

Analyses of Structures for a Synthetic Leather Made of Polyurethane and Microfiber

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ABSTRACT: A gradient extraction method was developed and used for a synthetic leather made of polyurethane (PU) and microfiber polycaprolactam (PA-6), by which the two components were separated using DMF and formic acid as solvents, respectively. Their chemical structure was confirmed by FTIR spectra, and the result showed that the PU is a kind of polyester polyurethane with phenylene rings in the molecule. The condensed phase structure was analyzed using X-ray diffraction (XRD). The crystallinity of the PA-6 is about 65.6%, and for the PU, there was not distinct crystalline character shown in the XRD pattern but a phase separation structure of hard block-soft block with the hard domains con-

tent about 58.7%. SEM images showed that the PA-6 microfibers transfixing the PU matrix form a net bundle structure, and there are two kinds of porous structures in the synthetic leather, with one type of pore sized 5–80 μm between the components of PU and PA-6, and the other in PU matrix with a size of 0.1–2 μm . The multipores run through the synthetic leather as three-dimensional channels, benefit for transportation of air, water, dyes, and so on. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 903–908, 2007

Key words: synthetic leather; microfiber; structure; polyamide; polyurethane; porous structure

INTRODUCTION

Natural leathers, e.g., chamois leather, with beautiful appearance, softness, and a porous structure that give them high water absorption and vapor permeability, are popular in the market. However, these are less and less in markets because of their restricted source, exorbitant price, as well as more and more awareness of protecting animals. As an alternative, man-made leather based on nonwoven support material coated with polyvinylchlorides or polyurethanes is usually used for habiliments and shoe upper materials.¹ Among them, articles manufactured from new synthetic leathers based on polyurethanes and composite fibers of “matrix–fibril” type² have been gaining steady increase in demand in recent years. One of the matrix–fibril composite fibers is named as “sea–island” fiber, in which one portion is in a dispersed phase (called after island component) and the other is in a continuous phase (sea component). It is made by the conjugate spinning with two components immiscible in thermodynamics. Commonly, sea–island fibers consist of bicomponent such as PET/COPET (polyester/water-soluble copolyester), PA-6/COPET,³ PA-6/LDPE (low density polyethylene),⁴ etc. In the postprocessing step for the fabric base of synthetic leather, it is necessary to remove the sea component, and then the island

component reserved usually becomes microfibers. In a typical processing procedure for synthetic leather, the nonwoven fabric of the sea–island microfiber with a reticulate structure is treated by wet-cured polyurethane process, followed by extraction of the matrix polymer using an organic solvent. As a result, some properties of the synthetic leather are even better than those of natural leathers, such as soft handle, crease resistance, strength and elongation at break, hygroscopic ability, ventilation, easy-care, easy volume-producing, and so on.⁵ On the other hand, there are also disadvantages of the synthetic leather, such as poor dye fastness resulted from larger surface area of microfiber, when compared with those of the natural ones.

The performances of the synthetic leather must be correlative with its chemical structure, microstructure, or submicrostructure. Unfortunately, information about subtle structures of the new synthetic leather has hardly been found. In this study, a synthetic leather made of PA-6 microfiber and PU was separated into its constituent elements to determine either their delicate nature by use of FTIR, SEM, and XRD to understand the functions of the fabric, although the chemical structure is approximately known.

EXPERIMENTAL

The synthetic leather was from the Dongtai Chemical Fiber, which is one of the factories producing man-made leathers in larger scale in China. The synthetic leather with high quality was manufactured from a nonwoven fabric base with PA-6/LDPE sea–island

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fiber, via a wet-cured polyurethane process, and followed by a process dissolving out the sea component of low-density polyethylene in the sea-island fibers using toluene. The fabric density is 525 g/m², with the composition 45% of PA-6 fiber (about 0.5 dtex in fineness) and 55% of PU.

N,N-dimethylformamide (DMF) and formic acid (HCOOH), most suitable for dissolving PU and PA-6 components, respectively, were analytical reagents available in the market.

