Influence of UV Irradiation on the Properties of Tanned and Fatliquored Goatskin Leather[#]

Xuejing Zheng, Kun Wang, Keyong Tang*, Shufa Qin, Jie Liu

College of Materials Science and Engineering, Zhengzhou University, Henan 450052, P.R. China

Abstract: Collagen based biomaterials are sometimes subject to the action of UV irradiation from sunshine or from artificial sources during sterilization. Prolonged exposure to UV irradiation will cause excessive molecular fragmentation and denaturation. However, limited data appear to be available concerning the influence of UV irradiation on the collagen matrices modified by chemical crosslinking and physical plastisizing. The present work investigated the influence of UV irradiation on the mechanical properties, water vapor permeability, dimensional stability and surface morphology of the tanned (by chrome, glutaraldehyde and quebracho extract, respectively) leathers and fatliquored (by emulsified chlorinated paraffin, soybean lecithin and sulphitated soybean lecithin, respectively) leathers before and after UV irradiation. It was found that the tensile strength of all the samples slightly increase during 4h of UV irradiation, then followed by a rapidly decrease with irradiation time increasing. It was indicated that limited exposure of collagen to UV results in an intermediate state consisting of molecules that are cross-linked but partially denatured because of multiple chain scissions along the helix. Long time irradiation may result in UV-induced chain scission and an impaired mechanical performance. The water vapor permeability of tanned and fatliquored collagen matrices decrease during the initial 4h of UV irradiation, and then increase after long time irradiation (4-64h). The resistance to UV irradiation is apparently related to the tanning agents applied. This is probably due to the role of different tanning agents and different tanning mechanisms. For fatliquored samples, the amount of double bonds of fatliquoring agents is a dominate parameter affecting the UV-resistance properties.

Keywords: collagen matrix; tanning; fatliquoring; UV irradiation; properties

1 Introduction

Collagen is the most abundant biopolymer in animals where it provides the principal structural and mechanical support. Biomaterials based on collagen have found a wide range of applications, including leather, sutures and haemostatics. Leather is a biomaterial made of collagen fibrous protein. In order to avoid putrefaction and to lubricate the collagen fibers, collagen is usually industrially modified by tanning and fatliquoring.

Leather products are often used under the explosion to the sunshine. The solar spectrum is a complex band of radiation including UVC (220-290nm), UVB (290-320nm) and UVA (320-400nm) as well as visible light and infrared radiation. Recently, stratospheric ozone depletion has been observed on the earth, and this induces the enhancement of UVB radiation reaching the earth's surface. It is important to understand the photodegradation mechanism of collagen and to take measure to improve the anti-UV ability of collagen materials [1-4]. This work investigated the influence of UV irradiation on the properties

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[*] Corresponding author. Tel.: +86-371-67763216. E-mail: keyongtang@yahoo.com.cn

of different tanned and fatliquored collagen matrices, trying to understand the chemical and physical modification on the anti-UV ability of leather products.

2 Experimental

2.1 Materials and Chemicals

Pickled goatskins were supplied by Heitian Mingliang Leather Co., Ltd., Xinxiang, China.

The tanning agents used were chrome power, glutaraldehyde and quebracho extract. The fatliquoring agents used were emulsified chlorinated paraffin, emulsified soybean lecithin and emulsified sulphited soybean lecithin. Chrome powder (Cr_2O_3 content of 25% and basicity of 33%), quebracho extract, chlorinated paraffin and soybean lecithin, commercial grade, were supplied by Sichuan Decision Chemicals Co., Ltd., Deyang, China. The other chemicals, glutaraldehyde (50%), NaCl, $NaHCO_3$, and sodium acetate are all analytical reagents.

2.2 Preparation of Tanned and Fatliquored Samples

Tanning and fatliquoring processes were carried out by using laboratory-scale tanning drums (DJDf 350 tanning drum, Xibeitang Leather Machinery Company, Xishan, China). Standard laboratory conditions are applied for tanning and fatliquoring procedures for each agent.

