Development of products from Caesalpinia spinosa

Anna Bacardit, Jorge Díaz, Concepció Casas, Luís Ollé
A3 Chair in Leather Innovation. Escola d'Enginyeria d'Igualada (EEI). Universitat Politècnica de Catalunya (UPC). Avda. Pla de la Massa, 8. 08700 – Igualada (Spain)
Corresponding author: anna.bacardit@eei.upc.edu

Abstract

In previous studies chemical and physical modifications have been developed in order to obtain a modified tara with a higher percentage of tannins and with a better ability to penetrate and fix in leather by sieving and milling. The milled and sieved Tara with particle sizes around 40-50 microns gives better results in terms of organoleptic properties and reduction of the pollutant loads of final baths; from now on, this product will be used as the basis for different applications and optimizations, and it will be referred to as modified tara.

The aim of this work is to study different combinations of modified tara with other products, i.e. quebracho, mimosa, dispersants and synthetic tannins in order to reduce its astringency, and therefore, improve the penetration into the leather structure.

Keywords: tara, vegetable tannage, pre-tannage.

1 Introduction

Cæsalpinia spinosa (Molina) Kuntze, commonly known as tara, is a small leguminous tree or thorny shrub. Tara is cultivated as a source of high value products from its pods and seeds as tannins based on a galloylated quinic acid structure, used in the leather industry and gum for food industry. It is also grown as an ornamental plant because of its large colorful flowers and pods1-4.

Having its origin in the Andean Region, pre-Incas civilizations used the fruits of the tree to produce dyes for textiles and ceramics, tannins for leather and medicines. Known, therefore, as "Incas green gold", there is a strategic interest in Peru, Bolivia and Ecuador, supported by international organizations for cooperation, to promote productive processes under environmental sustainability criteria and social benefit5.

Due to its wildness, there exists a variety of plants according the regions and the living conditions, thus the content of tannins, e.g., can vary from 30% to 80%. Currently, institutions and universities carry out researches to characterize the genetic variability.

Caesalpinia spinosa can be found growing throughout northern, western and southern South America, from Venezuela to Argentina, subtropical and semitropical regions between 4º to 20º S latitudes. It has been introduced in dry parts of Asia, the Middle East and Africa and has become naturalized in California.
Normally tara grows in areas with a yearly rain of 400 to 1.100 mm, and on sanded or degraded soils. It is a wild tree, normally isolated, but sometimes, can form small forests. Generally resistant to most pathogens and pests, it will grow between 0 and 3,000 meters above sea level. Trees begin to produce after 4–5 years. If well irrigated, they can continue to produce for another 80 years, though their highest production is between 15 and 65 years of age6-8.

The fruit of tara tree as and its derivates have a high interest in a number of industries and, thus, a great worldwide economic potential for commerce. The properties of pods and seeds result in a sustainable and quality raw material for several applications.
The weight of the fruit of tara is composed by: 60-64 % of pods, 34-38 % of seeds and 2 % of non-valuable residues. It is important to point out that from tara powder, 45- 50% is

composed by tannins, and tara gum can be obtained from 24% of the weight of the seeds.

Tara powder is obtained by simply mechanically milling and sifting the gross powder after threshing the pods and separate the seeds. The tara powder is a fine (100 to 200 mesh) yellowish sawdust. Further than the leather industry, it is used, as well, in the chemical industry to obtain tara extract, also used in the leather industry and to other applications.

The leather industry appreciates the tara powder as a source of vegetable tannins to obtain light colors, with good light fastness, and full and soft leather articles, with a firm and smooth grain. Tara is easily soluble in water and do not contain color substances like other vegetable tannins.

In our previous publication, the physical modification process of tara not gave an extract with high tannin content like obtained with the alternate aqueous extraction method. (see Low carbon products to design innovative leather processes. Part I: determination of the optimal chemical modification of tara)9, But, as this current study showed, the physical modification of tara improved the penetration/fixation of its tannins into the leather, reduced the suspended matter and chemical oxygen demand in the spent floats.

The best physical modification of tara was obtained by milling, sieving and using the particle size fraction of 50-40 microns (see Low carbon products to design innovative leather processes. Part II: determination of the optimal physical modification of tara)10.

2 Experimental methodology

The aim of this work is to study different combinations of modified tara with other products, i.e. quebracho, mimosa, dispersants and synthetic tannins in order to reduce its astringency, and therefore, improve the penetration into the leather structure.

More specifically, seven trials with different mixtures have been developed at laboratory scale to determine their tanning power, their degree of penetration, the stabilization on the hide structure, as well as the physical and organoleptic properties acquired.

