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Short Communication

Pickling of sheepskin by benzene sulphonic acid with low-salt content to enhance shrinkage and mechanical properties

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This study aims to investigate the effectiveness of a novel eco-friendly pickling method using benzene sulphonic acid with reduced salt content to improve the mechanical properties of sheepskin leather while minimizing environmental impact. Sheepskins are treated using five different ratios of benzene sulphonic acid ($C_6H_6O_3S$)/ sodium chloride (NaCl), while one sample was pickled using the conventional NaCl/sulphuric acid method. The remaining ingredients, formic acid and water, are kept constant. Among the treated samples, S1 treated with 5% of $C_6H_6O_3S$ with 4% NaCl exhibits the highest tensile strength (80.83 N/mm^2), elongation at break (45.7%), tear strength (60 N/mm), and shrinkage resistance temperature (107 °C). On the contrary, the sample treated with 4% $C_6H_6O_3S$ and 3% NaCl shows the lowest mechanical and shrinkage properties. Statistical analysis confirms significant differences among the pickling treatments. The findings demonstrate that the proposed novel pickling of benzene sulphonic acid with low-salt content has the potential to enhance the mechanical properties of sheepskins, reduce environmental pollution, and be affordable cost since sulphonic benzene acid can replace the sulphuric acid application, which is used in the conventional process.

Keywords: Benzene sulphonic acid, Pickling, Sheepskin leather, Tensile strength

Environmental pollution is a global challenge, with the leather industry identified as a major contributor that generates vast amounts of waste, particularly in the form of tannery effluents[1]. Among the most critical pollutants are chromium and chloride salts, especially sodium chloride (NaCl), which is extensively used during the pickling stage of leather processing[2]. The discharge of these salts into the environment not only elevates salinity levels in water bodies but also increases treatment costs and threatens the viability of the tanning sector. Sodium chloride is a leading cause of salinity in tannery effluent, and its high concentration adversely affects both wet-blue leather properties and agricultural ecosystems by contaminating irrigation and potable water sources. The traditional pickling method, which employs sulphuric acid and NaCl, often leads to uncontrolled float conditions and elevated pollution loads[3]. Excessive salt usage results in stiffer leathers with reduced mechanical strength and poor organoleptic characteristics. Furthermore, low-efficiency effluent treatment systems and increasing regulatory pressure have intensified the need for eco-friendly and salt-free pickling alternatives[4-6].

In response, researchers have investigated aromatic sulfonic acids—notably benzene sulphonic acid—as a substitute for mineral acids in the pickling stage[7,8]. Aromatic sulfonic acids have strong donors on their benzene rings, which allow them to create a rather stable ionic bond with the collagen side chains, preventing acid swelling. By adopting salt-free pickling and making minor changes to the pickling and tanning conditions, at least 80% of NaCl consumption may be lowered while chromium absorption might be significantly[9-11].

Additional approaches to salt-free pickling include aldehyde-functionalized cross-linkers for pre-tanning the skins/hides, notably aldehyde derivatives like oxazolidine, which can generate covalent bonding before pickling[10,12]. Essa *et al.* showed that using salt-free pickling, the eco-friendly tanning process reduces pollution caused by chromium and chloride salts[10,13,14].

Other research highlights the effectiveness of aliphatic epoxy compounds, which catalyze the tertiary amine to produce a covalent link between the epoxy group and the amino group in the collagen side chain. A salt-free pickling and chrome tanning process has been developed using an epoxy compound as a salt-free pickling auxiliary to remove the need for sodium chloride in pickling[15]. Before tanning, an intermediate pickling step is commonly used to bring the entire protein matrix to consistent chemical and physical conditions, preventing the skin substrate from combining with chrome too quickly[16].

