic leather as shoes and clothes.^{17,18} In addition, moisture absorption is also a crucial indicator to the sanitary properties of material.¹⁸ Generally, the water contact angle characterizes the hydrophilicity of materials.^{1,14,18} Water penetration time describes the time taken by a needle drop of water from the start to completion of penetration when dropped on the base.¹⁷ Moreover, the liquid wicking rate refers to the measurement of the materials' capillary effect. It can assess the fabric's moisture absorption ability.⁷ Air permeability is also a valuable hygienic property of MSLB and relates to porosity, fiber bundle dispersion, and fiber morphology.¹ The softness is another key concern in its application.¹⁴

The difference in the hygienic properties of the natural leather and microfiber synthetic leather comes about due to the existence of more hydrophilic groups in the collagen fibers of natural leather than the ones in microfiber synthetic leather.¹⁸ Collagen is a typical amphoteric polyelectrolyte. It has outstanding biocompatible and hydrophilicity properties because of having active groups and several amino acids.¹⁷ On the other hand, microfiber (e.g., polyamide) has fewer active groups than natural leather. Ultimately, the main research topic in the microfiber synthetic leather field has been improving moisture absorption and WVT of MSLB.¹⁴ Increasing the reactive groups in fibers improves the hygienic properties of MSLB. Typically, hydrophilic groups of microfibers are increased through acid hydrolysis, enzymatic modification, and grafting of hydrophilic materials.¹ This paper reviews various modification types that have been investigated to ameliorate the sanitary properties of microfiber synthetic leather. It will be conducive for the future researchers to understand the sanitary property of MBSL.

Modifications to improve sanitary property

Various types of modification performed by different researchers in order to improve the sanitary property of microfiber synthetic leather base are mentioned as follows:

According to a research by Zhao et al., fabricated microfiber synthetic leather had better properties than commercial synthetic leathers of different leather bases concerning hygienic properties such as WVT and air permeability. Their research involved preparation of nylon/polyester 6 hollow segmented pie bicomponent spunbond hydro-entangled microfiber nonwoven (PET/PA6 HSBSYMNW) and using it as a leather base in the production of microfiber synthetic leather for apparel.⁹

The nylon/polyester (N/P) split microfiber nonwoven as the base while waterborne polyurethane (WPU) was used in the preparation of the split microfiber synthetic leather through dry transfer-coating. The resultant split microfiber synthetic leather had better properties than both real leather and knitted synthetic leather.¹⁵

MSLB modification is done through collagen and sulfuric acid pretreatment for enhanced sanitary properties. Under an appropriate action conditions, compared to untreated base, carboxyl group content increased by 196.03%, hygroscopicity increased by 179.72%, water vapor increased by 65.16%, and amino acids content increased by 114.52%.¹⁹

Xingyuan et al.²⁰ established that hydrolyzing the surface of polyamide hyperfine fiber with a suitable enzyme produces a better loosed fiber bundle. Therefore, the structure of the fiber could be changed and the surface of the hydrophilic group fiber could be increased. Essentially, the suitable hydrolyzation of the enzyme could improve the physical/mechanical properties, dyeing capacity, moisture absorption properties, and the handle of the hyperfine fiber synthetic leather base.²⁰

Using glutaraldehyde as the crosslinking agent, modification of MSLB was performed by collagen extracted from leather wastes. Compared with nontreated sample and sulfuric acid pre-treated sample, the collagen modified sample had an increased moisture absorption by 28.58% and 53.43% respectively. The reason for this is the hydrophilic groups increase on the base surface after modification by collagen and loose effect of fiber, which illustrates that the collagen modification improves sanitary properties of MSLB. After modification by collagen, it leads to production of relatively smooth fabric surface; its relative average roughness is 28.47nm, the roughness becomes much lower (relative of roughness of sulfuric acid treated MSBL was 267.5nm).¹⁸