Separation of components from the synthetic leather

The synthetic leather was cut into bits of 1 cm² pretreated using 5 g/L of a neutral detergent with 1:50 of bath ratio for 30 min at 95°C. After rinsing with clean water, the bits were put into a vacuum oven at 60°C for drying, until they were dried to a constant weight. Then, they were placed into an exsiccator.

The component of PA-6 was obtained from the sample using gradient extraction as follows. The dried sample of 1 g was put into a flask with 50 g of DMF, the flask was plugged, and then was placed into an ultrasonic oscillator (KO-50B Ultrasonic Cleaner, Kunshan Ultrasonic Instrument, China) to release the air bubble from the sample for 2 min. After that, the flask was put still for 4 h at room temperature for the extraction, and was vibrated lightly for 1 min at every intervals of 0.5 h. Then, the DMF was poured out from the flask and the sample was washed twice with 20 mL of fresh DMF. The whole process was repeated up to five times. Subsequently, the resultant sample was rinsed using distilled water to remove the solvent DMF, and finally it was put into the vacuum oven at 60°C for drying. The dried sample was PA-6 component, needed for characterization.

The separation steps for the component PU from the synthetic leather sample were similar to the process mentioned earlier, while the only difference was that the DMF was replaced by HCOOH as a solvent to eliminate the PA-6 portion. The resultant sample was PU component.

Determinations

Instruments of 170SX FTIR (Nicolet Company), JSM-5900 LV SEM (JEOL Company, Japan), and D/maxIIIa XRD (Japan) were utilized to analyze the chemical, morphological, and the crystalline structures for the synthetic leather sample and its components, respectively.

For determining the crystallinity, we adopted the integral area distribution method⁶ that fits for a polymer having a limited number of crystalline peaks on its X-ray diffraction pattern $I = f(2\theta)$. In this way, the sharp diffraction peak(s) of the crystalline region could be differentiated from the scattering of the amorphous.

That is, after the background scattering had been deducted from the XRD pattern, the total diffraction area under the curve, S_0 , and the area of crystalline portion in the XRD pattern, S_k , were integrable. Then, the crystallinity K is calculated as

$$K = S_k \times 100 / S_0 \quad (1)$$

RESULTS AND DISCUSSION

Chemical structure of the components

In PA-6 molecule, $-\text{[(CH}_2\text{)}_5\text{CONH]}_n-$, there are some polar groups of $-\text{CONH}-$, $-\text{COOH}$, and $-\text{NH}_2$, with hygroscopicity, and soft hexylidene chains with hydrophobicity and soft handle. The amphiphilic chemical structure is suitable for the fiber to be dyed using acid dyes and disperse dyes.

Figure 1 shows the FTIR spectrum of the PA-6 component separated. In this figure, two middle absorption peaks at 3304 and 1543 cm⁻¹ and a strong absorption band at around 1642 cm⁻¹ are assigned to $-\text{NH}_2$ and $-\text{CONH}$; in addition, there is a wide absorption band at about 3413 cm⁻¹, which is the character of $-\text{COO}-$. Furthermore, two absorption bands around 2932, 2861 cm⁻¹, and a weak band at 720 cm⁻¹ are attribute of five $-\text{CH}_2-$ joined together. This absorption curve is consistent with the standard pattern of PA-6.

General chemical structure of PU is $-\text{[O(CH}_2\text{)}_4\text{]}_m-\text{[X]}_n-$ and $-\text{[COOR]}_m-\text{[X]}_n-$, in which $-\text{[X]}_n-$ is hard segment: $-\text{[OCONHC}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NHCONHCH}_2\text{CH}_2\text{NHCONHC}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NHCO]}_n-$; $-\text{[O(CH}_2\text{)}_4\text{]}_m-$ is polyether soft segment in a polyether urethane and $-\text{[COOR]}_m-$ is polyester soft segment in a polyester urethane, respectively.

As shown in Figure 2, for the FTIR spectrum of the PU component, there are two absorption bands of N—H stretching vibration around 3427 and 3452 cm⁻¹.

