



Laser-drilled micro-hole arrays on polyurethane synthetic leather for improvement of water vapor permeability



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ABSTRACT

Three kinds of lasers at 1064, 532 and 355 nm wavelengths respectively were adopted to construct micro-hole arrays on polyurethane (PU) synthetic leather with an aim to improve water vapor permeability (WVP) of PU synthetic leather. The morphology of the laser-drilled micro-holes was observed to optimize laser parameters. The WVP and slit tear resistance of the laser-drilled leather were measured. Results show that the optimized pulse energy for the 1064, 532 and 355 nm lasers are 0.8, 1.1 and 0.26 mJ, respectively. The diameters of the micro-holes drilled with the optimized laser pulse energy were about 20, 15 and 10 μm , respectively. The depths of the micro-holes drilled with the optimized pulse energy were about 21, 60 and 69 μm , respectively. Compared with the untreated samples, the highest WVP growth ratio was 38.4%, 46.8% and 53.5% achieved by the 1064, 532 and 355 nm lasers, respectively. And the highest decreasing ratio of slit tear resistance was 11.1%, 14.8%, and 22.5% treated by the 1064, 532 and 355 nm lasers, respectively. Analysis of the interaction mechanism between laser beams at three kinds of laser wavelengths and the PU synthetic leather revealed that laser micro-drilling at 355 nm wavelength displayed both photochemical ablation and photothermal ablation, while laser micro-drilling at 1064 and 532 nm wavelengths led to photothermal ablation only.

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1. Introduction

Water vapor permeability (WVP) of polyurethane (PU) synthetic leather is of great importance when PU synthetic leather is used for the manufacture of shoes and garments [1]. In order to keep human bodies warm and comfortable, shoes and garments should have high WVP value which allows perspiration to evaporate promptly, especially when human bodies are in hot environments. Relative humidity inside the shoes and garments will decrease when water vapors transfer through the PU synthetic leather into the environment. This subsequently leads to a decrease in thermal conductivity of the insulating air, resulting in guarding against a damp feeling [2–6]. In this way, WVP has significant influence on thermal comfort properties of shoes and garments. However, PU synthetic leather exhibits low WVP, despite the excellent physical properties it has. The low WVP of the PU synthetic leather is mainly caused by the PU film on the top layer. The PU film has a remarkably negative impact on the WVP, though its thickness is small [3,7,8]. According

to the results reported by Lewin [9], WVP of PU synthetic leather decreased by 30–50% when compared with unfinished leather. Many researches have been done to improve the WVP of PU film. The present investigations mainly focused on the ways to promote surface hydrophilic property and porous structures of the PU film by chemical process. Zuo et al. [10] prepared blend membranes of PU and superfine chitosan powder by immersion precipitation phase inversion method. They found that the WVP was improved remarkably with increasing superfine chitosan powder content. Chen et al. [11] enhanced WVP of PU synthetic leather by oxygen plasma treating. Liu et al. [12] used solution casting method to blend down powder with PU to improve the WVP of PU membrane. They found that large pore size of composite membranes and hydrophilic groups on the surface of down powder lead to improvement of the WVP. Han et al. [13] modified PU by hydrophilic DMPA segments to improve the WVP of PU. Chwang et al. [14] used ethylene glycol and other strong hydrophilic compounds to prepare modified PU. In this way, the WVP was raised.

Slit tear resistance is of great value to leather when they are used to manufacture shoes and garments, since better slit tear resistance enables leather to withstand tearing stresses. As a result, decrease in slit tear resistance can affect durability of leather.

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Compared with other manufacturing methods, laser micro-drilling has many advantages. For example, it has good flexibility, high efficiency, as well as the ability to control the duration of the energy deposition process [15,16]. Many researches on laser micro-drilling have been reported up to now. Pan et al. [15] fabricated hole arrays with a 50 μm thick PI film by using a 248 nm excimer laser. They found that laser fluence has a great influence on the diameter of the hole. Chen et al. [16] used UV excimer laser drilling a submicron via hole inside a bigger via hole. They thought that the refocusing of the reflected laser light from the side-wall of the bigger hole and the wave-guide effect of the light trapped inside the smaller hole led to the formation of the smaller via hole. Tokarev et al. [17] developed a model of multipulse excimer laser drilling in polymers. They tried to investigate the particular mechanism of radiation propagation and absorption inside the keyhole, to identify the factors that control the formation of the keyhole and to optimize the drilling. Tan [18] achieved 20 μm holes in a 250 μm thick silicon substrate by using a nanosecond UV laser. He successfully eliminated the deformation caused by plasma shielding with a multi-burst pulse train. Seet et al. [19] got hole arrays on PVC templates by using a 355 nm diode-pumped solid state Nd:YAG laser. He pointed out that the laser fluence, laser irradiation time, number of pulses and focal point all could affect the quality of the drilled holes. Liu et al. [20] formed circular and rectangular via holes in 300 μm thick bulk 4H-SiC substrates by a 193 nm UV laser. Yalukova et al. [21] compared the drilled holes in fiber reinforced polymer and non-reinforced thermoplastic sheets using three wavelengths, 1064, 532, and 266 nm. They pointed out that by using UV light, bond breaking rather than thermal material removal occurred.