PAN-PET/PA6 micro/nano MSLB was prepared by mixing polyacrylonitrile (PAN) nanofibers with PET/PA6 microfibers through alkali treatment and hydro-entanglement. According to the results, when the nanofibers content was 20%, the base water vapor permeability increased by 15.19%, softness increased by 38.17%, and the moisture absorption increased by 23.53%. Moreover, after the treatment of alkali, base hydrophilicity improved obviously. Softness had a 23.20% increment, moisture absorption also increased by 42.26%, water vapor permeability increased by 23.81%.²¹

Duo et al. prepared MSLB through a mixture of polyacrylonitrile electrospun nanofibers and PET/PA6 hollow segmented pie microfibers. The used nanofibers were 950nm, 450nm and 200nm respectively. They found that PAN nanofibers were uniformly mixed with microfibers, interpenetrated and randomly dispersed, simulating natural leather in structure. It is mentioned that the hollow segmented pie bicomponent microfibers formed wedges when split and tend to pack tightly. After nanofiber addition, the reduced porosity of MSLB makes it denser. Therefore, the MSLB permeability was reduced with the decreased nanofiber diameter. Furthermore, there was a decrease in the water contact angle from 107.3 to 97.3, with the reduced fineness of the nanofibers from 950nm to 200nm. Adding more nanofibers makes more fibers to contact the water droplets which enhance the MSLB's capillary effect and affecting moisture absorption to some extent. This indicated that the hydrophilicity of MSLB surface was not significantly changed. Moreover, the study also examined the impact of fiber fineness on moisture absorption and WVT. After the addition of nanofibers, there was a decrease in air permeability from 102.04mm/s to 84.88mm/s, an increase in softness from 4.68mm to 6.54mm, increase in softness from 4.68 mm to 6.54mm, and an increase in WVT from 3112.37g/(m².24h) to 3990.11g/(m².24h) with the decreasing fineness of nanofibers. An increase in the specific surface area of fiber results in an increase in moisture absorption capability as well as the capillary effect, enhancing the transport capacity of water molecules (WVT) and the percentage of moisture absorption respectively. Moreover, the bending rigidity of the fiber reduced with the addition of nanofibers and thus softness of MSLB was improved.¹

Zhao et al. studied the impacts of sulfonated polysulfone (SPSF) and thermoplastic polyurethane (TPU) electrospun nanofibers content

on the structure and properties of the MSLB. The production of TPU/SPSF nanofibers was through electrospinning and that of the PET/PA6 (70%/30%) hollow segment pie bicomponent fibers was through spun bonding. It was indicated that the fabricated nanofibers and microfibers had average diameters of 0.12mm and 4.75mm respectively, thus a similarity with monofilaments and fibrils of natural leather. The increase in the content of TPU/SPSF nanofibers from 5% to 30% led to a gradual decrease in the contact angles of MSLB from 90.40 to 67.07. Therefore, it is certain that nanofibers have an impact on the hydrophilicity of the MSLB. The amount of water molecules to be absorbed on the surface of the fiber through hydrogen-bond or physical interactions have been increased with the increasing content of the TPU/SPSF nanofiber in MSLB. This is because the increasing content of the TPU/SPSF nanofiber can increase the number of active group. On the extension of the nanofibers content from 0 to 30 wt. %, the WVT value indicated a 55.19% improvement (from 2868.96 to 4452.24g/ (m².24 h)) while moisture absorption increased by 26.25% (from 628.70% to 793.75% mm/s). They explained increased fiber specific surface area with the increase of the content of nanofiber as well as the presence of the hydrophilic sulfonic acid groups (-SO₃-) on the SPSF chains, resulting in the MSLB with high moisture absorption and WVT. It found that an increase in the content of nanofibers from 0 to 30 wt. % led to a decrease in air permeability of the MSLB from 145.23 (M0) to 135.37mm/s (M30). Air permeability decreased by 6.79% which relates to the nonwoven structure in which the nanofibers adhered on the bundles. The MSLB softness increased from 6.70 to 8.56mm as the content of nanofiber increased from 5 to 30 wt. % respectively whereas without adding any nano fibers gives only 4.54mm. The fiber bending rigidity is relative to the fiber linear density or the fiber diameter. Therefore, it is expected that smaller fiber diameters will produce softer base.¹⁴