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As a result, the uniform penetration of chromium into the protein matrix is accelerated. Throughout pickling, salt, occasionally the binary compound, 6-8 % of limed pelt weight, is utilized to keep skins and hides from swelling due to acids and low pH[17]. In fact, according to a recent assessment, almost 300,000 tons of salt are used annually in the pickling process of leather manufacture all over the world[18]. The low level of cleansing technology has typically resulted in environmental issues, prompting researchers to seek a new way to manufacture raw property methods. Pickling is done in various ways, each adding to the pollution load generated by excessive salt consumption[19-22].

Despite these advancements, the mechanical properties of sheepskins subjected to salt-free pickling methods remain underexplored. Currently, good mechanical strength combined with an environmentally friendly technique is in high demand[23-26].

This study, therefore, aims to evaluate the mechanical and shrinkage resistance properties of sheepskins pickled using a novel formulation of benzene sulphonic acid with minimal salt content. It hypothesizes that lower salt levels can prevent excessive dehydration of the pelt, improve flexibility, and yield stronger leather while mitigating environmental impact. Another hypothesis in this study is that high salt content causes skin dryness, which results in thin leathers with decreased mechanical strength.

Experimental

This study used enzymatically bated sheepskins, each weighing 1 kg with an average thickness of 0.7 mm, which were collected from Bahir Dar Tannery, Ethiopia. The pickling of skins was carried out using a combination of formic acid (HCOOH), aromatic sulphonic acid ($C_6H_6O_3S$), and sodium chloride (NaCl). All chemicals used were of commercial grade and applied as per experimental formulations.

Sample Preparation

Five enzymatically bated sheepskin samples were processed under experimental pickling conditions, varying the concentrations of NaCl and benzene sulphonic acid ($C_6H_6O_3S$) while keeping the amount of water (80%) and formic acid (0.5%) constant across all samples. The amount of NaCl and $C_6H_6O_3S$ used in each experiment was varied, as shown in Table 1. Additionally, a conventional control sample was prepared using 8% NaCl and 0.8% sulphuric acid (H_2SO_4), following the traditional pickling method. The skins were tumbled in a rotating drum, and after 10 min, the specified amount of $C_6H_6O_3S$ and 0.5% formic acid (CH_2O_2) were added to the pickling drum. All pickling processes were conducted at a 21–26 °C temperature range.

Testing Methods

The pH level of the pickling float was assessed using standard litmus paper based on SLC (Standard Leather Committee) procedures. An optimal pickling pH was considered between 2.5 and 3.0, indicating complete penetration and fixation of acids within the skin matrix.

Tensile Strength and Elongation

The ISO 3376 standard was used to determine the tensile strength and elongation of a leather sample pickled with sulphonic acid with minimal salt content. The test was performed using a standard tensile testing machine, with samples conditioned under controlled temperature and humidity before testing. Results were recorded in N/mm² (tensile strength) and percentage (elongation).

Tear Strength

The tear strength is the force required to rupture the specimen per unit area of the cross-section. The resistance of a leather sample to ripping force was measured using an ASTM D1424 digital tear strength tester during the experiment.

Shrinkage Property

The temperature at which the samples shrank was evaluated using SATRA TM17 quality; the temperature at which the samples shrank reveals the qualities of the pickled leather linked with temperature resistance.

Results and Discussion

Tensile Strength and Elongation

Figure 1 presents the tensile strength and elongation values of the sheepskin leathers pickled with different concentrations of benzene sulphonic

Table 1 — Pickling formulations with 80% water and varied chemical contents

Sample code	NaCl, %	$C_6H_6O_3S$, %	CH_2O_2,%	H_2SO_4,%
S1	4.0	5.0		
S2	4.5	3.5		
S3	3.0	4.0		
S4	3.5	3.0	0.5	
S5	3.75	3.25		
Conventional	8.0			0.8

acid and low salt, compared to the conventional pickling method. This analysis is essential to understand the skin's resistance to axial loads and its capacity to stretch without rupture.

