

Preparation and Characteristics of Leather-like Material from Shark Intestines

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Every year fish skin, bone and intestines are discarded as processing waste material. The use of fish processing waste material is more economical and environmental-friendly. The leather-like material was produced using shark intestine. Physical characteristics such as tensile strength, elongation, tongue tearing strength, and bursting strength of the leather-like material were measured, and compared with those of a commercial leather product. The values of tensile strength, elongation, tongue tearing strength, and bursting strength of the leather-like material were 3.3 kg/mm², 53%, 13.0 kg/mm and 18 kg/cm², respectively. Elongation (109%) of the leather-like material coated with lacquer was higher than that of a commercial leather material, and the other factors were similar. The tensile strength and tongue tearing strength of the leather-like material was higher than those of shoes leather, but bursting strength was lower. These results suggested a potential value to use the leather-like material from shark intestines as a substitute for commercial leathers.

Key words: Shark intestine, Leather-like material, Physical characteristic

Introduction

Considerable amounts of fish processing waste material such as fish skin, bone and intestines are discarded every year in the fisheries industry (Kim et al., 2001a). Marine bio-source based producers are no longer allowed to discard their offal directly into the sea, resulting in a very high cost of refining the material before it is discarded.

However, development of processes for waste recovery and utilization is more economically beneficial for the industry than discarding wastes. Some studies related to the effective utilization fish processing wastes, have reported the extraction of bio-active peptides from fish skin and frame (Kim et al., 1997; Byun and Kim, 2001; Kim et al., 2001b), purification of various enzymes from fish tissues and intestines (Kim and Kim, 1991; Haard, 1992; Jeon et al., 1998), extraction of soluble calcium and gelatin from fish bones (Kim et al., 1996; Choi et

al., 1999; Kim et al., 2001c).

In the case of large fish, sharks were taken in large quantities beyond the Pacific coast of North America, near Ireland, and in South African and Australian waters (Brogstrom, 1969). The sharks classified *Subclass Elasmobranchii* of which there are about 400 species of sharks in the world (Compagno, 1984). In Southern coast of Korea, there are about 40 species.

In the past, shark waste materials were either discarded or used as fishmeal due to the limited harvest (King and Clark, 1987). Apart from fillets, some of the current products from shark include skin, fins, fish meal, corneas, cartilage, chondroitine, liver oils, and indirect products such as surfactant, aromatics, artificial silk and pharmaceuticals (Buranudeen and Richards-Rajadurai, 1986; McCurdy et al., 1995; Miller et al., 1998; Suzuki, 1999). Particularly, liver oil purified from shark exhibits anti-coagulative, antibacterial, anticholestermic, antitumor, and antimicrobial activities (Akiyama et al., 1982; Bordier et al., 1996; Baskaran et al., 1996; Lee

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et al., 1999).

The skin of the shark or whale was used for the preparation of leather shoes in Japan before the World War II. After the war, the production of these came to a halt due to the increment of imported land animal hides (Tanikawa, 1971). The leather industry produces a range of indispensable consumer goods, including shoes, bags, clothes, belts, wallets and gloves. Worldwide production of leather was expected to grow to 2.4 billion square meters by end of the year 2000 (Muchie, 2000).

Leather made from animal hides was used in various industries, but very little information is available of the leather related to large fish intestine. Shark intestines are mostly discarded due to bad smell and the appearance. However, efficient utilization of shark waste should be given a higher priority.

For effective utilization of shark intestines, it was suggested to prepare leather using shark intestines. The physical properties of this leather-like material were tested for the use in various leather industries.

Materials and Methods

Materials

The shark (*Squalus brevirostris*) intestines were purchased from the Southern coast of Korea. Lipapron used for deliming process of leather was purchased from Korea-Samhyup Co. (Busan, Korea), formic acid and basic chromium sulfate from Sigma Chemical Co. (St. Louis, USA). Tannin and olive oil were purchased from Junsei Chem. Co. (Tokyo, Japan). All the other reagents were of special grade reagents.

