Tanning Chemicals' Influence in Leather Tensile and Tear Strength Review

by
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Abstract

For over 100 years of tanning research, it is still arguable whether tanning chemicals weaken, strengthen or have an effect on the skin's original collagen fibers.

The current paper is a review of the literature regarding the impact of the tanning process on the mechanical properties of leather specifically, tensile and tear strength, that raises several questions about this topic. A call is made for the scientific and technical community to address these questions.

Findings about Hides and Leathers

Since the beginning of last century, it was broadly accepted in the trade as a fact that vegetable and chrome tanned leathers diminished their original hides strength. In 1920, Bowker and Churchill[1], found that the lower the tannage degree, the higher the tensile strength value of vegetable harness leather. Later, Downing[2] reported the fact found in his tannery, that the tensile strength value of vegetable belting leather produced during 1925 and 1926, decreased with the increase of the degree of tannage. In 1947, Highberger[3] considered that the decrease in the tensile strength value of collagen occurring during tanning, was inconsistent with the formation of strong crosslinks.

In 1949, regarding chrome tanned leather, Noerr and Classen,[4] observed that the strength of chrome tanned leather decreased as the chrome (Cr_2O_3) content was increased.

In 1951, Stather and Schmidt[5] found that for each tanning process there was a reduction in absolute tensile strength of about 10 to 25% compared to delimed pelts.

In 1952, Kanagy et al.[6] showed that chrome-retanned leathers were weaker than those that had been straight chrome tanned.

From 1953 onwards, discrepancies among different researchers and technicians were evident. Benskin[7] reported that the absolute tensile strength of limed and splitted hides, vegetable tanned, increased by 18-19% compared to the pelt from which it was made, while tear strength decreased 16%. Similar results were found for chrome tanned.

In 1959, Toth and Ribli[8] drew opposite conclusions than those of Stather and Schmidt[5] under the same trial conditions, according to the first. They found an increase in both tensile strength and stitch tear resistance. Lower values were measured only for the resistance to continuous tear. In both works from Benkins and Toth et al., the samples were first cut from limed hides, the thickness was measured, then tanned and resistance tests were carried out on the samples in the wet state.

Zissel[9] in 1974 studied the influence of three types of tanning on the mechanical resistance of leather. His findings demonstrated that in leathers that were not deliberately fatliquored, and air dried at 25°C, compared to chrome tanning, glutaraldehyde tanning causes lower absolute and relative tensile strength values. Vegetable tanning, on the other hand, lowers the relative tensile strength value only due to its strong filling effect.

As for absolute and relative tear resistance, Zissel found that when compared to chrome tanning, vegetable tanning and glutaraldehyde have the same effect on reducing resistance.

In 1977, Leberfinger[10] et al. did not find any reduction in absolute tensile and tear strength neither in chrome nor in vegetable tanning. On the contrary, the relative resistances showed a decrease in their values due to the associated increase in the thickness of the leather. They worked with pickled pelts, after tanning the leathers did not receive further post-treatment or fatliquoring. Fatliquored leathers are subject to a certain amount of fiber adhesion and this residual adhesion can be of different magnitude depending on the type and intensity of the tanning process. In order to eliminate this factor, instead of normal drying, dehydration with acetone and anhydrous calcium chloride was carried out.

In 1978, Bitcover and Everett,[11] found significant inverse correlations between chrome content and tensile strength (in both directions) and slit tear strength (in one direction). The authors minimize the possible influence of different raw hides used in the experiments and emphasize the influence of chemical composition of crust leather, to arrive to these conclusions. Nevertheless, they recognized that their results would have been more reliable if the experiments had been designed specifically to study the effects of varying chrome content on leather strength at a constant fat content and the effects

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of varying fat content at a constant chrome content. It would have been valuable also to know the original strength of raw or pickled hides either in wet state or dried with acetone, to verify the levels of starting strength values.

Findings about Collagen Fibers

Regarding the behavior of individual tanned collagen fibers and their physical resistances, the findings are equally contradictory. In 1950, Mao and Roddy[12] and later Roddy[13] in 1952, arrived at the conclusion, working with individual collagen fibers, that there was no loss of resistance after both vegetable and mineral tannages. In 1953, Michailov[14] demonstrated that the tensile strength of individual fibers increased considerably with tannage. The same conclusion was reached by Okamura and Shirai[15] tanning with cationic chrome complexes.