In table 1, the mixtures composition can be seen.

Sample	Composition	% Theoretical tannins		% Theoretical tannins
		Tara	Product	
1	Modified tara/Mimosa	47	70	52.8
2	Modified tara/Quebracho	47	70	52.8
3	Modified tara/Naftalensulphonic	47	49	47.6
4	Modifed tara/phenolic	47	50	48.0
5	Modified Tara/ Dihidroxidiphenilsulphone	47	41	44.8
6	Modified tara/Sodium pyrophosphate acid	47	-	36.1
0	Original Tara	47	-	47.0

Table 1. Theoretical tannins of the different mixtures of tara

A determination of tannins for each mixture has been conducted, so we can establish with certainty their real content of tannin. This is done to know the actual quantities, and to apply the same amount of tannins in each test, in order to perform comparable tests. The results of the characterization of the samples can be seen in Table 2.

Determination	1	2	3	4	5	6	0
Soluble solids (%)	66.0	67.1	72.1	72.3	87.3	57.4	57.5
Total Solids (%)	92.0	90.7	92.6	89.0	85.1	73.9	87.7
No tannins (%)	15.9	14.2	31.7	26.7	43.0	21.3	13.6
Tannins (%)	50.1	53.0	40.4	45.7	44.3	36.1	43.9
Insoluble matter (%)	25.9	23.5	20.4	16.6	0.0	16.4	30.2
Water (%)	8.0	9.3	7.4	11.0	12.7	26.2	12.3
pH	3.7	3.8	3.8	3.7	3.7	3.9	3.7

Table 1. Characterization of different mixtures of tara

The results of theoretical and real tannic content are described in Table 3. This is a comparative study to know if there is a big difference between the two of them.

Samples	Composition	% Theoretical tannins, mixture	% Real tannins, mixture
1	Modified tara/Mimosa	52.8	50.1
2	Modified tara/Quebracho	52.8	53.0
3	Modified tara/Naftalen sulphonic	47.6	40.4
4	Modified tara/phenolic	48.0	45.7
5	Modified tara/Dihidroxidiphenilsulphone	44.8	44.3
6	Modified tara/Sodium Pyrophosphate acid	36.1	36.1
0	Original Tara	47.0	43.9

Table 3. Analysis of theoretical and real tannin content

There are some differences between theoretical and real tannin content. Due to the fact that the theoretical content is given by the brand, it is better to use the real figures that were obtained.

It is observed that the content of tannins in the commercial tara is 44%.The vegetable extracts, quebracho and mimosa, increase their tannin content considerably, followed by the synthetic products like naphthalene sulphonic and phenolic.

Regarding the Dihidroxidiphenilsulphone, more than a synthetic tanning, it could be considered as a dispersant; this means that it improves the penetration of the tannins without reacting with the collagen of the hide.

Such is the case of the sodium pyrophosphate acid, which could be considered as a dispersant, and can also act as sequestering of iron.

The application of mixtures of tara on leather was performed using pickled cowhide at pH 3.5. Then, a neutralization at pH 5.0 is done using DD Simplex Drum (10 rpm). Once neutralized, the hide is divided into several pieces of about 250 g each, to perform the pre-tannage tests.

The pre-tannage is performed in Drum SIMPLEX-4 (12rpm). The process and formulation applied are described in Table 4.

OPERATION	ºC	%	PRODUCT	TIME	Observation
Pre-tannage	20				
		X	**Modified Tara mixture with product**		
		7	Synthetic S-3		
		2	Sulphited oil	night	
		0.8	Formic acid	2 hours	pH=3.59, drain
Wash	20	300	Water	20 min.	Drain
					Rest
					Samming
					Air drying

Table 4. Formulation of pre-tannage using mixtures of tara

The 'X' value in table 4 is referred to the % of mixes with modified tara and the different products mentioned in Table 5.

Test	Composition	%Real tannins	% Applied respect to commercial Tara
1	Modified tara/Mimosa	50.1	7.90
2	Modified tara/Quebracho	53.0	7.45
3	Modified tara/Naftalen sulphonic	40.4	9.80
4	Modified tara/phenolic	45.7	8.60
5	Modified tara/Dihidroxidiphenilsulphone	44.3	8.90
6	Modified tara/Sodium pyrophosphate acid	36.1	11.0
0	Original Tara	43.9	9.00

Table 5. Products and quantities applied

The different products are compared with the application of the original Tara (test 0). This means that a 9% of commercial tara, with 43.9% of real tannins, is applied; therefore, for each test the amount of mixture to be applied is calculated to obtain comparable results.