Preparation of leather

Preparation of leather using shark intestines was performed by the method of Yun et al. (1999) as shown in Fig. 1. First of all, the shark intestine (rectum) was separated from shark, and then the intestine was washed with water for the removal of the excreta and blood on the intestine surface.

For the removal of soluble proteins and lipids of the intestine (liming process), the intestine was treated with 3% (w/v) calcium oxide solution for 1 hr. After the removal of calcium oxide (deliming process) and proteins (bating process), the intestine

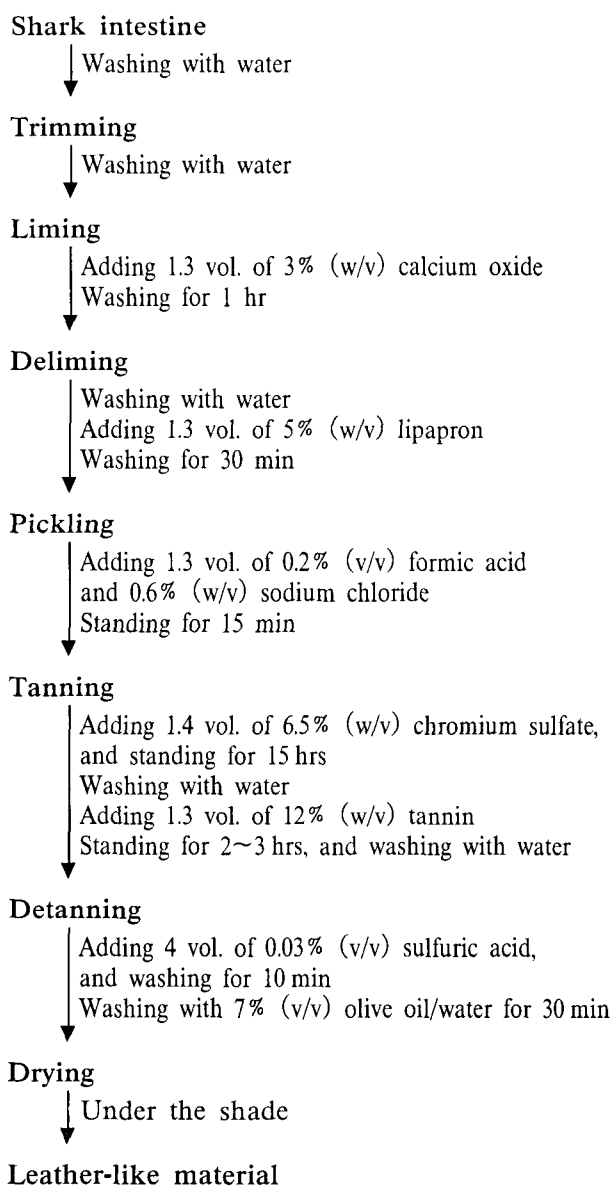


Fig. 1. Schematic procedure for preparation of the leather-like material from shark intestine.

was enlarged by treating 5% (w/v) ripapron solution for 30 minutes. Before the tanning process, the intestine was treated with a mixture solution of 0.2% (v/v) formic acid and 0.6% (w/v) sodium chloride for 15 minutes (pickling process).

The intestine was treated with 6.5% (w/v) basic chromium sulfate solution for 20 minutes, and then it was limed for 15 hrs in the same solution until become colorless from its initial green color. After washing the intestine in water, the intestine was limed in 12% (w/v) tannin solution for 2~3 hrs

(tanning process). Tannin was removed by using 0.03% (v/v) sulfuric acid for 10 minutes, and then was washed with 7% (v/v) olive oil/water for 30 min. Finally, the leather product was dried in the shade.

