A NEW SYSTEM TO MEASURE LEATHER SHRINKAGE TEMPERATURE

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Abstract. A characteristic of leather is that if it is gradually heated in aqueous solution it reaches a temperature where sudden and irreversible shrinkage occurs (shrinkage temperature). This phenomenon is related to the denaturalization of the collagen protein that conforms the hide and is known as leather shrinkage. Specifically, the internal bonds break thus causing a shortening of the leather that can be up to a 35% from its original length. The method that describes the ISO 3380:2015 standard uses a device where the determination of the shrinkage temperature is performed visually by the laboratory technician. Consequently, the method tends to be imprecise and subjective. It should also be noticed that the device proposed by the standard does not allow differentiation between the different stages of the contraction process. There are other methods to determine leather shrinkage temperature including differential scanning calorimetry, microscopic hot table, thermogravimetric analysis, differential thermal analysis and thermomechanical analysis. All these methods involve complex devices and are only suitable for specialized personnel. In this work, a new device is developed to precisely measure the leather shrinkage temperature and to distinguish the different contraction stages. In addition, the proposed device is simple, easy to use and inexpensive, which facilitates its use in any industry. The developed system consists basically of a load cell to measure the strength produced by the shrinkage of the leather. With the logged data during the test a strength versus temperature graph is built. By means of its interpretation, the different stages of shrinkage can be determined. Different mathematical analysis of the logged data is proposed to determine the shrinkage stages temperatures, thus achieving a high degree of certainty and repeatability.

1 Introduction

One of the most used methods to check the quality of the leather tanning process is the determination of the shrinkage temperature according to the ISO 3380:2015 standard. This method measures the leather shrinkage when constantly increasing the sample temperature. The shrinkage temperature (T_S) corresponds to the temperature when the sample suddenly contracts. The value of this temperature indicates the degree of collagen stability and therefore, when higher, the leather will have better quality and resistance.

The process of leather shrinkage can be divided in different stages. Several authors discriminate temperature A1 (when the first fibre starts to shrinkage), temperature C (when there is a massive shrinkage) and finally temperature A2 (when the last fibres are contracted individually). [2,3]

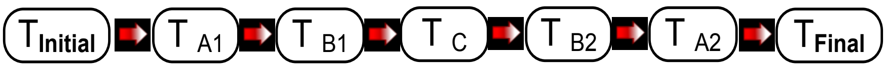

Fig. 1.Temperatures defining each step according to fibers shinkrage: Tinitial (the material fibers are inactive), A1 (the first shrinkage of individual fibers is noticed), B1 (the individual fiber shrinkage is immediately followed by another fiber shrinkage consecutively), C (most fibers experience simultaneous shrinkage), B2 (the last fibers experience simultaneous shrinkage), A2 (the shrinkage of the last individual fibers is noticed), Tfinal (fibers shrinkage is complete).

The device presented in this work is based on the isometric method that measures the fibers tension (in terms of strength) of a leather sample that occur when its temperature increases. This method has been used by different authors to study the different types of cross bonds of collagen [4]. Other authors define the different stages of the strenght-temperature curve and place the shrinkage temperature where the curve tends to intersect with the abscissa axis or the onset temperature [5-7]. These methods do not consider that if the leather suffers a previous contraction, the results of the Ts differ from those obtained according to the ISO 3380:2015 method, as shown in **Figure 2**.

