Low Carbon Products to Design Innovative Leather Processes. Part II: Determination of the Optimal Physical Modification of Tara

by

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Abstract

This study considers the fruit of the tara bush as a sustainable source for tanning agents and proposes alternatives to chromium and other mineral salts and vegetable extracts. Specifically, physical modifications have been developed in part II of the study to obtain a modified tara with a higher percentage of tannins and with a better level of penetration (see Low carbon products to design innovative leather processes. Part I: determination of the optimal chemical modification of tara).[1] The physical modification of tara focused on milling and sieving. The different products obtained have been characterized and applied to leather samples in order to evaluate the degree of penetration and stabilization in the leather structure.

Introduction

Cæsalpinia spinosa (Molina) Kuntze, commonly known as tara, is a small leguminous tree or thorny shrub. Tara pods and seeds are a source of high value products, which contain tannins of a galloylated quinic acid structure, used in the leather industry and gum for food industry.[2] Tara powder is obtained by simply mechanically milling and sifting the gross powder after threshing the pods and separating the seeds.[3,4]

During the last two decades, some auto manufacturers have required new tanning processes that replace the traditional chrome tanning. Tanners and the chemical industry have developed alternative processes using organic tannins with the aim to obtain a fully degradable material at the end of its cycle life. The leather obtained using these organic tanning processes can be composted after use.[5] This measure is compulsory in Europe. The End-of-Life Vehicle Directive (or ELV Directive 200/53/CE) requires that the vehicle manufacturers be responsible for taking back and scrapping cars in the future. This directive specifies that 95% of the vehicle weight must be reused by 2015.[6]

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"Wet-white" is the intermediate leather commodity using the tanning properties of aldehydes, mainly, glutaraldehyde. Other "wet-white" systems use metals, when applicable, such as Aluminum, Zirconium, Titanium, vegetable tannins or syntans (molecules obtained by organic synthesis with specific properties similar to the vegetable tannins). Up until today, tara tannin has been used to produce automotive "wet-white" as a retanning agent after pre-tanning with glutaraldehyde and carrying out mechanical operations. The properties of light fastness and relative colorlessness have not been improved using other substances despite the efforts of the chemical industry to find out a "synthetic tara tanning agent".[7-11]

To point out one of the most important advantages for tara products when compared with syntans and other vegetable tannins, is that they are exempted of such Registration as defined in:

"Substances occurring in nature, if they are not chemically modified, unless they meet the criteria for classification as dangerous according to Directive 67/548/EEC"

In order to propose the use of tara tannins for a sustainable pretanning process, we developed physical modifications to obtain a modified tara with a higher percentage of tannins and with a better level of penetration.

MATERIALS AND METHODS

This study was conducted in three steps:

1st step. Separation by screening of tara.

2nd step. Milling and sieving of the tara in different particle sizes.

3rd step. Application of the modified tara to leather.

Separation by Screening of Tara
A screening process is applied to a sample of tara powder using a sieve of a 20 cm diameter and 90 microns light. Two fractions of tara were separated:

i) Tara powder with a particle size above 90 microns.

ii) Tara powder with a particle size below 90 microns.

To determine the quality of the tara obtained, the following parameters were examined:

-Tannin content by the filter method.

-Non-tannin content by the gravimetric method.

-Insoluble matter by the gravimetric method.

-Total solids by the gravimetric method.

-Soluble solids by the gravimetric method.

-Water.

-pH.

Milling and Sieving of the Tara in Different Particle Sizes
A screening process is applied to a sample of original tara powder. The methodology follows these steps:

- The powder tara sample is placed in canisters of 1L capacity to 1/3 of its capacity.

- Bearing steel balls of various sizes are put in the canisters.

- Shake for 50 h in laboratory rotary shaker (speed 15 rev / min.).

After the screening process, a sieving process is applied using the digital electromagnetic sieve shaker Filtra. The digital electromagnetic sieve shaker is suitable for particle fractionation in grain size determination from 0.040 mm in dry state. The body of the casing is made of steel, digital power regulation, intermittence and operation timer. This sieve shaker causes a three-dimensional movement of the test sieves, which is necessary to obtain an optimal separation of the grain-size fractions. The sieving time was 9 minutes and the vibration power 9.