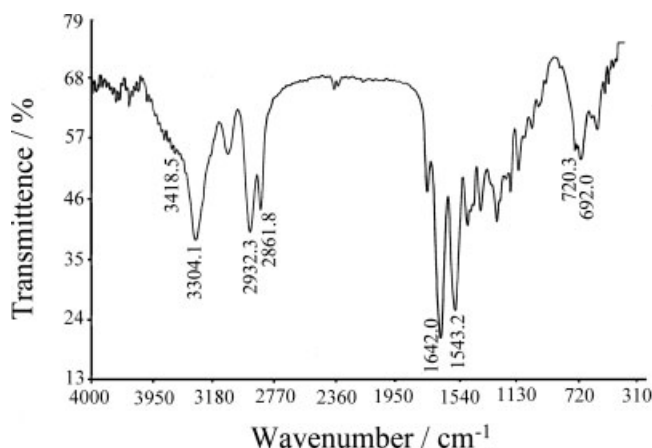


Figure 1 FTIR spectrum of the PA-6 component.

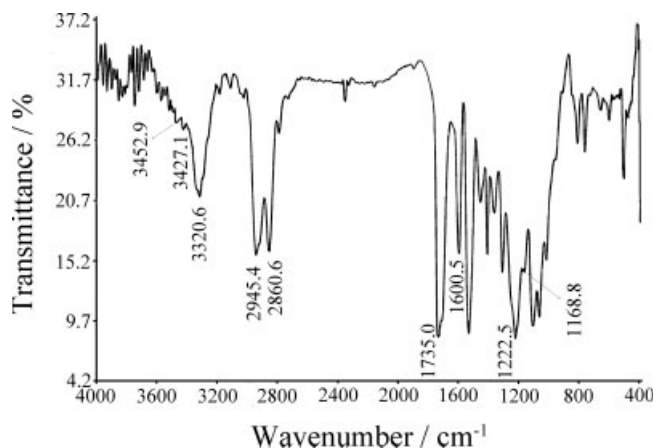


Figure 2 FTIR spectrum of the PU component.

Three absorbance bands around 1735, 3320, and 1600 cm^{-1} are assigned to —NHCOO— group. In general, the absorption bands of 1250–1180 cm^{-1} indicate ester groups, so that two absorbance bands around 1222.5 and 1168.8 cm^{-1} indicate that there are ester groups in the polymer. There are several peaks between 1460 and 1600 cm^{-1} owing to absorption of phenylene ring. The two absorption bands of C—H stretching vibration around 2945 and 2860 cm^{-1} are attribute of alkylene in the compound, and illuminate that it belongs a kind of thermoplastic polyester polyurethane. There are significant differences between the ether and ester soft segment in polyurethane. The low glass transition temperature for the polyether (-50°C) was attributed to the flexibility of the ether linkages, whereas a glass transition at -30°C was found for the ester soft segment polyurethane owing to segment rotation round the axis of C—O—C. When compared with ether soft segment polyurethanes, polyesters are known to provide a more polar bond structure and more basic oxygen with which stronger dipole and hydrogen-bonding interactions can occur with the NH groups on the urethane hard segments.

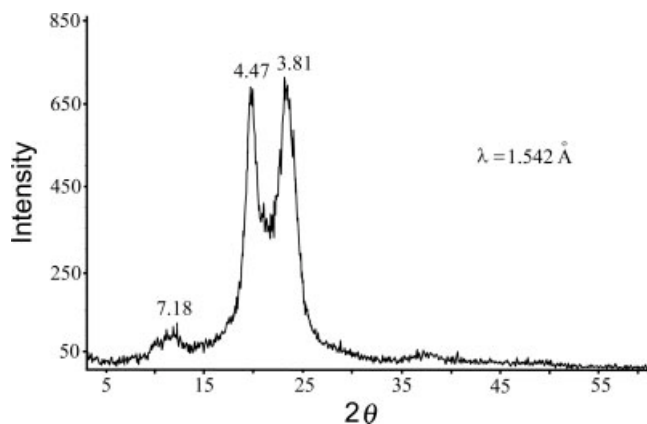


Figure 3 XRD pattern of the PA-6.