Among all samples, Sample S1, treated with 4% of NaCl with 5% of $C_6H_6O_3S$, exhibits the maximum tensile strength (80.83 N/mm^2) and elongation (45.7%), followed by sample S2 which is treated with 4.5% of NaCl and 3.5% of $C_6H_6O_3S$. In contrast, sample S4 records the least tensile strength (67.83N/mm^2). An ANOVA test was conducted to assess whether these differences were statistically significant. As presented in Table 2, tensile strength and elongation values differ significantly among the samples, with a *p*-value of 0.001, F-value of 521.65 (tensile strength), and F-value of 103.61 (elongation), at a significance level of $\alpha=0.05$. These values confirm that the pickling method using benzene sulphonic acid with reduced salt content has a statistically significant impact on the mechanical properties of sheepskin. The five sheepskin leathers pickled by benzene sulphonic acid with low salt, and conventional method had different tensile strength and elongation characteristics. The fundamental reason these pelts have superior tensile and elongation capabilities than the other samples is that sections of acid are more physically and mechanically trapped between the fibre bundles of the pelt. Furthermore, using benzene acid as an additive in low salt pickling serves two purposes: first, it helps to bring the bated pelt to an acidic medium, which aids in the preservation of the pelt for a longer period prior to tanning on behalf of pickling acids such as sulphuric acid or hydrochloric acids. Second, benzene sulphonic acid can simultaneously be employed as a salt and an acid in skin pickling operations at tanneries, reducing chloride-based environmental pollution in tannery effluents[27].

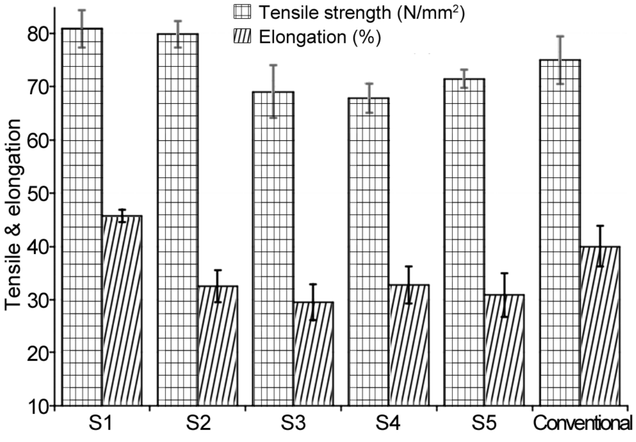

Fig. 1 — Tensile strength and elongation of pickled sheepskins

Tear Strength

As shown in Figure 2, Sample S1 again demonstrates the maximum tear strength (60 N/mm), which is better than the remaining samples, including the conventionally pickled sample (51 N/mm). As a result, the pickled pelt in the S1 can resist external forces that could cause sequential breakage of leathers. Although samples S2, S4 and S3 had lower tear strength of 45.69, 48.19 and 48.26 N/mm, respectively, they still perform comparably to conventional treated sample. The relatively lower tear strengths in Samples S2–S4 may be due to an improper ratio of sulphonic acid to salt, which likely hinders the effective integration of acids between the fibre bundles. These findings are consistent with previous reports that identified the importance of acid retention for structural strength[28,29].

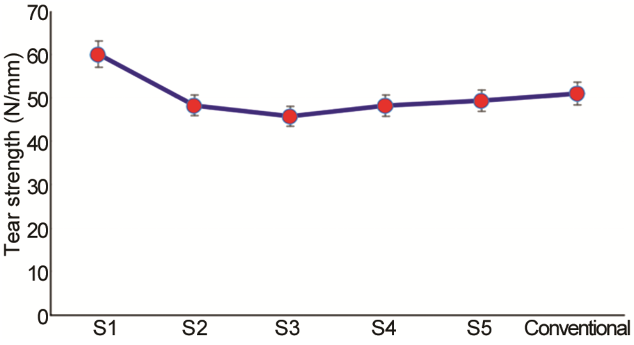

Fig. 2 — Tear strength of pickled leathers

Table 2 — One-way ANOVA results for mechanical and shrinkage properties of pickled sheepskins ($\alpha=0.05$)