The mesh sieves with stainless steel AISI 316 complies with UNE 7050-3, ISO 3310-1 and ASTM E11. Different mesh sieves of 20 cm of diameter were used: 200 microns, 160 microns, 125 microns, 100 microns, 80 microns, 63 microns, 45 microns and 40 microns. Figure 1 shows the digital electromagnetic sieve shaker Filtra.

Figure 1. Digital electromagnetic sieve shaker Filtra.

To determine the quality of the tara obtained, particle size was figured out and the following parameters:

-Tannin content by the filter method.

-Non-tannin content by the gravimetric method.

-Insoluble matter by the gravimetric method.

-Total solids by the gravimetric method.

-Soluble solids by the gravimetric method.

-Water.

-pH.

The tannin content, the non-tannin content, the insoluble matter, the total solids, the soluble solids, and water, were determined following the ISO 14088:2012 Leather — Chemical tests — Quantitative analysis of tanning agents by filter method standard.

Application of the Modified Tara to Leather
Finally, the application of modified tara in the pre-tanning process was studied. Bovine pickled hides (pH 3.5) were used to perform the experiment. The formulation of the pre-tanning process is shown in Table I.

RESULTS AND DISCUSSION

Separation by Screening of Tara
Table II shows the results of the analysis of the three samples of tara: original tara, tara powder with a particle size above of 90 microns and tara powder with a particle size below 90 microns.

As can be observed, there is variability across the different samples. The tara powder with a particle size above 90 microns presents low values of soluble solids, total solids, non-tannins and tannins. In contrast, it presents a high amount of insoluble matter. Concerning the tara powder with a particle size below 90 microns, it presents better values for tannins and a low content of insoluble matter. Following these results, we will proceed with the study by milling and sieving the tara powder in different particle sizes.

Milling and Sieving of the Tara in Different Particle Sizes
To obtain a tara extract with high tannin content and low content of insoluble matter, the milling and sieving processes were carried out.

TABLE I
Pre-tanning formulation.

STAGE	ºC	%	PRODUCT	Time	
Pre-tanning	20	50	Water with salt	15’	10 ºBé
		11	Modified tara		
		7	Synthetic S-3		
		2	Sulphite oil	Aut. night	Cross section testing
		0.8	Formic acid	2h	pH=3.59
					Drain
Washing	20	300	Water	20’	Drain
					Rest on horse
					Samming
					Drying

Table III shows the weight distribution according to the mesh sieves used with the original tara.

Table III shows that using a sieve above 106 microns, all tara is retained in the mesh sieve (no tara pass through the mesh sieve). Table 3 also shows which amount of tara is retained in each mesh sieve. For instance, using a sieve of 106 microns, 1.18% of tara is retained in the mesh. In addition, Table 3 shows the % of tara retained accumulated in all meshes. That is, after using a sieve of 106 microns, 96.65% of tara is retained. And finally, the test indicates that a loss of 2.23% of the sample is produced due to the fact that 97.7% of the tara was retained in the mesh sieves and no more tara pass through the last mesh sieve.

TABLE II
Characterization of the three samples of tara powder.

Parameter	Original	Tara > 90 microns	Tara < 90 microns
Soluble Solids (%)	59.7	37.1	62.0
Total Solids (%)	92.9	90.3	91.9
Non-Tannins (%)	14.7	11.7	14.0
Tannins (%)	45.0	25.4	48.0
Insoluble Matter (%)	33.2	53.2	30.0
Water (%)	11.0	9.7	8.1
pH	3.8	3.9	3.7

Table IV shows the weight distribution according to the mesh sieves used of the milled tara.

As can be seen in Table IV, when using milled tara, all tara is retained in the mesh sieve of 106 microns (no tara pass through the mesh sieve). Table IV also shows which amount of tara is retained in each mesh sieve. For instance, using a sieve of 106 microns, 4.39% of tara is retained in the mesh. In contrast, when using original tara only 1.18% of tara is retained in the mesh. In addition, Table 4 shows the % of tara retained accumulated in all meshes. That is, after using a sieve of 106 microns, 97.28. In contrast, when using original tara, only 96.65% of tara is retained. And finally, the test indicates that a loss of 2.72% of the sample is produced.