Thus, the polyester urethane with phenylene rings forms a more cohesive polymer, with less hard segment-soft segment microphase segregation and less flexible soft segment polyester chains. Therefore, the PU has both hard segment and soft chains, offering good elasticity to the material. This, in the mass, is a hydrophobic polymer with some polar groups, such as —NHCOOR— , —NHCONH— , and —O— , which provide the PU with dyeability using disperse dye-stuffs. In sum, the chemical structure of the PU is $\text{—[COOR]}_m\text{—[X]}_n\text{—}$, in which $\text{—[X]}_n\text{—}$ is hard segment and $\text{—[COOR]}_m\text{—}$ is polyester soft segment.

Condensed phase

The XRD pattern of a polymer reflects in its condensed texture. For PA-6, as shown in Figure 3, the crystallinity calculated by use of eq. (1) is 65.6%, which means the crystalline region in the PA-6 is more than the amorphous. In other words, the microfiber PA-6 has a more compact supermolecular structure, which provides the nonwoven textile as well as the synthetic leather with good strength. On the other hand, larger crystallinity could influence absorption of dyes, so does the depth of dyeing.

Figure 4 shows the XRD pattern of the PU component. There is a dispersion peak at about $2\theta = 21^\circ$ in the pattern, which means a noncrystalline structure in the PU,⁷ and is associated with the phase separation (hard block-soft block) of the PU. The hard segments (two urethane groups and one chain extender unit) may give rigid and high melting temperature microdomains. Soft segments (hydrocarbon chains of polyglycol) may give flexible, elastomeric, and low softening temperature microdomains. The crystallization of PUs is correlated with their molecular weight, constituents, and the component ratios of the soft-hard segments.⁸ Since, there are aromatic rings in the PU molecule as indicated in the FTIR spectrum, which may increase rigidity to the polymer and make against arrangement of chains, so as to effect the crystallization.⁹ The hard

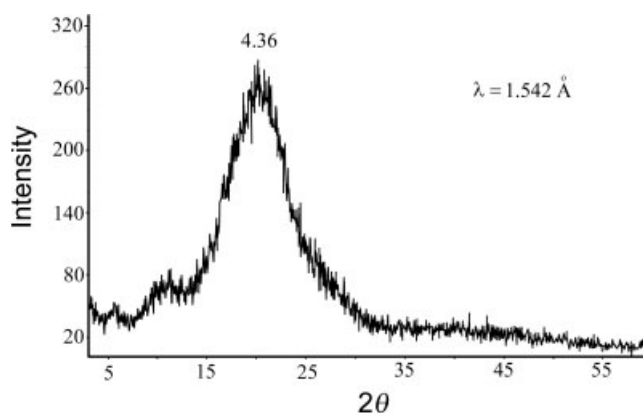


Figure 4 XRD pattern of the PU.