Duo et al. explored the impact of polyhydroxy butyrate (PHB) nanofibers content on the properties and structure of PET/PA6 hollow segmented-pie MSLB. From the obtained results, it is found that the polyhydroxy butyrate nanofibers (average diameter = 0.40μm) were distributed evenly in all directions of MSLB. They reported that an increase in the content of nanofibers from 0% to 20% led to a significant improvement in MSLB hydrophilicity. Moreover, there was a decrease in water contact angle from 111.640 to 59.310, an increase in WVT by 44% (from 3112.37g/ (m².24 h) to 4350.53g/ (m².24 h)), a 22.3% improvement in the moisture absorption (from 649.12% to 812.92%). Furthermore, nanofiber addition made the MSLB denser, resulting in a 24.0% air permeability decrease and a 42.18% increase in softness of MSLB.⁸

The “two-step method” was adopted to modify the polyamide MSLB. Firstly, the process involved cross-linking of the amino-terminal hyperbranched polyamides (NH₂-HBP) to microfiber synthetic leath MSLB base that was pretreated with formic acid, whereby the crosslinking agent was glutaraldehyde. Secondly, a crosslinking of Gelatin hydrolysate to the preliminary modified MSLB was done with glutaraldehyde as the crosslinking agent. As a result, there was a significant improvement in the surface roughness, water absorption ability, and the wettability of the modified base through the “twostep method” compared to the unmodified base. Besides, there was an improvement in hygroscopicity for the base with an increase in glutaraldehyde dosage. Similar trend was exhibited with the change in the permeability of the water vapor of the base caused by the same reason. There was an increase in activity groups that could syndicate with NH₂-HBP following an increase in the dosage of glutaraldehyde, resulting in an increased combination of gelatin hydrolysate with the

base. Moreover, improved water vapor permeability of the base is also related with an increase in the activity groups. With the increase in NH₂-HBP dosage, there was an increase in the degree of looseness of the fiber bundles, making the fiber bundles slightly scattered. Thus, the fiber bundles in the base were dispersed at a greater degree, which improved the hygienic property of base. Also, the hygroscopicity and water vapor permeability increased by 86.7% and 48.8% respectively in comparison with that of the unmodified base.³

The grafting of amino-terminated hyperbranched polymers (NH₂-HBP) onto the polyamide microfiber synthetic leather was done using organic phosphine as a cross-linking agent. After modification, there was a slight improvement in the hygienic properties of base, as an increase in amino content improves the hygienic properties.²²

The sulfuric acid pretreated polyamide MSLB was modified by Collagen, and the organic phosphine FP was utilized as a cross-linking agent to increase the active groups and improve its properties. When the amino content modified by collagen was compared with the pretreated base, it was double, while the carboxyl content was thrice. The water vapor permeability of modified base intensified by 65% while absorption of moisture heightened by 181%. The increase in the amino and carboxyl groups in the base after collagen modification triggered the improvement of moisture absorption and water vapor permeability. The dispersion of the modified base microfiber increased significantly, the hydrophilicity enhanced, and the average roughness decreased. The base surface became comparatively smooth after modification by collagen with FP as the modified base combines with a huge amount of collagen to fill the vacant space between the fibers, triggering the decline of the surface roughness. The contact angle of the base modified by collagen (42.3°) reduced greatly, thus improving the hydrophilicity of the modified base compared with the blank base (89.4°). The water penetration time of the modified base by collagen was 4 sec, which is 78% shorter than that of the pretreated base.¹⁷

