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Surface shrinkage: Determination of stress at high temperatures on leathers of different origins using DMA

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Abstract

When exposed to high temperatures, leather undergoes a phenomenon of dimensional contraction (shrinkage) closely related to the protein and fibrous nature of the material. The studies of thermal shrinkage on leather have been focused on automotive applications, but no statistical analysis of the effect of anisotropy and inhomogeneity in the different areas have been carried out. In the present study a test method to assess the shrinkage of leather at 120°C in terms of forces by means of DMA has been proposed. The method has been applied for mapping the shrinkage stresses in the 3 segments of ISO 2418 (butt, shoulder and belly) in the two directions parallel and perpendicular to the backbone. Different leather articles, tanned with different chemicals and different intended use (automotive, furniture, footwear, clothing and gloves) have been analyzed. The aim is to increase the knowledge of the phenomenon with a correlation with the fibrous structure of the material by means of an innovative test method.

Introduction

Dimensional change due to environmental variations is one of the typical phenomenon related to leather. In particular, when exposed to high temperature, leather shows a negative thermal expansion (NTE) with a subsequential partial permanent loss of surface that could determine problems in different applications as for footwear production (lasting process), automotive applications or, in general, during drying processes of leather [1]. From the quantification point of view, shrinkage has been studied in terms of stresses developed using a capacitive stress measurement transducer method [1] or by placing force-measuring systems in climate chamber in a cyclic environmental ageing (heat and relative humidity) [2]. Furthermore, in the studies available on leather [1-3] all the assessments have been carried out without any reference to the anisotropy of the materials due to its typical structure. Finally, with reference to quality control of incoming materials, most of the technical specification (i.e for automotive industry) take into account large test pieces both in terms of force and deformation [4]. Finally, test methods of official standardization bodies are available only from a dimensional point of view [5].

In this study a new test method (SSIP 1701-21) for the quantification of the forces involved in the shrinkage at high temperature is proposed using DMA techniques on small samples. To verify the effects of the inhomogeneous fibrous structure of leathers on the results, shrinkage stresses have been measured in the three segment area of ISO 2418 (shoulder, butt and belly) [6] and in two reference directions: parallel and perpendicular to leather backbone. Different leather articles, with different animal origin, tanning and destination of use have been analyzed to verify an eventual correlation with leather structure and characteristics.

Material and Methods

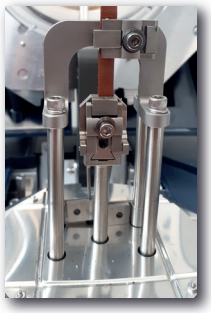
The measurements were performed using a DMA 850 (TA Instruments, USA), in tensile mode from room temperature till the target isothermal temperature of 120°C at a rate of 20°C/min. The forces have been assessed in iso-strain mode fixing a deformation of 0,1% and a preload of 0,05 newtons.

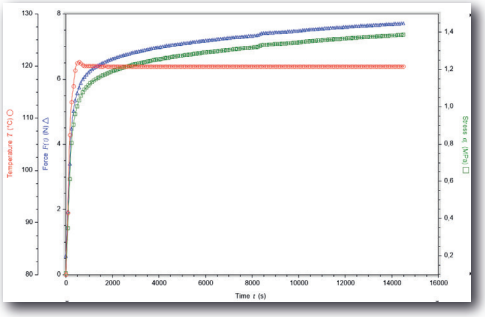
Rectangular test pieces (30,0 ± 0,5) mm x (5,0 ± 0,5) mm have been analyzed sampling in accordance with ISO 2419 [7]; the iso-strain mode have been carried out at the reference distances of the clamps of (20,0 ± 0,5) mm. The isothermal has been applied for 240 minutes, as required in some automotive specifications [4], and the results have been expressed in kPa dividing the force with the transverse section of the specimen. Values after 10, 60, 120 and 240 minutes have been reported.

For the validation of the test methods, two different leathers have been used: bovine for automotive tanned using glutaraldehyde and ovine chrome tanned leather for gloves. For each, 10 measurements were carried out in both sampling directions and only in the butt (ISO 2418 [6]). Afterwards, the mapping of the shrinkage in the 3 areas of ISO 2418 (shoulder, butt and belly) [6] were carried out on several leather samples, for which have been determined the elastic modulus in stress-strain tests (up to 15 newtons) and dimensional shrinkage (ISO 17130) too.

Results and Discussion

In the following tables the characteristics o the sample analyzed are reported.