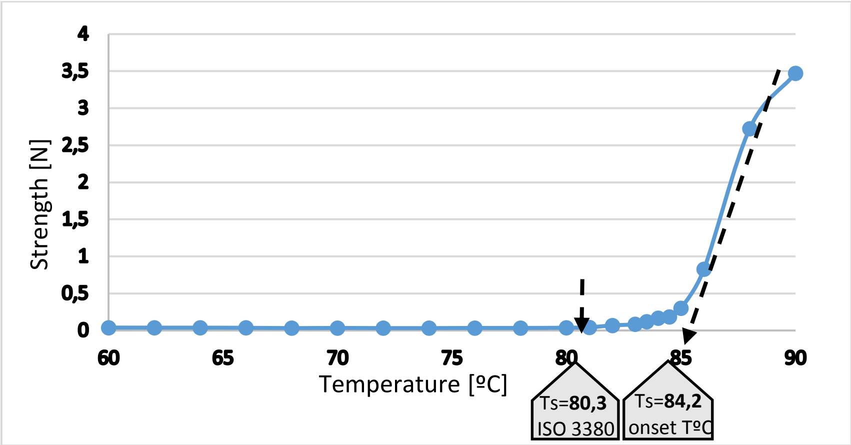

Fig. 2. Differences of T_S based on the determination method. Strenght vs. temperature of a vegetable tanned leather probe.

To avoid this differences in temperature the present work proposes to take into account the derivative of the presented curve and determine the point where it begins to increase. In this way, this method intends to find a way to determine if the Ts from the strenght-temperature curve is equivalent to the one obtained through the method according to the ISO 3380:2015.

2 Experimental design

In order to be able to verify the new measurement method of Ts, a new device has been prepared, which allows the T_S to be measured according to the ISO 3380:2015 method and at the same time registering the probe strenght to determine the T_S from the strenght-temperature curve. The two samples are tested simultaneously, submerged in a bath with agitation and temperature control. The strength and temperature data are initially calibrated and then recorded and mathematically treated to obtain the strenght-temperature curve and its derivative. Figure 3 shows the device developed to measure T_S.

Fig. 3. Experimental device used to measure T_S and tanned leather probes.

The samples tested on the device are vegetable tanned leather probes. The sample 1 was from a leather tanned with mimosa and the sample 2 was from a leather tanned using quebracho and mimosa. Three repetitions have been performed and the T_S has been determined using the following methods:

- Method 1: Ts according to the ISO 3380:2015 method.
- Method 2: Ts Onset temperature
- Method 3: Ts from the strenght-temperature curve derivative, corresponding to the sampled data where the derivative starts to increase.

The value of the T_S according to the ISO 3380:2015 (method 1) is determined directly. However, to obtain the value of the T_S according to methods 2 and 3, it is necessary to register the value of the strenght vs temperature during the test.

3 Results and Conclusions

Figure 4 shows the table of results obtained from testing six different leather samples along with the calculation of the error "ε" and the arithmetic mean "ẋ". The samples have been tested according to the methods described in the previous section and it can be seen that the results of method 3 proposed in this work are close to the results of method 1 (ISO 3380:2015).

		T_s method 1	T_s method 2	T_s method 3
		ISO:3380	*On set*	*New*
Sample 1	1	78,8	79,5	78,0
	2	77,5	79,3	77,7
	3	77,5	78,9	77,9
calf	ẋ	77,9	79,3	77,9
	err	0,8	0,3	0,1
Sample 2	1	81,5	84,3	79,0
	2	79,5	84,0	79,0
	3	81,8	84,2	78,0
cow hide	ẋ	80,9	84,1	78,7
	err	1,4	0,2	0,7
Sample 3	1	82,3	84,2	80,6
	2	81,3	84,6	81,5
	3	81,7	84,0	81,5
cow hide	ẋ	81,8	84,3	81,2
	err	0,5	0,3	0,6
Sample 4	1	74,5	79,4	73,5
	2	74,8	78,7	73,0
	3	75,3	78,1	72,0
calf	ẋ	74,8	78,7	72,8
	err	0,4	0,6	0,7
Sample 5	1	76,5	84,4	73,0
	2	73,3	84,6	74,0
	3	75,4	84,4	74,0
calf	ẋ	75,1	84,5	73,7
	err	1,8	0,1	0,7

Fig. 4. T_S results obtained using the three tested methods.

The T_S results using method 2 clearly show differences comparing to the ones according the ISO standard. Methods 3 shows T_S results similar to the ones from the ISO standard but some slight differences can be seen.

4 References

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