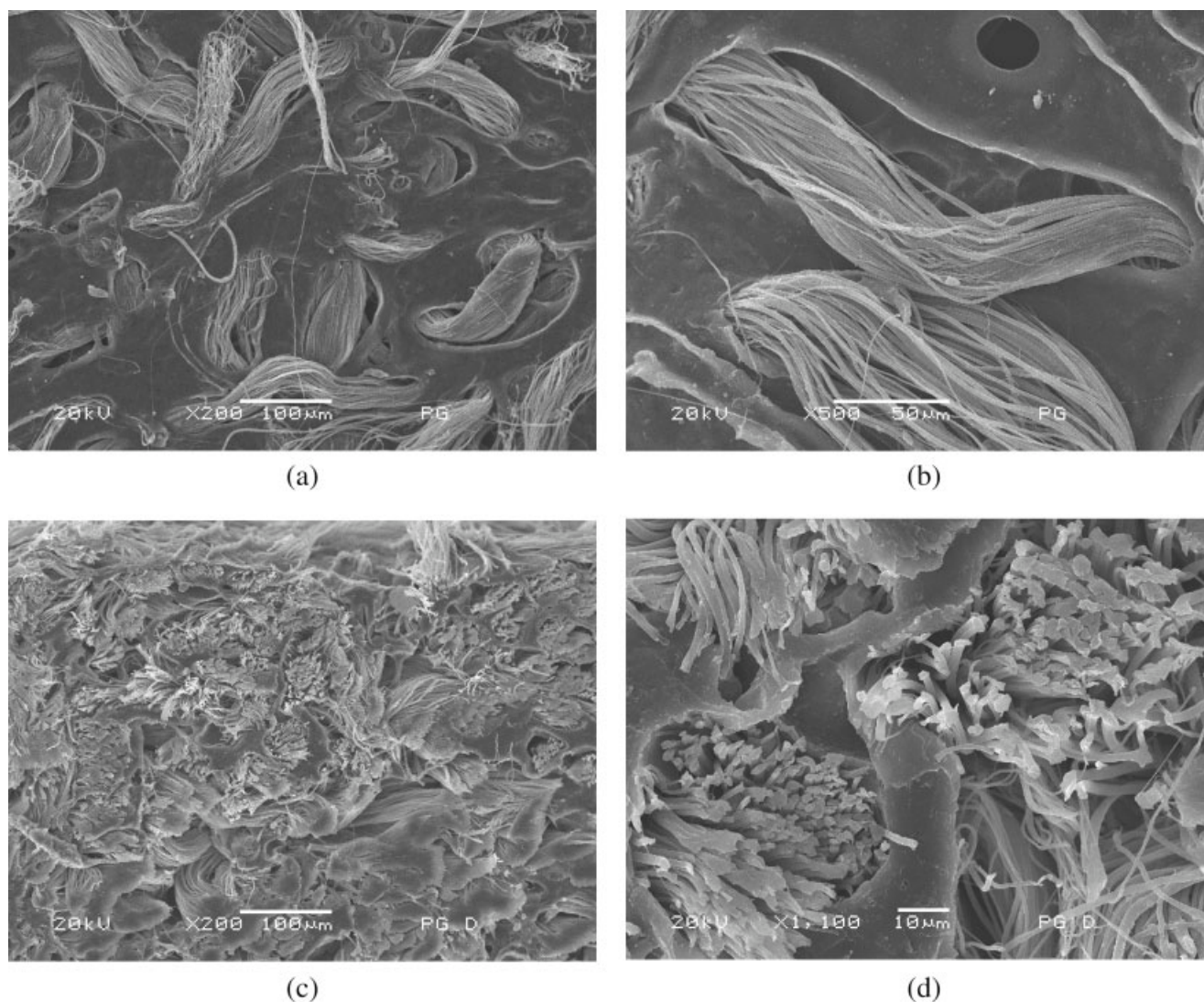


Figure 5 SEM micrographs of the synthetic leather. (a) and (b) for the surfaces; (c) and (d) for the cross sections of the synthetic leather. (a) $\times 200$, (b) $\times 500$, (c) $\times 200$, and (d) $\times 1100$.

segment domains act as physical crosslink at temperatures above the glass-rubber transition point of the soft segments, and stability of the physical links may exhibit shape memory effect.¹⁰ The content of the hard domains in the PU is 58.7%. A larger hard segments proportion means more rigid than an ordinary PU, and may make the leather better shape retention.

Morphological structure

Figure 5 shows the scanning electron micrographs of the original synthetic leather. It was observed from Figure 5 that the PA-6 microfiber yarns are inserted in the PU component, forming a net structure. Figure 5(a) shows that the annular fiber bundles distribute on the surface of the textile, making it floss-like in a sense of soft handle. After magnification of the picture, as shown in Figure 5(b), the loose fiber bundles are clearer, together with some holes and trenches in

the PU matrix with size of 25 μm or above, which could be ascribed to both treatments of wet-cured polyurethane process and extraction of the matrix LDPE from the sea-island composition fibers using toluene. Figures 5(c) and 5(d) show the cross section images of the leather. It was shown that many microfiber bundles are distributed in the textile, just like the structure of a ferroconcrete, which will endow the synthetic leather with excellent mechanical properties.