2.3 UV irradiation

The samples were UV irradiated under air at room temperature using a UV-resistant Climate Testing Machine (Model ZN, Shanghai Linpin Experiment Equipment Co., Ltd., China), which emits light mainly at a wavelength of 312 nm. Irradiation experiments were carried out on aluminum shutter at a distance of 50 mm from the light source. Various doses of UV irradiation were obtained by varying irradiation time (0-64h). After irradiation, all the samples were air-conditioned in a desiccator with relative humidity of 65% (controlled with 36.7wt% H_2SO_4) for at least two weeks to a constant weight.

2.4 Mechanical Properties

The mechanical properties were measured with a Universal Testing Machine Model CMT6104. The tests were carried out at a crosshead speed of 100 mm/min.

2.5 Hydrothermal Stability

Samples were cut into a definite shape and the hydrothermal shrinkage temperature was tested in glycerin with a shrinkage temperature tester (PS-83, China).

2.6 Water Vapor Permeability

All the samples were air-conditioned in a desiccator with relative humidity of 65% (controlled with 36.7 wt% H_2SO_4) for at least two weeks to a constant weight. Water vapor transmission rate (WVTR) was measured by permeation cup method.

3 Results and Discussion

3.1 Mechanical Performance

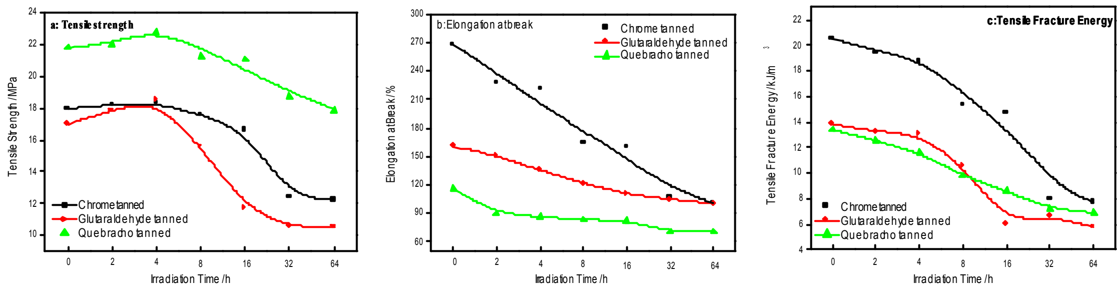

Fig. 1 Influence of UV irradiation on the mechanical properties of tanned goatskin matrices

Results of the mechanical properties of different UV-irradiated tanned goatskin matrices against irradiation time are shown in Fig. 1. From Fig. 1a it is seen that tensile strength of tanned samples increases slightly after irradiation for 4 h, then follows with a significant decrease after longer irradiation time. Fig. 1b shows that the elongation at break for each sample is decreased continually with the increase of irradiation time, which suggests that the samples become more brittle due to the UV irradiation. It also can be seen that the elongation at break of quebracho extract tanned matrices varied in a small range with irradiation time. It indicates that UV irradiation exerts less influence on the stretching ability of quebracho extract tanned leather. The tensile fracture energy determined from the area under the tensile load-offset curves of the samples can give the information of the toughness of the material [5]. The influence of the irradiation time on the tensile fracture energy is shown in Fig. 1c. The tensile fracture energy of all the tanned samples decreased with increasing the irradiation time, showing that the toughness of the materials was impaired by UV. Quebracho extract tanned leather shows a stable change in the mechanical properties after UV irradiation. It is deduced that during UV irradiation the phenolic structure of quebracho extract may produce phenoxyl radicals and renders possible photooxidation.