Test of physical properties of the leather

Characterization of physical properties of leather was performed at the Korea Institute Footwear & Leather Technology (Busan, Korea). Tensile strength, elongation, and tongue tearing strength of the leather were measured by the test method of KS M 6882 (Korean Agency for Technology and Standards, 1995). Bursting strength was measured by the test method of KS M 7082 (Korean Agency for Technology and Standards, 1997).

Results and Discussion

Preparation of leather-like material from shark intestine

Sharks intestines are composed of collagen, keratin, and elastin, which is same compositions as commercial leathers. Therefore, leather-like material from shark intestines could be prepared by the same processing method of land animal leather. As shown in Fig. 1, leather-like material was prepared through the trimming, liming, deliming, pickling, tanning, detanning and drying processes.

The retannage of chrome tanned leather was carried out to improve the characteristics such as the fullness and the softness (Burkinshaw and Kitching, 1995; Covington et al., 2001). Tanning of shark intestine is a leathering effect, which is characterized by a change in the appearance and feel of the intestine, especially the effect of drying. Modern leather production employs a variety of agents, but tanning with chromium (III) salts predominates (Covington et al., 2001)

Photographs of the surfaces of the leather-like material prepared from the rectum of the sharks intestines shown the same appearance of leather (Fig.

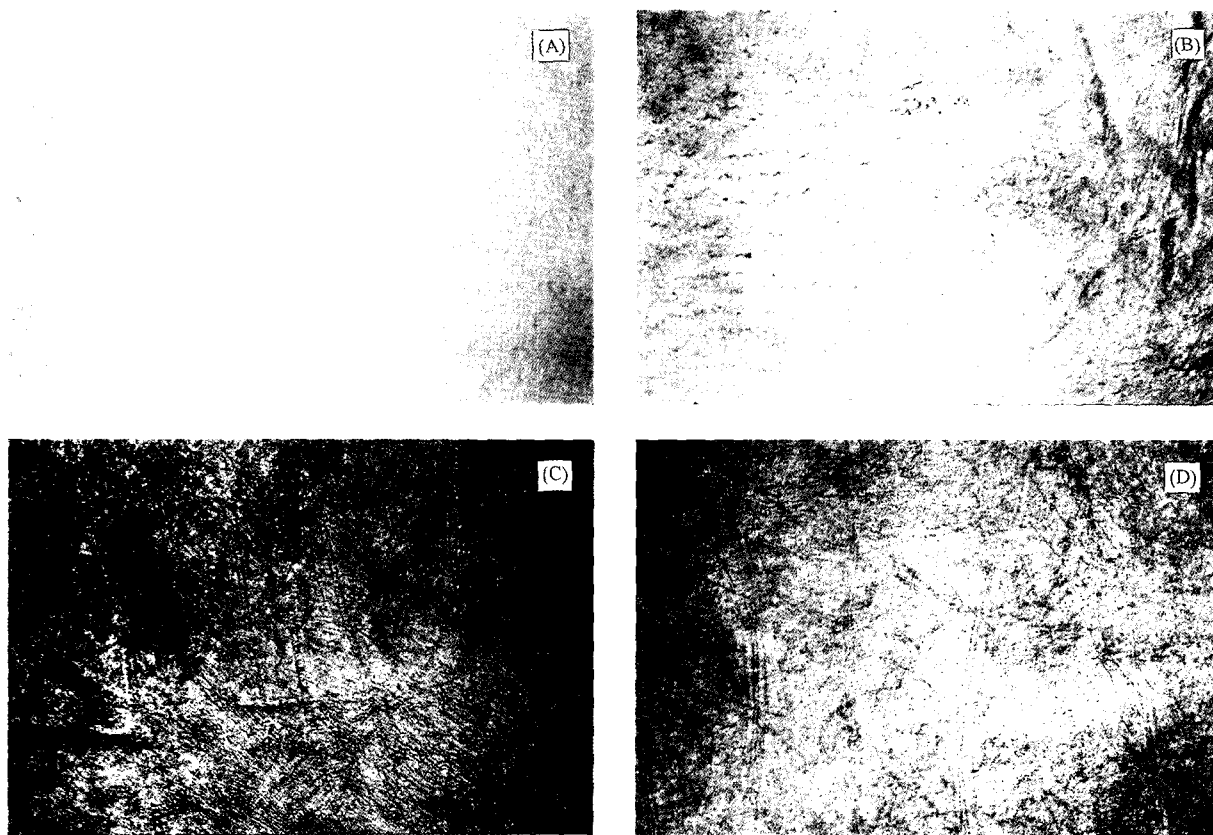


Fig. 2. Photographs of the surfaces of various leather-like materials prepared from the rectum (A, B, C and D) of shark intestine. (A) gray leather, (B) dark gray leather, (C) light violet leather, (D) light brown leather

2). Different colors of the leather-like materials were dependant on the pretreated dyeing. Colors (A), (B), (C) and (D) of the leather-like material prepared using rectum of shark intestine were gray, dark gray light violet, and light brown, respectively.

Physical characteristics of the leather-like material