Figure 2 shows the comparison of particle size distribution between the original and the milled tara.

It can be seen that milling and sieving the original Tara has increased particle fraction smaller than 63 microns, homogenizing the particles to a size of 45 microns. We can see a wider range of sizes in the original Tara.

TABLE III
Weight distribution of original tara after sieving.

Sieve	Aperture (µm)	% Partial retained	%Accumulated retained	% pass
92	200	1	1	96.77
94	160	0.88	1.88	95.89
96	125	2.86	4.74	93.03
98	100	10.63	15.37	82.4
100	80	6.61	21.98	75.79
102	63	27.29	49.27	48.5
104	50	17.26	66.53	31.24
105	45	28.94	95.47	2.3
106	40	1.18	96.65	1.12
< 106	< 40	1.12	97.77	0

TABLE IV
Weight distribution of milled tara after sieving.

Sieve	Aperture (µm)	%Partial retained	%Accumulated retained	% pass
92	200	1.74	1.74	95.54
94	160	1.32	3.06	94.22
96	125	4.14	7.2	90.08
98	100	2.25	9.45	87.83
100	80	5.89	15.34	81.94
102	63	10.67	26.01	71.27
104	50	8.31	34.32	62.96
105	45	58.57	92.89	4.39
106	40	4.39	97.28	0
< 106	< 40	0	97.28	0

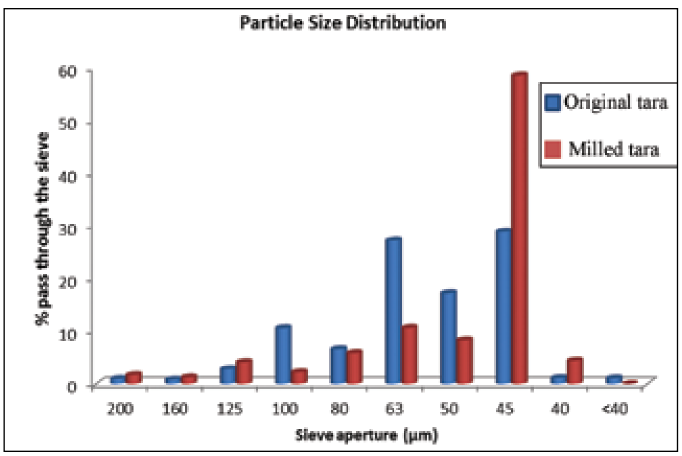


Figure 2. Comparison of the particle size distribution of original and milled tara.

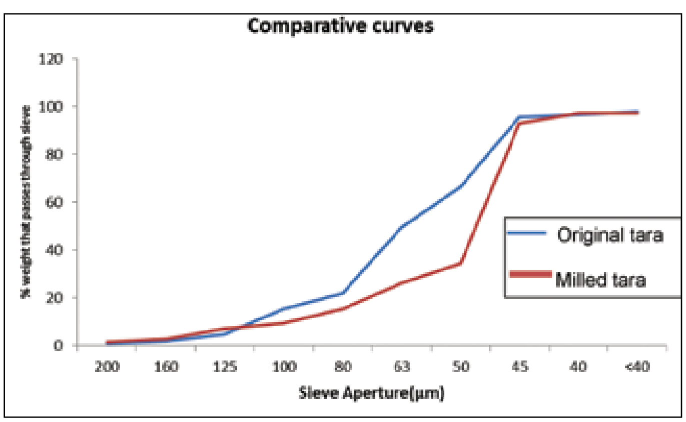


Figure 3. Comparison of the grading curves of original and milled tara.

Figure 3 shows the comparison of the grading curves between the original and the milled tara.

Following the same pattern as particle size distribution, when comparing the weight distribution, a wider range of weights can be observed in the original tara. Milling and sieving the tara has increased the weight that passes through the mesh sieve when working with a sieve aperture of 45 microns. Therefore, we can conclude that the milling and sieving process allows particle size to be reduced to values below 50 microns.