In 1960, Morgan and Mitton,[16] working for the BLMRA* with single raw fibers, found that chrome tanned fibers were about 25% weaker than raw collagen fibers and that vegetable tannage did not alter the strength of the fibers significantly.

In 1983, Bienkiewicz[17] came up with the concept that with the introduction of tanning agents into the hide, some "dilution" effect of native collagen properties could be expected.

Possible causes of confusion

It seems to be several reasons or causes that promote such confusions, divergences and contradictions.

One of them may be semantic, when naming the term "tanning". Some refer to tanning processes and others, to the tanning process in particular. When, for example, vegetable harness leather is mentioned, it includes several chemical and physical processes that raw hides are put through, that have the harness leather as a final result, and in which only one of them is the vegetal tanning process itself.

Another cause of confusion can be the term "leather resistance or leather strength". It is important to differentiate between absolute tensile or tear strength from the same relative, N/cm^2 and N/cm respectively. In this regard, a tannage that does not affect the absolute strength of a hide before and after being processed but increases its substance, will show a decrease in its relative strength.

Benskin[7] points out that differences of their findings with other workers "may be due to the fact that they may have worked on one or two hides so that variations in raw material may have offset differences caused by experimental changes."

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In addition, Leberfinger[10] states: "The influence on tensile strength and progressive tear is based on very complex relationships. Both measurements depend not only on the type and quantity of the tanning agent, but also on other factors (condition of the skin, topographical sampling, work in the tanneries, fatliquoring, retanning, conditioning, finishing, etc.). Therefore, if you want to know about the influence of tanning alone, you have to eliminate the secondary factors."

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In 2015, Tournier[18] studied changes in tear resistance of bovine hides along the processes of a certain tannery, up to wet blue state. The author followed a protocol for the assessment of the tear strength absolute and relative of four fresh hides, processed in normal tannery lots, by means of a statistical sequential sampling. The full sampling and testing methodology is outlined in Tournier.[18] The tongue (or trouser) tear method (ALCA method E10) was used to measure tearing strength. The samples were tested in the wet state in fresh, limed, lime split, chrome tanned, chrome tanned full substance and wet blue split. The study showed, among other findings, that in this particular tannery, the processes from raw hides up to chrome tanned, decreased substantially the original fresh hides tear resistance in both processes, lime split and wet blue split.

The author noted that this tannery had opportunities for improvement on the tanning processes, namely, in deliming, bating, pickling and chrome tanning itself. Tournier suggested the tannery technicians using the new developed methodology to determine the impact of each one of the processes mentioned above in the decrease of the tearing resistance of their leather and to act later on, in reverting it.

In 2016, Sizeland[19] et al. studied the effect of tanning agents on collagen structure and response to strain in leather. Pickled pelts were tanned as standard, with 4,5% chromium sulfate, retanned with 4% of mimosa extract and fatliquored with 5% of two different types of oils. Zirconium leathers were tanned with 5% of zirconium sulfate, retanned with 3% of a commercial syntan and same fatliquor of chrome tanned. THPS* leathers were tanned with 2% of THPS, retanned with 2% of the commercial syntan and fatliquored with the same fatliquor of chrome tanned. Oxazolidine + Mimosa leathers were tanned with 2% of the commercial syntan, 6% of mimosa extract and 2% of oxazolidine. After the addition of a further 8% of mimosa extract, the standard fatliquor followed.

Regarding the results of tear and tensile strength of these leathers the authors found that "chromium or zirconium tanned leathers were higher than those of oxazolidine or THPS".

*Tetrakis hydroxymethyl phosphonium sulfate

These results give the idea that metal tannages yield stronger leathers than metal-free ones. With so many different products used, in different proportions and applied in different manners, without mentioning the crusting procedures, this statement seems, at least, risky, and misleading.