TIME (MIN)	AUTOMOTIVE LEATHER				LEATHER FOR GLOVES			
	PARALLEL		PERPENDICULAR		PARALLEL		PERPENDICULAR	
	MEAN	ST.DEV	MEAN	ST.DEV	MEAN	ST.DEV	MEAN	ST.DEV
10	51	10,8	85	21,6	213	69,2	32	11,5
60	89	14,8	154	51,5	532	133,7	93	25,3
120	96	15,8	166	56,2	622	148,6	115	30,5
240	103	16,9	178	60,9	720	161,0	141	36,9

SAMPLE	DESCRIPTION	DIR.	SHRINKAGE (kPa)			E(5-15N)			LINEAR SHR (%)	AREA SHR (%)
			BUTT	SHOUL.	BELLY	BUTT	SHOUL.	BELLY		
MIS_1	WASHED BOVINE	0°	37,3	25,7	42,5	45,1	32,1	31,3	0,0	5,5
	(VEGETAL) UPPER FOOTWEAR	90°	16,8	29,1	15,2	31,2	32,3	15,0		
MIS_2	WRINKLED BOVINE	0°	884,3	432,5	188,5	49,6	30,4	15,0	3,0	8,3
	(CHROME) UPPER FOOTWEAR	90°	317,2	419,9	116,7	23,8	27,9	15,0		
MIS_4	CALF BOVINE	0°	1401,4	597,4	314,1	74,5	47,3	28,0	4,0	7,5
	(VEGETAL) LEATHER GOODS	90°	1897,6	2216,5	1251,2	102,8	107,8	70,4		
MIS_6	LAMB OVINE	0°	60,8	101,7	79,5	45,9	45,2	49,6	4,0	7,5
	(CHROME) GLOVES	90°	347,9	322,6	599,2	48,9	47,4	48,9		
MIS_7	SUEDE GOAT	0°	24,8	14,4	23,1	22,5	18,9	16,8	2,0	5,6
	(CHROME) UPPER FOOTWEAR	90°	64,4	123,9	63,4	27,1	32,7	21,7		
MIS_10	CALF BOVINE	0°	53,1	14,5	35,9	19,4	28,3	12,4	4,0	7,5
	(CHROME) APPAREL	90°	36,7	60,4	7,0	16,9	24,6	9,7		
MIS_11	CALF BOVINE	0°	900,3	504,8	38,6	46,0	38,1	5,2	4,0	9,2
	(CHROME) UPPER FOOTWEAR	90°	182,3	997,7	262,7	23,4	48,0	26,5		
MIS_14	SPLIT OVICAPRINE	0°	448,0	510,5	160,3	71,4	83,1	53,8	4,7	6,4
	(CHROME) APPAREL	90°	260,7	636,6	400,1	38,4	63,2	57,6		
BCD_O	OVINE	0°	744,9	226,5	617,2	8,9	7,4	21,2	3,0	6,5
	ACETONE DRIED	90°	190,5	131,6	352,1	5,9	5,5	8,1		
BCD_B	BOVINE	0°	1144,1	777,7	242,5	58,9	34,5	5,4	4,7	9,9
	ACETONE DRIED	90°	319,1	220,2	849,1	16,9	13,2	33,5		
CP294_2	BOVINE	0°	240,7	138,9	607,5	23,9	37,9	39,8	2,1	6,8
	(GLUTARDEHYDE) AUTOMOTIVE	90°	182,0	388,6	30,7	32,7	17,4	7,4		
ML1	BOVINE	0°	458,3	600,3	208,3	32,5	30,9	33,2	4,2	7,1
	(GLUTARDEHYDE) AUTOMOTIVE	90°	203,2	216,7	127,5	34,1	21,1	12,6		
N245	OVINE	0°	81,1	55,0	77,3	43,3	34,9	41,1	2,7	4,4
	(VEGETAL) APPAREL	90°	55,2	35,0	49,5	24,7	27,9	36,2		
PF23	BOVINE	0°	73,2	61,2	40,4	22,2	20,5	18,0	3,7	8,9
	(VEGETAL) UPHOLSTERY	90°	69,1	105,2	38,0	22,4	23,9	13,3		
PF25	BOVINE	0°	203,2	257,5	333,7	21,8	21,5	29,1	3,0	6,5
	(CHROME) UPPER FOOTWEAR	90°	251,8	264,9	151,2	20,8	22,3	18,2		
PF29	BOVINE	0°	244,0	234,5	654,8	30,8	24,3	46,4	3,3	8,6
	(METAL FREE) LEATHER GOODS	90°	222,2	463,6	62,8	38,8	34,0	18,4		
PF31	BOVINE	0°	253,7	162,5	560,4	35,7	21,9	44,1	3,7	10,7
	(CHROME) FURNITURE	90°	328,9	331,9	121,3	25,8	28,1	16,6		

Conclusion

From the results reported in the tables and with the observations limited to the samples analyzed, we can conclude that:

- DMA Method shows good repeability performances
- Leather with the same dimensional behavior could have very different values in terms of force or shrinkage stress
- In the different sampling area there is a certain correspondence between the trend of the force values with the modulus
- In many cases the shrinkage stresses have been resulted:
  - higher parallel to the backbone for butt
  - higher perpendicular to the backbone for shoulder
- Shrinkage behavior can be affected by drying or toggling processes
- Shrinkage is directly related to the fibrous structure of leather
- The stress trend suggests that the time of testing can be reduced to 120 minutes; the linear forecast error to 240 minutes is lower than 2% than the measured value.

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