The Polyamide MSLB was filled with filling agent (e.g., Desoaten RST) to improve the sanitary properties, and a zirconium tanning agent served as a cross-linking agent in the research study conducted by Qiang et al. The study discovered that an increase in the dosage of the filling agent increases the trend of the water vapor permeability and the moisture absorption although different filling agents had different optimum dosages. The filling agent comprises a large number of active groups. The hydrophilic group crosslinked with the base increased gradually to improve the sanitary properties of base. In a nutshell, the comfortability of the MSLB advanced after the filling process. The moisture absorption of the base filled with Desoaten RST (filling agent) compared with the blank base augmented by 43.33% while the permeability of water vapor increased by 52.17%. The results revealed that the time of the water penetration of the blank base was 19 s, while the water penetration time of the bases filled with Desoaten RST filling agents was 4s. The duration for water penetration lowered by 84.21%, showing that the filling agent filled in the MSLB can progress its wettability. Besides, the unit mass adsorption quantity of filled base was greater than that of the blank base accredited to the greater level of the specific surface area.¹²

Ren et al. research indicates that the cross-linking of polyamidoamine dendrimers (PAMAM) to polyamide MSLB pretreated with sulfuric acid were performed by the use of glutaraldehyde and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide as crosslinking agents. After the modification, the microfiber base showed enhanced dispersion and the surface of base-PAMAM was coarse as well. The changes ensued from the disclosure of sufficient

number of active groups after hydrolysis and the crosslinking of PAMAM to the microfiber base. Amino content, moisture absorption, and water vapor permeability values increased respectively by 330.61%, 349.59%, and 96.72% for modified base compared to the untreated base. This improvement of moisture absorption and the water vapor permeability is occurred due to the broadening of water channels among the fibers. Ren et al. argued that the increasing number of active groups in the modified base influences hygienic property greatly as the microfiber pores are opened moderately and roughness of the fiber is increased.²³

Nylon superfine synthetic leather (SFSLB) provides a hot feeling because of its poor transfer abilities and moisture absorbent when compared with natural leather. Without finishing, native leather has a static water-vapor transmission rate (SWVT) of 700g/m².24 h while the SFSLB has 400g/m².24 h. Wang et al. conducted a research to escalate the sanitation performance of the superfine fiber synthetic leather base where collagen-chrome tannins (C-CrT) is grafted with nylon SFSLB fiber. The research revealed that the rates of the SWVT and liquid wicking of the C-CrT grafted SFSLB were 986g/m².24 h and 1.323 mm/s, enhanced by 90.35% and 344% in comparison with untreated SFSLB (SWVT was 518g/m².24 h and liquid wicking rate was 0.298mm/s) respectively. The results of the water contact angle indicated that the C-CrT grafted SFSLB surface had better wettability than the untreated SFSLB. Besides, the SWVT of the unfinished native leather was 700g/m².24 h, and that of C-CrT grafted SFSLB was 986g/m².24 h, showing that the SWVT of C-CrT grafted SFSLB had surpassed that of native leather using this modification.⁷

Conclusion

The limited resources of natural leather have increased the research and attention of developing excellent synthetic leather to supplement the natural leather. The performance and appearance of the high-grade microfiber synthetic leather fairly resembles that of natural leather, even presenting better mechanical and physical properties. Unfortunately, the sanitary properties i.e., air permeability and water vapor transmissions are not satisfactory for the microfiber synthetic leather compared to natural leather. In this context, several modifications by various researchers attested the advanced sanitary properties, increasing MSBL possibility levels in future for the leather industry. Chemical modification such as acid treatment, enzyme hydrolysis, incorporating nanofiber and collagen waste, changing the dimensions of incorporated nanofiber as well as microfiber, integrating polyamide structure in base are may be considered as effective ways to improve the sanitary properties of MSLB. However, MSBL researchers still have a scope to study further in this field.

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Conflicts of interest

The authors declare there is no conflict of interest in publishing the article.

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