The shrinkage temperature of the hides is determined to evaluate their stability at the temperature.

3 Results

Table 6 shows the results obtained from the tests of shrinkage temperature, hardness (softness) and appearance of the cuts of hides (penetration rating products):

Test	Composition	Ts (°C)	Softness (mm)	Cuts photos
1	Modified Tara/Mimosa	60	1.1	
2	Modified Tara/Quebracho	59	1.0	
3	Modified Tara/ Naftalen sulphonic	64	0.7	
4	Modified Tara/ phenolic	64	0.6	
5	Modified Tara/ Dihidroxidiphenilsulphone	62	1.1	
6	Modified Tara/ sodium Pyrophosphate acid	62	0.9	
0	Original Tara	61	0.6	

The best results regarding the shrinkage temperature were observed with the naphthalene sulphonic mixture and with the phenolic syntan mixture, followed by the pyrophosphate and Dihidroxidiphenilsulphone ones.

Table 7 shows the results in terms of assessing the color of the hide samples

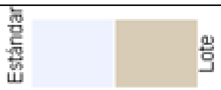
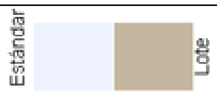
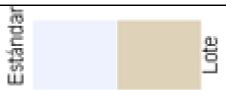
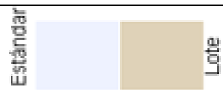
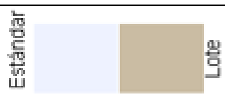
Test	Composition	Data Color				
			DL	**Da**	**Db**	Strength **(%)**
1	Modified tara/Mimosa		-23.09	2.59	17.99	9108
2	Modified tara/Quebracho		-16.76	4.42	22.16	6505
3	Modified tara/ Naphthalene sulphonic		-12.61	0.39	19.39	4077
4	Modified tara/ phenolic syntan		-19.65	0.95	20.65	8092
5	Modified tara/ Dihidroxidiphenilsulphone		-10.53	0.03	20.51	3585
6	Modified tara/ Sodium pyrophosphate acid		-10.53	0.25	21.17	3749
0	Original tara		-18.00	0.69	21.16	7361

Table 7. Results of Data Color

Differences in color with respect to the Original Tara correspond to the mixtures of tara with vegetable extracts, due to their intrinsic characteristics (brown or reddish color) and ease of oxidation. Among vegetable extracts, Tara is characterized for contributing with little coloration to the skin.

The data color test shows good results for the modified Tara and Naphthalene sulphonic mixutre, as well as with the Dihidroxidiphenilsulphone and sodium Pyrophosphate acid one.

4 Conclusions

In general, the hides obtained are rigid, and the level of penetration achieved is not the most adequate due to the fact to doing the test at laboratory level.

As a conclusion, the auxiliary product Naphthalene sulphonic acid has been chosen to use in the optimization of a pre-tanning process, due the results obtained in shrinkage temperature, data color and organoleptic properties.

Sodium acid pyrophosphate also possesses dispersant qualities, and also acts as an iron sequestrate. Because good organoleptic properties of the pyrophosphate and tara mixture have been observed, further tests will be developed using this product. And it will be evaluated, for its ability to improve the behaviour of tara against contamination of iron particles generated from the shaving processes of leather. Furthermore, the possibility of removing salts by decreasing the amount of sodium chloride in the tanning process will be considered.

Here is a sample of the iron sequestering power of pyrophosphate, by applying a drop of ferric chloride in the wetted surface of the leather, and by observing the color change compared with a sample of leathers without pyrophosphate.

The following photographs, shows the change of color after two hours and two weeks for trial 6 (tara with pyrophosphate) and trial 0 (original tara).

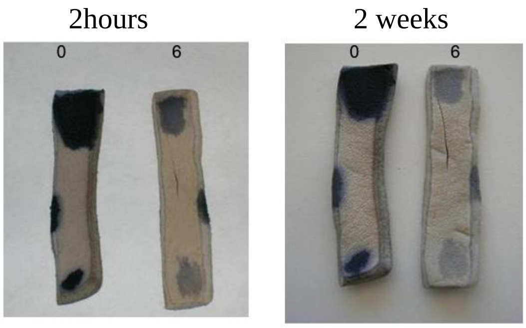


Figure 1. Ferric chloride reaction after 2 hours and after 2 weeks

Obviously, when iron pyrophosphate is added, the stain fades over time; unlike the sample with original tara where the stain remains. The difference between both is noticeable. This is a clear proof of the iron sequestering power of pyrophosphate, and the big importance to use it in terms of reducing the possibility of stains resulting from iron in shaving process.

5 Acknowledgement

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