The leather-like material prepared from shark intestines was tested for physical characteristics such as tensile strength, elongation, tongue tearing strength and bursting strength. As shown in Table 1, the tensile strength, elongation, tongue tearing strength and bursting strength of the leather-like materials were 3.3 kg/mm², 53.0%, 13.0 kg/mm and 18.0 kg/cm², respectively. The values in shoes (upper) made out of a commercial leather tested in this experiment are 2.8 kg/mm², 64.0%, 17.4 kg/mm and 50.8 kg/cm², respectively. In the case of clothes, these values are 10 kg/mm², 40~90%, 10 kg/mm and 20 kg/cm², respectively.

Table 1. Physical characteristics of the leather-like material prepared from shark intestine

Test items	Unit	Leather-like material	Shoes ¹⁾		Clothes ¹⁾
			Upper	Lining	
Tensile strength	kg/mm ²	3.3	2.8	2.7	10
Elongation	%	53.0	64.0	50.0	40~90
Tongue tearing strength	kg/mm	13.0	7.4	4.6	10
Bursting strength	kg/cm ²	18.0	50.0	40	20

¹⁾ Quality standard.

Elongation and bursting strength of the leather-like material were lower than those of the commercial leather used in shoes, but tensile strength and tongue tearing strength were higher. Tensile strength, elongation and bursting strength of the leather-like material were lower than those of the commercial leather in clothes, but the tongue tearing strength was higher.

Elongation and bursting strength of the leather-like material were lower compared with the commercial leather, because thickness of the shark intestines was very thin. Elongation of the leather-like material was enhanced by about 105% when coated with lacquer (Table. 2). Product was made out of the leather-like material prepared using shark

Table 2. Comparison of physical characteristics of the leather-like material, coated leather-like material, and commercial leather used for shoes and clothes

Test items	Unit	SILLM ¹⁾	CSILLM ²⁾	Shoes ³⁾		Clothes ³⁾
				Upper	Lining	
Tensile strength	Kg/mm ²	3.3	3.6	2.8	2.7	10
Elongation	%	53.0	109.0	64.0	50.0	40~90
Tongue tearing strength	Kg/mm	13.0	13.8	7.4	4.6	10
Bursting strength	Kg/cm ²	11.0	10.0	50.0	40	20

¹⁾ SILLM: shark intestine leather-like material

²⁾ CSILLM: coated shark intestine-like material

³⁾ Quality standard

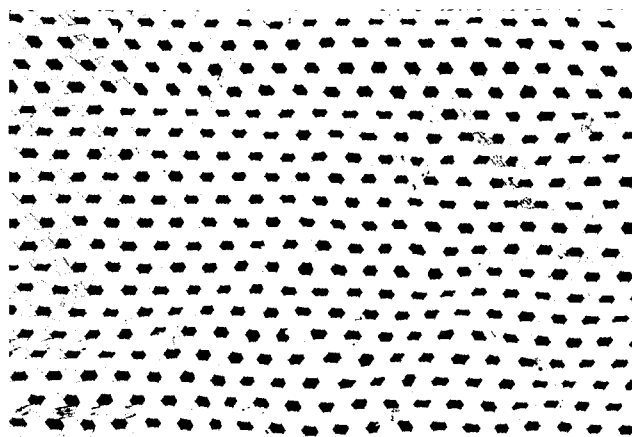


Fig. 3. A photograph of leather product made from the leather-like material.

intestines as shown in Fig. 3.