Test parameter	Source of variation	SS	df	MS	*F*-value	*P*-value	F crit
Tensile strength	Between Groups	1108.444	5	221.6888	521.65	0.001	2.620654
	Within Groups	10.19952	24	0.42498			
Elongation	Between Groups	1415.815	5	283.1631	103.61	0.001	2.620654
	Within Groups	65.59304	24	2.733043			
Tear strength	Between Groups	101.2395	5	20.2479	18.071	0.001	2.620654
	Within Groups	26.8899	24	1.120413			
Shrinkage	Between Groups	1265.8	5	253.1601	102.35	0.001	2.620654
	Within Groups	59.36088	24	2.47337			

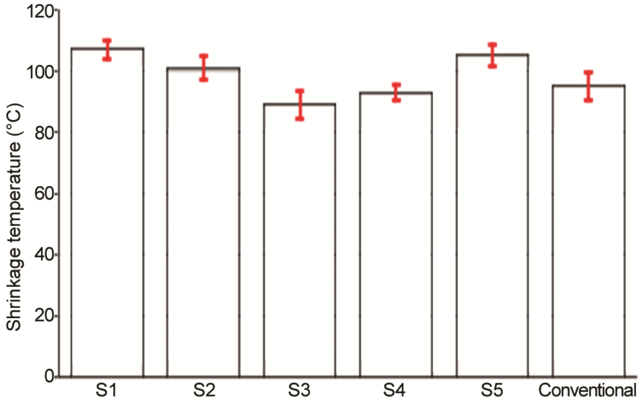

Fig. 3 — Shrinkage resistance pickled sheepskins

Statistical analysis reveals significant differences among the groups, with a *p*-value of 0.001 and an F-value of 18.08 at α = 0.05, indicating strong evidence that the pickling formulation affects tear resistance. The lower the *P*-value, the stronger the significance of the effect.

Shrinkage Property

The usefulness of the shrinkage property of the pickled skins has an implication with moist heat relation[26]. The temperature at which skin collagen fibers contract is similar to the melting temperature of proteins. The shrinkage properties of the pickled pelt of this study utilizing the components listed in Table 1 are compared to the values of conventional pickling leathers in this section. As indicated in Figure 3, S1 exhibits the highest shrinkage temperature (107 °C), indicating superior thermal resistance. In contrast, Sample S3 has the lowest value (89 °C), suggesting reduced fibre bonding due to its lower acid concentration.

The enhanced shrinkage resistance in S1 is likely due to the increased availability of benzene sulphonic acid, which promotes cross-linking between acid functional groups and the collagen matrix. Overall, samples pickled with benzene sulphonic acid and minimal salt consistently show better shrinkage resistance than the conventionally treated sample. These findings support the previously reported results[30,31]. The ANOVA results also prove this trend, yielding a *p*-value of 0.001 and an *F*-value of 162.35 at α = 0.05, demonstrating a statistically significant effect of the treatment on shrinkage resistance.

In this research work, a unique pickled process is proposed using benzene sulphonic acid with low-salt content to improve the mechanical and shrinkage properties of sheepskin leathers by reducing the environmental effect of salt. Of the six formulations evaluated, sample S1 (5% $C_6H_6O_3S$ + 4% NaCl) shows superior performance in all measured parameters: tensile strength (80.83 n/mm²), elongation (45.7%), tear strength (60 n/mm), shrinkage temperature (107 °C). In contrast, Samples S3 and S4 recorded the lowest tensile, tear strength, and shrinkage resistance. Though functional, the conventional method outperformed most sulphonic acid-based treatments and has a higher environmental burden due to high NaCl content. The results suggest pickling with benzene sulphonic acid in optimized ratios can effectively enhance mechanical strength, reduce environmental pollution, and be a sustainable alternative to traditional pickling practices.

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