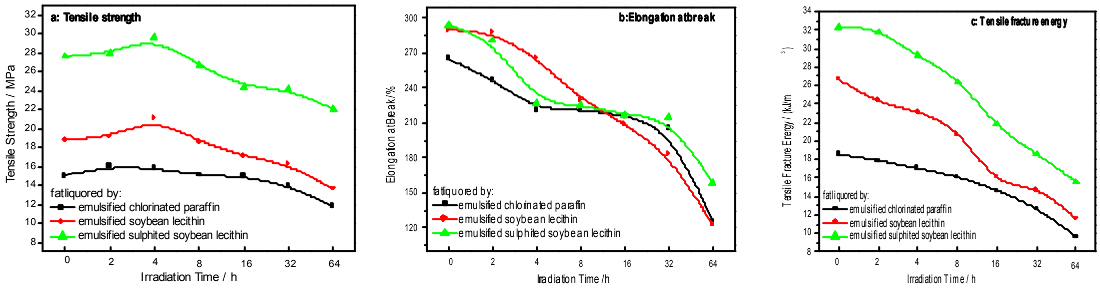

Fig. 2 Influence of UV irradiation on the mechanical properties of fatliquored goatskin matrices

Three fatliquoring agents were applied to lubricate the collagen fibers in the matrices. Chlorinated paraffin, a saturated mineral oil, is a complex mixture of polychlorinated n-alkanes. Soybean lecithin is a group of phospholipids having the general composition CH_2OR_1 - $CHOR_2$ · CH_2OPO - OHR_3, in which R_1 and R_2 are fatty acids and R_3 is choline. When the native soybean lecithin is sulphited, the unsaturation degree is decreased and amount of the double bonds is reduced significantly. The current work tries to investigate the effect of the double bonds in fatliquoring agents on the UV resistance of the collagen matrices. Results of the mechanical properties of UV-irradiated different fatliquored goatskin matrices against irradiation time are shown in Fig. 2. The tensile strength of fatliquored collagen matrices increases slightly with increasing irradiation time up to 4h, and then decreases significantly after long time irradiation (Fig. 2a). The elongation at break decreases continually with irradiation time (Fig. 2b), indicating an impaired stretching ability. The tensile fracture energy results show that smaller energy is required to destroy the material after UV irradiation (Fig. 2c). The three fatliquoring agents investigated endows collagen matrices with apparent different anti-UV ability. The changes in mechanical properties of different fatliquored samples irradiated for 4h and 64h are shown in Table 1.

Tab. 1 Mechanical properties of fatliquored collagen matrices irradiated for 4h and 64h.

	Emulsified chlorinated paraffin fatliquored			Emulsified native soybean lecithin fatliquored			Emulsified sulphited soybean lecithin fatliquored		
	4h	64h	decrease	4h	64h	decrease	4h	64h	decrease

Tensile strength (MPa)	15.8	11.8	25.3%	21.1	13.6	35.5%	29.7	22.1	25.6%
Elongation at break (%)	221	126	42.9%	266	123	53.8%	227	159	30.0%
Tensile fracture energy (kJ/m^3)	17.0	8.1	52.4%	23.1	11.5	50.2%	29.2	15.6	46.6%

It is seen that, as a saturated mineral oil, emulsified chlorinated paraffin fatliquored samples have small change in mechanical properties. Native soybean lecithin fatliquored collagen matrices show a significant change in mechanical tests. A gentle change in mechanical properties is observed in the case of the sulphited soybean lecithin fatliquored samples. The data in Fig. 1 and Table 1 suggest that the number of double bonds in fatliquoring agents may have great influence on the resistibility to UV irradiation of the collagen matrices.

3.2 Hydrothermal Stability

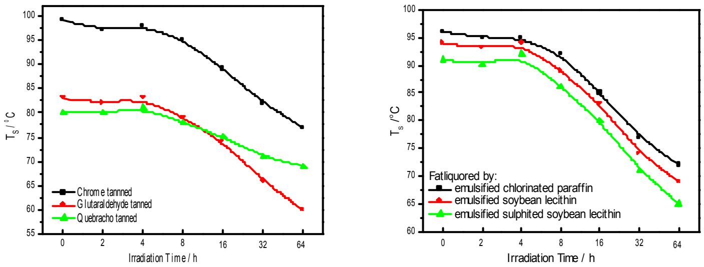

Fig. 3 Influence of UV irradiation on the hydrothermal shrinkage temperature of tanned and fatliquored goatskin matrices.