Suresh et al. (2001) reported that physical characteristics were higher in chrome syntan tanned leathers compared to basic chrome sulfate (BCS) tanned leathers. Tensile strength, elongation tongue tearing strength, and bursting strength of leather tanned with chrome syntan were enhanced about 12%, 37%, 28%, and 73% compared to leather tanned with BCS (Suresh et al., 2001).

Weak characters of shark intestines were less thickness and colorlessness, but these can improve during the process. It is the most important for making leather using shark intestine that no difference between the inside and outside appearance is observed. The leather-like material prepared from shark intestines was proved to be a valuable substitute for commercial leather materials in leather industry.

References

- Akiyama, F., N. Seno and K. Yoshida. 1982. Anticoagulant activity of dermatan polysulfates. *Tohoku J. Exp. Med.*, 136, 359~365.
- Baskaran, S., M.H.A. Baig, S. Banerjee, C. Baskaran, K. Bhanu, S.P. Deshpande and G.K. Trivedi. 1996. An efficient and stereoselective synthesis of (2R, 2'S)-1-O-(2'-hydroxy-hexadecyl)glycerol and its oxo analogs: Potential antitumor compounds from shark liver oil. *Tetrahedron*, 52, 6437~6452.
- Bordier, C.G., N. Sellier, A.P. Foucault and F. Le Goffic. 1996. Purification and characterization of deep sea shark centrophorus squamosus live oil 1-O-alkylglycerol ether lipids. *Lipids*, 31, 521~528.
- Brogstrom, G. 1969. Trends in utilization of fish and shellfish. In *Fish as Food*, Vol. II, G. Brogstrom ed. Academic Press, Inc., New York, pp. 637~725.
- Buranudeen, F. and P.N. Richards-Rajadurai. 1986. Sequelene. *Infotish Marketing Digest.*, 1, 42~43.
- Burkinshaw, S.M. and L. Kitching. 1995. Further studies of the use of chitosan in the dyeing of full chrome and heavily retanned leather with anionic dyes. *Dyes and Pigments*, 27, 17~34.
- Byun, H.G. and S.K. Kim. 2001. Purification and characterization of angiotensin I converting enzyme inhibitory peptides from Alaska pollack skin. *Process Biochemistry*, 36, 1155~1162.
- Choi, J.S., C.K. Lee, Y.J. Jeon, H.G. Byun and S.K. Kim. 1999. Properties of the ceramic composites and glass-ceramics prepared by using the natural hydroxyapatite derived from tuna bone. *J. Kor. Ind. & Eng. Chem.*, 10, 394~399 (in Korean).
- Compagno, L.J.V. 1984. *FAO species catalogue*. Vol. 4, *Sharks of the world*. An annotated and illustrated catalogue of shark species known to date. Part 1-*Hexanchiformes* to *Laminiformes*: VIII, Part 2-*Carcharhiniformes*: X, *FAO fisheries synopsis*, 125, 1~655.
- Covington, A.D., G.S. Lampard, O. Menders, A.V. Chadwick, G. Rafeletos and P. O'Brien. 2001. Extended X-ray absorption fine structure studies of the role of chromium in leather tanning. *Polyhedron*, 20, 461~466.
- Haard, N.F. 1992. A review of proteolytic enzymes from marine organisms and their application in the food industry. *J. Aquatic Food Prod. Dev.*, 1, 65~72.