In 2019, Kaijun Li et al.[20] reported the action of a new tanning agent, Chromium loaded PPA*copolymer Nanoparticles (Cr-PPA NPs). This product was used for tanning one sample of pickled sheep skin and comparing it with two other samples of the same sheep skin tanned with commercial chrome tanning as control (one sample with 4% and the other one with 8%). The control samples were cut from the left side of the skin, and the trial sample from the right side of the skin. Wet blue leather samples were further treated with 16% of a fatliquoring agent. It was not specified if all samples were treated together or separately and there was no information about crusting procedures. The authors claim higher hydrothermal stability of the novel product vs. chrome tanned (4 and 8%), and highest tearing strength, whereas the tensile strength and breaking elongation were nearly the same.

It is curious that the chrome tanned leathers reached a shrink temperature of only 89.5° and 98.1°C respectively. Also, regarding the physical properties, it would have been of interest to consider the following:

- a statistical design of experiments
- standard sample preparation: samples would have been cut in such a way that bilateral symmetry differences were minimized,
- to provide more information about crusting processes,
- to report chrome and oil content of each leather samples,
- to report tearing and tensile absolute values.

In 2020, Xiu He et al.[21] assessed the correlation between fiber dispersion and physical properties of chrome tanned leather with different quantities of chrome sulphate powder. As a parallel finding, they reported that the tensile strength, tear strength and elongation at break of crust leathers increased with the increase of chrome powder.

The sample preparation consisted in four pieces of pickled pelts that were tanned with 2, 4, 6 and 8% of chrome powder, the wet blue obtained was wrung and sampled. Afterwards, the remaining wet blue were rewetted, neutralized and fatliquored (each piece separately[22]) while following post-tanning processes of horsing-up, drying and staking, and finally, sampling of the crust leather

*Poly (PEG-co-AA)

Table IV
Mechanical properties of crust leathers.

Crust leather	Tensile strength (N/mm2)	Tear strength (N/mm)	Elongation at break (%)
Cr-2	22.84±0.68	96.94±0.53	47.21±5.55
Cr-4	24.86±1.63	97.27±1.17	53.21±4.87
Cr-6	25.24±0.58	117.82±3.12	55.50±1.15
Cr-8	23.29±2.04	110.28±4.11	64.32±2.87

The data about mechanical properties is shown in Table IV of their paper and reproduced here with authors[21] permission. It seems that the conclusion reported, regarding the physical properties increasing with increasing chrome powder, is not accurate due to some weakness in the methodology. The author of this manuscript humbly suggests that this method would have provided better information about the real influence of chrome itself, if it had included in the table:

- the absolute and relative strength data of the original pickled pelts,
- the absolute and relative strength data of the tanned pelts in wet blue state, before going on with the fatliquor and the rest of the crusting processes,
- if instead of informing the chrome powder offered in each trial, the amount of chromium actually uptaken by the pelts was informed.

Conclusions

There is no doubt that there are many unanswered questions and issues to be clarified in the critical field of leather strength and its relationship with tanning products.

There are lots of publications regarding the structure of leather fibers and collagen, and research trying to elucidate which are the characteristics that define the strength of fibers, but not that many to explain the effect of tanning materials on them. A lot of work is needed in the scientific area, in laboratories and tanneries to shed light on these questions.

For tanneries in particular, the method suggested by the author[18] can be very useful to know how robust their formulations are and take advantage of an easy internal research method to surpass competition in this respect. Special care must be taken by scientists and technicians in the design of their tests and experiments as well as in the expression of results and conclusions.

It is both important and urgent to clarify the action of tanning agents on collagen and hides and their influence on tensile and tear resistance as new products are constantly being developed and released to the market in the need of less environmental impact.

Perhaps, IULTCS could take the lead on this subject by defining rules or a standard test method to systematize experimental design, statistical sampling and assessment of results. This may help in doing research and the expression of results specifying whether certain products are tanning or not and whether they increase the physical properties of collagen fibers and hides or not.

In the meantime, technicians working in the shop floor must take care of the critical points of the processes where it is known for sure, that native collagen fibers can be damaged. Bear in mind the concept of Bienkiewicz[17,] mentioned above, and act in consequence, constantly checking the results.

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