Rather than promoting neither the surface hydrophilic property nor the porous structures of PU synthetic leather by chemical process, we fabricated micro-hole arrays on the PU synthetic leather by a laser micro-drilling process to improve the WVP of the PU synthetic leather in this study. In order to obtain small drilled micro-holes, lasers with different wavelengths were used. The influence of pulse energy on the morphology of the micro-holes was investigated. The interaction mechanism between laser beams at three kinds of wavelengths and the PU synthetic leather was studied. After micro-hole arrays being drilled on the PU synthetic leather, the WVP and slit tear resistance were then tested.

2. Materials and methods

In this study, the thickness of the PU synthetic leather is about 1.3 mm, and the thickness of the PU layer is about 60–70 μm . Laser micro-drilling of PU synthetic leather was carried out by adopting three kinds of lasers with different wavelengths, i.e., a SPI 20W/HS laser at 1064 nm wavelength, a Huaray Cedar-532/20B diode-pumped Nd:YAG laser at 532 nm wavelength and a Huaray Cedar-355/10B diode-pumped Nd:YAG laser at 355 nm wavelength. The specifications of the lasers are given in Table 1. Focal length of objective lens adopted by the 1064, 532 and 355 nm lasers is 100, 120 and 100 mm, respectively. Numerical aperture of objective lens equipped the 1064, 532 and 355 nm lasers is 0.22, 0.15 and 0.18, respectively. For the 1064 nm laser, magnification of beam expanding lens is 75. For the 532 and 355 nm laser, magnification of beam expander is 10. The morphology of the laser-drilled micro-holes was observed by a JEOL-7600F scanning electron microscope (SEM) and a Dino-Lite digital microscope. The micro-hole density was varied from 10,000 to 40,000 micro-holes per square centimeter to investigate the effect of the micro-hole density on WVP and slit tear resistance.

WVP was measured in a round mouth plastic cup filled with distilled water. Laser-drilled PU synthetic leather was placed over

the top of the cups. The cups were placed in a chamber where the temperature was constant at 20 °C and the relative humidity was at 70%. The weight loss after 24 h was measured. For each WVP measurement, on an average of three different readings was used. The result of WVP was calculated using the following equation:

$$\text{WVP} = \frac{G}{tA} \quad (1)$$

where G is weight change in milligram, t the duration of measurement in hour and A the measurement area in square centimeter.

The slit tear resistance of laser-drilled PU synthetic leather was evaluated with a universal material testing machine (Zwick/Roell, Z020) according to ASTM D2212. The speed of the clip was 100 mm/min.

3. Results

3.1. Laser micro-drilling parameters of the PU synthetic leather

The morphology of micro-hole arrays, front view of micro-holes and cross section of micro-holes drilled by different lasers under variable pulse energy are shown in Figs. 1–4, respectively. When the 1064 nm laser was adopted, it could be seen from Fig. 1 that no micro-hole but only some thermal degradation and shrinkage were observed at the laser pulse energy lower than 0.2 mJ, and obvious micro-hole was observed at the laser pulse energy higher than 0.3 mJ. Fig. 2 shows that micro-holes could be drilled using the 532 nm laser at the pulse energy higher than 0.5 mJ, and there was no burning but a heat affected zone (HAZ) around the micro-holes. Micro-holes could be drilled using the 355 nm laser at the pulse energy higher than 0.18 mJ, as shown in Fig. 3. It was clear that the variation of pulse energy had a remarkable influence on diameter and depth of the micro-holes. With an increase in pulse energy, diameter of the laser-drilled micro-hole at 1064 nm wavelength increased from 15 μm to 20 μm ; diameter of the micro-hole drilled with the focused 532 nm laser beam increased from 12 μm to 15 μm ; the diameter of the micro-hole drilled by the 355 nm laser increased from 8 μm to 10 μm . In addition, diameter of the HAZ in Fig. 2 increased from 27 μm to 32 μm , with an increase in pulse energy. Moreover, depth of the micro-hole drilled with the focused 1064 nm laser beam increased from 31 μm to 69 μm with an increase in pulse energy from 0.23 mJ to 0.26 mJ; depth of the micro-hole drilled by the 532 nm laser increased from 34 μm to 60 μm with an increase in pulse energy from 0.7 mJ to 1.1 mJ; depth of the laser-drilled micro-hole at 355 nm wavelength increased from 31 μm to 69 μm with an increase in pulse energy from 0.23 mJ to 0.26 mJ. Furthermore, in comparison with 1064 nm-laser and 532 nm-laser drilled specimens, thermal influence was significantly reduced when the 355 nm laser was adopted.

It is of great significance that the depth of the laser-drilled micro-holes should be deep enough in order to penetrate the PU films that cover the synthetic leather. Taking the results of the earlier parameters studies into consideration, the optimized pulse energy was used for different kinds of lasers to drill different micro-hole densities. The optimized laser parameters for three kinds of laser wavelengths are summarized in Table 2.

3.2. The effect of laser wavelength and micro-hole density on the WVP

Fig. 4 shows the WVP value of the laser-drilled PU synthetic leather. The samples for WVP test were prepared according to the optimized laser parameters listed in Table 2. It could be observed that the WVP showed an upward trend with a decrease in laser wavelength. The WVP values of all laser-drilled samples were significantly influenced by laser beam wavelength at the fixed

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