- Jeon, Y.J., P.J. Park, H.G. Byun, B.K. Song, W.S. Kim and S. K. Kim. 1998. Preparation of an immobilized enzyme for enhancing thermostability of the crude proteinase from fish intestine. *Korean J. Life Sci.*, 8, 627~637 (in Korean).
- Kim, S.K., P.J. Park and Y.T. Kim. 2001c. Study on acute subcutaneous toxicity of hydroxyapatite sinter produced from tuna bone in Sprague-dawley rats. *Korean J. Life Sci.*, 11, 97~102 (in Korean).
- Kim, S.K., S.H. Moon, I.C. Jung, H.G. Byun, P.J. Park and J. T. Jang. 2001a. Recovery of calcium from fish bone and development of calcium absorption accelerating materials. Ministry of Maritime Affairs & Fisheries, Seoul, Korea, pp. 1~168 (in Korean).
- Kim, S.K., Y.J. Jeon and H.G. Byun. 1997. Enzymatic recovery of cod frame proteins with crude proteinase from tuna, *Pyloric caeca*. *Fisheries Science*, 63, 421~427.
- Kim, S.K., Y.J. Jeon, B.J. Lee and C.K. Lee. 1996. Purification and characterization of the gelatin from the bone of cod, *Gadus macrocephalus*. *Korean J. Life Sci.*, 6, 14~26 (in Korean).
- Kim, S.K., Y.T. Kim, H.G. Byun, K.S. Nam, D.S. Joo and F. Shahidi. 2001b. Isolation and characterization of antioxidative peptides from gelatin hydrolysate of Alaska Pollack skin. *J. Agric. Food Chem.*, 49, 1984~1989.
- Kim, Y.T. and S.K. Kim. 1991. Purification and characterization of the collagenase from the tissue of filefish, *Novoden modestrus*. *Korean Biochem. J.* 24, 401~409.
- King, K. and M. Clark. 1987. Sharks from the upper continental slope-are they of value. *Catch*, 14, 3~6.
- Korean Agency for Technology and Standards. 1995. Testing method for leathers. *Korean Industrial Standards*, KSM 6882.
- Korean Agency for Technology and Standards. 1997. Paper and board-determination of bursting strength by mullen high-pressure tester. *Korean Industrial Standards*, KSM 7082.
- Lee, J.S., J.G. Im, K.S. Song, J.B. Seo and T.H. Lim. 1999. Exogenous liooid pneumonia: high-resolution CT findings. *Eur. Radiol.*, 9, 287~291.
- McCurdy, L., W.W. Chatham and W.D. Blackburn. Jr. 1995. Rheumatoid synovial fibroblast adhesion to human articular cartilage. Enhancement by neutrophil proteases. *Arthritis. Rheum.*, 38, 1694~1700.
- Miller, D.R., G.T. Anderson, J.J. Stark, J.L. Granick and D. Richardson. 1998. Rhase I/II tial of the safety and efficacy of shark cartilage in the treatment of advanced cancer. *J. Clin. Onco*, 16, 3649~3655.
- Muchie, M. 2000. Leather processing in Ethiopia and Kenya: lessons from India. *Technology in Society*, 22, 537~555.
- Suresh, V., M. Kanthimathi, P. Thanikaivelan, J. Raghava Rao and B. Unni Nair. 2001. An improved product-process for cleaner chrome tanning in leather processing. *J. Cleaner Production*, 9, 483~491.
- Suzuki, F. 1999. Cartilage-derived growth factor and antitumor factor: past, present, and future studies. *Biochem. Biophys. Res. Commun.*, 259, 1~7.
- Tanikawa, E. 1971. *Marine Product in Japan*. Koseisha-Kosekaku Co., Tokyo, Japan, pp. 476~478.
- Yun, S.G., S.H. Park, J.W. Na and M.H. Ko. 1999. Effective chrome removal process from shaving dust. *J. Kor. Ind. Eng. Chem.*, 10, 1104~1108 (in Korean).