To analyze the modified tara, 5 samples were selected according to the different particle size fractions:

Sample 1: Milled tara

Sample 2: Milled tara, particle size fraction of 200-80 microns.

Sample 3: Milled tara, particle size fraction of 80-50 microns.

Sample 4: Milled tara, particle size fraction of 50-40 microns.

Sample 5: Original tara

Table V shows the results of the analysis of the 5 samples of tara selected.

As can be observed in the table, there is variability across the different samples once again. The tara powder with a particle size between 200 and 80 micron, presents low values of

TABLE V
Tannin content of tara.

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Soluble Solids (%)	59.6	40.2	57.9	64.0	59.7
Total Solids (%)	86.0	76.0	95.4	93.6	92.9
Non-Tannins (%)	13.1	12.5	11.4	14.7	14.7
Tannins (%)	46.4	27.7	46.5	49.3	45.0
Insoluble Matter (%)	26.5	35.8	34.4	29.6	33.2
Water (%)	14.0	24.0	7.6	6.4	11.0
pH	3.7	3.7	3.7	3.7	3.8

TABLE VI
Shrinkage temperature, leather cross section and softness.

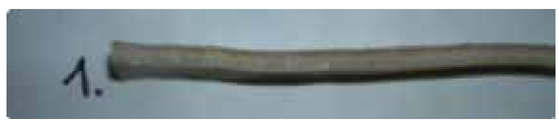
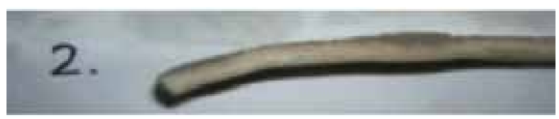
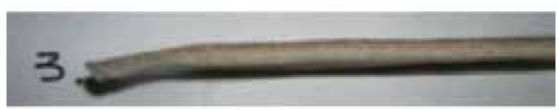
Test	Ts	Cut	Softness
Original tara	**69,5**		1.1
Milled tara	**69**		1.0
Milled and sieved tara (50-40 microns)	**70,5**		1.1

TABLE VII
Analysis of the residual floats.

Test	Suspended matter (mg/L)	Chemical oxygen demand decanted 2H (mg/L)	Chlorides (mg/L)
Original tara	22772	63700	33038
Milled tara	19773	44400	32385
Milled and sieved tara	11996	40600	33779

soluble solids, total solids and tannins. In contrast, it presents a high amount of insoluble matter. The tara of smaller particle size has a higher percentage of tannins and presents a low content of insoluble matter. Therefore, we will follow the work with the application of three samples of tara to the leather: i) original tara, ii) milled tara, and iii) milled tara, particle size fraction of 50-40 microns.

Application of the Modified Tara to the Leather

Shrinkage temperature was determined to evaluate the thermal stability of leathers obtained with the application of the three samples of tara: i) original tara, ii) milled tara, and iii) milled tara, particle size fraction of 50-40 microns. Leathers were evaluated regarding color and organoleptic parameters of hardness by applying the "Softness Test." The results obtained are shown in Table VI.

Table VII shows the analysis of residual floats in each of the test.

As can be observed, the cuts are very similar. Despite not being clearly visible from the picture, there seems to be thorough penetration throughout the cross section. The extract penetration into leather cross section was correct and the shrinkage temperature is similar in the three tests. The decrease of suspended matter and chemical oxygen demand is especially noticeable. Both the suspended matter and chemical oxygen demand decrease with the particle size, which is something to be taken into account. However, the softness obtained is not desirable; all the test leather samples were significantly hard.

CONCLUSIONS

The physical modification process does not allow for an extract with high tannin content to be obtained as it was with the aqueous extraction (see: Low carbon products to design innovative leather processes. Part I: determination of the optimal chemical modification of tara),1 but it improves the penetration of the extract into the leather and reduces the suspended matter and chemical oxygen demand of the residual floats. The best physical modification was obtained by milling and sieving at particle size fraction of 50-40 microns. We believe that in order to overturn the negative aspect of softness, some improvements need to be made. This work can be further broadened and developed by studying different mixtures of milled and sieved tara using other products: quebracho, mimosa, dispersants (protein) and synthetic tannins.

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