Figure 6 shows the SEM images of the PA-6 after separated from the leather. Figure 6(a) indicates that the basic character of the PA-6 nonwoven is well distributed at all directions, which will ensure symmetrical strength and elongation properties of the synthetic leather in all directions. As shown in Figure 6(b), after removing the PU component and the LDPE matrix, the PA-6 fiber has rounded cross section and slippery longitudinal shape. The average diameter is about 0.7 μm , with the highest about 2 μm and the lowest about

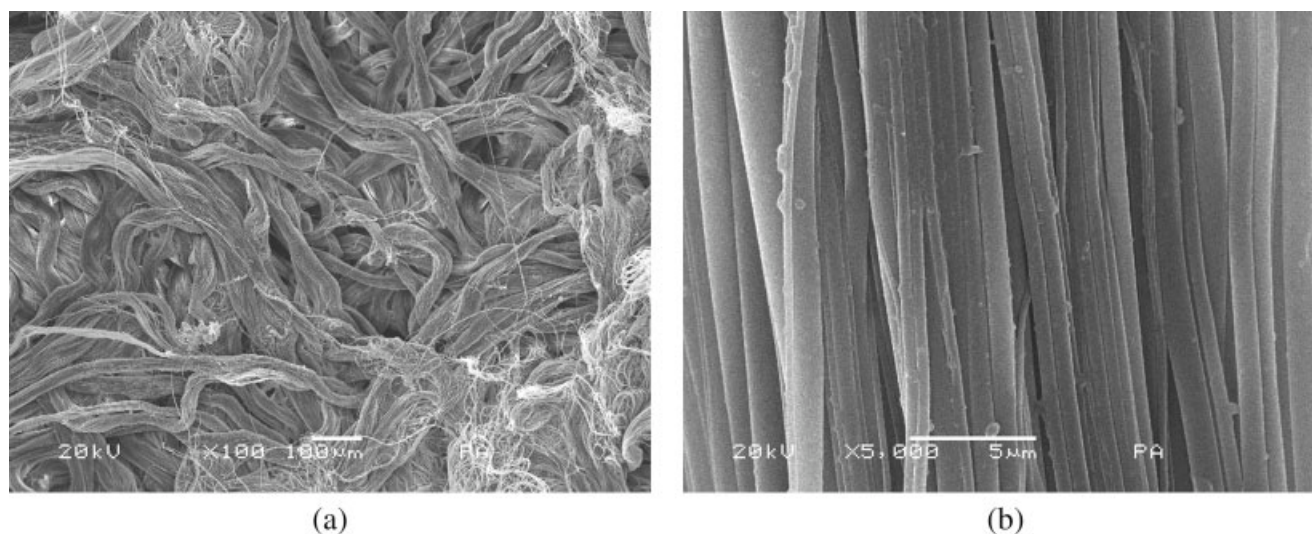


Figure 6 SEM micrographs of the PA-6 component separated (a) $\times 100$ and (b) $\times 5000$.

0.2 μm , in the range of microfiber category, contributing soft handle to the leather. Furthermore, the large surface area of the microfiber will enhance the ability to adsorb water and dyes, consequently, will provide the synthetic leather with a character of easy-to-dye but weak fastness.

Figure 7 shows the morphological structure of the PU component after the PA-6 component is removed from the leather. The SEM image of Figure 7(a) shows that the PU component is in a continuous phase, in possession of cavities or hollows connected with each other. The size of apertures is about 5–80 μm , just like the PU foam, enduing the leather with good elasticity and fluey handle. If relating Figure 7 with Figure 5, it could be seen that some tiny holes or apertures interlace from the surface throughout the synthetic leather

body, with sizes of about 25 μm or above those are much bigger than a free water molecule (about 0.18 nm) in gas or 280 associated water molecules (about 10 nm) in a colloid system.¹¹ Therefore, the porous structure is benefit for air and moisture permeability, hygroscopic ability, and desorption of moisture due to capillary action.