The influence of UV irradiation on the hydrothermal shrinkage temperature of tanned and fatliquored collagen matrices are shown in Fig. 3. It is seen that the hydrothermal shrinkage temperature decreases continually with increasing irradiation time, showing an impaired thermal stability. Furthermore, the hydrothermal shrinkage temperature of tanned and fatliquored samples changes little in the first 4h of irradiation, while decreases dramatically after long time irradiation. The results indicate that long time irradiation under UV light may break the collagen molecular structure to a large degree.

3.3 Water Vapor Permeability

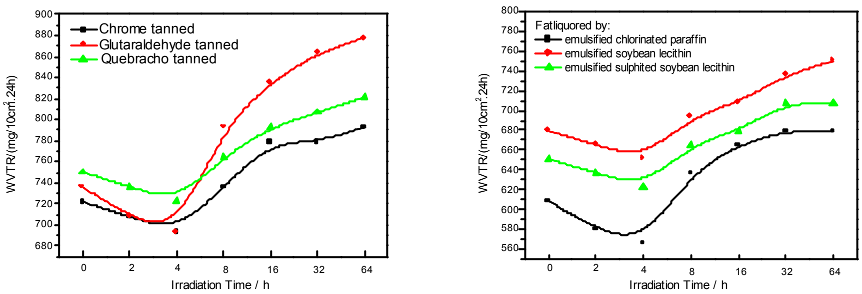

Fig. 4 Influence of UV irradiation on the water vapor permeability of tanned and fatliquored goatskin matrices.

Water vapor transmission rate is defined as the amount of water vapor passing through a given area of a sheet or film in a given time, when the sheet or film is maintained at a constant temperature and when its faces are exposed to a certain relative humidity. Water vapor permeability is an important property of leather to make successful breathable materials. Fig. 4 shows that water vapor transmission rate (WVTR) plays the similar trend for all the samples with UV irradiation time. The irradiation for less than 4 h results in a decrease in WVTR for tanned and fatliquored collagen matrices. This may have arisen from the additional crosslinking reactions due to the UV irradiation. The increasing of crosslink networks in the collagen matrix is obviously not in favor of the adsorption and diffusion of water vapor molecules throughout the leather matrices. Longer irradiation time (4-64 h) leads to a significant increase of WVTR. This is probably due to the macromolecular chain scission under UV energy, and therefore, an increase in pore volume of matrices.

3.4 Dimensional Stability

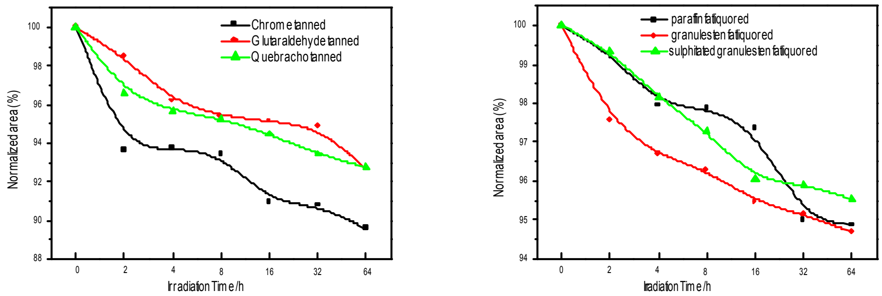

Fig. 5 Influence of UV irradiation on the dimensional stability of tanned and fatliquored goatskin matrices.

Products with a stable dimension are required in many applications. The area of each sample was measured before and after UV irradiation and the normalized areas are illustrated in Fig. 5. It can be seen that a progressive decrease in the area of the collagen matrices was found after irradiation. It is deduced that the chemical reactions in collagen macromolecules results in a decreased sample dimension.

4 Conclusions

Different chemical reactions happen in collagen macromolecules during UV irradiation. Short time irradiation results mainly in crosslink within and between collagen chains. Long time irradiation may result in chain scission. The tensile strength, tensile fracture energy and water vapor permeability are slightly increased at the beginning of irradiation, and then followed by a drastic decrease. The hydrothermal stability is impaired due to UV irradiation. The plant extract can endow the collagen with better capability against UV due to the phenolic structure. The number of double bonds of fatliquoring agent influences the UV-resistance properties of physical modified collagen matrices.

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