On the other hand, Figure 7(b) shows that the PU component (3000 times magnified) is not absolutely compact. Also, there are microapertures with diameters of about 0.1–2 μm randomly distributing in the PU matrix, may result in the process as the DMF was exchanged with water in the wet-cured polyurethane process. Therefore, the multiporous structure both in the PU matrix and between the PU and PA-6 will contribute excellent transportation of air or water in

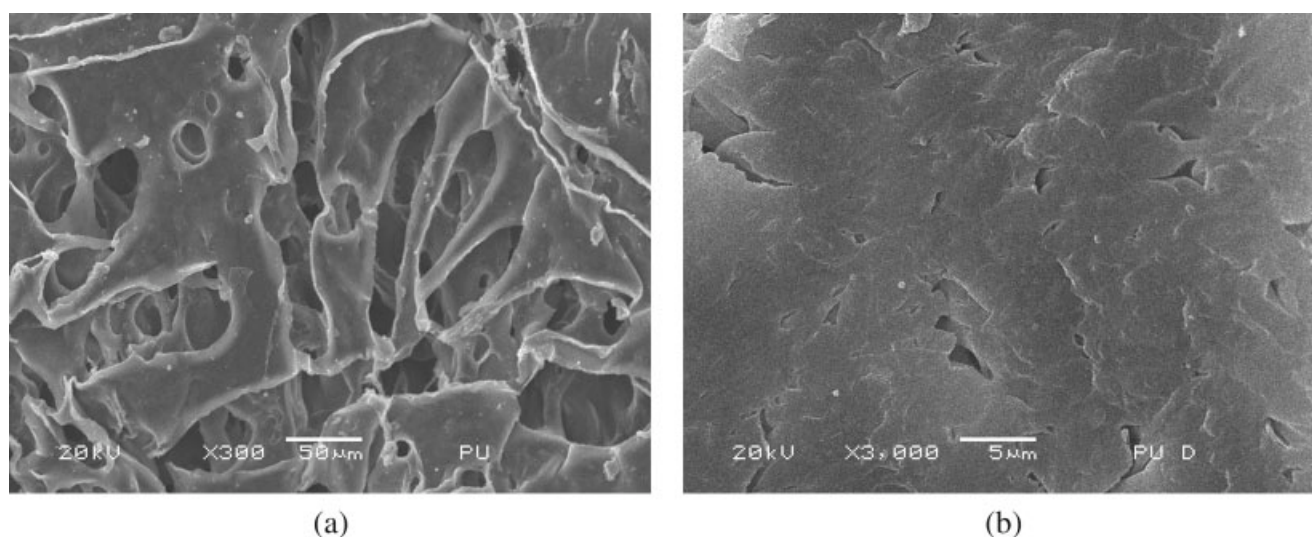


Figure 7 SEM micrographs of the PU component separated (a) $\times 300$ and (b) $\times 3000$.

and out, as well as dyeability, to the PU/PA-6 leather, although the PU and PA-6 are hydrophobic to some extent.

CONCLUSIONS

Synthetic leather, made of PA-6 microfiber and PU, was separated into its constituent elements using the gradient extraction by DMF and formic acid solvents, respectively. Each chemical structure of the components was characterized by FTIR spectra. The results showed the PU is a kind of polyester polyurethane. Although PA-6 and PU are both hydrophobic polymers, there are some hydrophilic groups in the molecules, which could provide them with dyeability and hydrophilicity to some extent.

It was shown from the determination of XRD that the crystallinity of PA-6 microfiber in the leather is 65.6%. It indicated that the crystalline portion occupies larger proportion in PA-6, which may offer the microfiber leather good mechanical property, and also could influence its dyeability. For the PU component, the XRD pattern showed a hard block-soft block phase separated structure lacking distinct crystalline, which may arise from aromatic rings in the PU molecule. The hard domains content in the PU was reckoned as 58.7%. A larger hard segments proportion means more rigid for the PU than an ordinary PU, and may make the leather better shape retention.

The performances of the synthetic leather must be correlative with its morphologic structures. From the

SEM images of the microfiber leather made of PA-6 and PU components, the morphological structures of them were clearly recognized. The PA-6 microfibrils transfixing the PU matrix form a net bundle structure, similar to collagen fibers in natural leathers, which could contribute mechanical properties for the microfiber leather. Furthermore, there are two kinds of porous structures, with one type of pore sized 5–80 μm between the components of PU and PA-6, and the other in PU matrix in a size of 0.1–2 μm . The multipores run through the synthetic leather as three-dimensional channels, benefit for transportation of air, water, dyes, and so on.

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