

Tanning with Pomegranate Peel Tannin

by

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Abstract

By-products of pomegranate juice enterprises are evaluated as a “green” raw material for many industries. In this study, pomegranate peels which are well known with high polyphenolic content were evaluated as a potential source of tanning agent for leather industry. For this purpose, firstly pomegranate peels were extracted in Koch extractor at 70°C for 8 hours. In order to determine the tanning ability, 30% of ground pomegranate peel powder (containing 7.2% of active tannin matter) was used in the tanning process and pomegranate peel tanned leather was evaluated in terms of increases in thickness and shrinkage temperature, color change and mechanical properties. The application of pomegranate peel tannin in the tanning process provided that an acceptable shrinkage temperature (68.5°C) and mechanical properties for vegetable tanned leathers. The results revealed that the tannin obtained from pomegranate peel has a remarkable tanning effect and can be used in the tanning process. Thus, it is concluded that pomegranate peels can be evaluated as a new source of tannin for leather industry.

Introduction

Polyphenol-rich plant extracts (vegetable tannins) bearing a large number of hydroxyl and other functional groups have ability to form strong linkages with collagen.¹ Therefore, vegetable tannins are taken into consideration as eco-friendly and manageable tanning agents and they contribute to remarkable improvement in leather properties by tanning process.² Vegetable tanning technology was prevalent process for leather industry over centuries until it has gradually been displaced to chrome tanning by the end of the 19th century.¹ However, vegetable tanning agents have recently regained their former popularity due to the increasing interest and even compelling trend towards more sustainable, greener and eco-friendly tanning processes. On the other hand, the vegetable tannin sources having commercial importance for tanning are limited due to scarce number of tannin rich plant materials. In recent years, numerous researchers have been focused on searching for new tannin sources that can be used in leather industry as tanning agent.³⁻⁶

Among the alternative tannin sources, pomegranate peels which are generated as waste in fruit juice enterprises have recently attracted

the attention of many industries.⁷⁻¹⁰ The peels constitute 30-40% of the pomegranate fruit and they remain as a byproduct after juicing fruit. On a global scale, there are 3 million tons of total pomegranate production, resulting in approximately 1.62 million tons of waste.¹¹ Due to their high polyphenolic content and antioxidant properties, pomegranate peels are no longer considered as waste, but as a valuable raw material source for sustainable, eco-friendly and green chemical production.

From the literature review, it was seen that there is limited data available concerning the possible usability of pomegranate peels as a source of tanning agent and its detailed tanning properties.^{2,12} So, as the first step pomegranate peel tannin was decided to be used as a retanning agent in leather processing and besides its retanning performance, its effect on prevention of Cr(VI) formation was investigated in a previous study.¹³ Especially the high tannin content and considerable filling properties obtained from the study drove to investigate its solo performance. Thus, as a complementary study, in the present part, it was focused on investigation of pomegranate peel tannin's tanning performance as a main tanning agent.

Materials and Methods

Materials

The pomegranate peels were supplied from a food company operating in Torbali/Izmir. Before experiments, pomegranate peels were rinsed, dried and broken into pieces similarly the previous study.¹³ Pickled sheep skins (breed of Métis) were used in tanning trials.

Methods

Tannin extraction: Extraction of pomegranate peels was carried out in a similar way as described in the previous study.¹³ From the evaluation of the findings obtained from the previous study, it was seen that higher extraction temperature did not have a significant contribution to the extraction yield and tannin content, so the extractions were carried out at 70°C in the present study.

Re-determination of the tannin content by repeating extraction processes has required due to following reasons: a) It should not be ignored that the tannin content of pomegranate peels may change more or less on account of different harvest times. The presence

of tannin can differ from plant to plant, and part to part of a plant since plant polyphenolic compounds are produced naturally. b) In order to accurately calculate the amount of tannin to be used in tanning process, the tannin content of the raw material to be used must be known exactly. Extraction yield was calculated according to Formula 1.

$$(\%) \text{Extraction Yield} = (\text{extract obtained (g)} / \text{pomegranate peels used (g)}) \times 100 \quad (1)$$

Tannin and non-tannin matter contents of obtained extract were determined according to the SLC 114,¹⁴ 115,¹⁵ 116¹⁶ and 117¹⁷ test methods. All analyses were repeated three times and mean data were given.

Tanning with Pomegranate Peel: Pomegranate peels were ground by micro mill (Super Mixer SM 108) into powder form before the tanning process. Approximately 30% of ground pomegranate peel powder (containing 7.2% of active tannin matter considering the determined tannin content) was weighed by taking in account the weight of intact pelt and used in tanning process in order to determine tanning effect. The applied tanning recipe is given in Table I. It should be pointed out that the recipe was not prepared to manufacture of garment, shoe upper etc., only a basic tanning recipe was applied to determine the tanning effect of pomegranate peels.

Determination of tanning properties of pomegranate peel: Filling coefficient and shrinkage temperature, the most important indicators

Table I
Tanning recipe

Process	Amount (%)	Product	Temperature (°C)	Duration (min.)	pH
Depickling	150	Water (8 °Be' NaCl)	28-30	15	
	1	HCOONa		40	
	0.3	NaHCO ₃		60	4.8
Draining - Thickness Measurement					
Tanning	70	Water	35		
	10	Ground Pomegranate Peel		90	
	10	Ground Pomegranate Peel		90	
	10	Ground Pomegranate Peel	37	90 (left in bath overnight 7-8 rpm)	
	0.1	Fungicide		20	
	0.7	HCOOH		60	3.7
Washing	200	Water		10	
Draining - Thickness Measurement					
Aging for 1 week - Shrinkage Temperature Measurement					
Retanning-Fatliquoring	200	Water	35		
	1	Neutralizing Syntan		30	5.0
	3	Amphoteric Acrylic Polymer		30	
	4	Sulphited Natural Fatliquor	45	75	
	3	Synthetic Fatliquor			
	3	Lanolin Fatliquor			
	0.8	HCOOH		90	3.6
Washing	200	Water		10	

for qualifying tanning effect, of tanned leather were determine in order to evaluate tanning properties of pomegranate peel. Before tanning (after depickling process) the thicknesses of pelt (T_1) and after tanning the thickness of leather (T_2) were measured from 8 different points in wet form according to ISO 2589¹⁸ and mean data were determined. Filling coefficient was calculated according to Formula 2.

$$(\%) \text{ Filling coefficient} = ((T_2 - T_1) / T_1) \times 100 \quad (2)$$

The shrinkage temperatures of intact pelt and tanned leather were determined according to ISO 3380¹⁹ with three repetitions and mean data was given.

Measurement of color: The color and color components of pomegranate peel tanned leather were measured by using the Minolta CM-2600d Spherical Spectrophotometer according to the CIE*Lab color system. Color measurements were taken from 15 different parts of the leather sample and the result was given as mean value.

Physical Properties of Tanned Leather: In order to determine the mechanical properties of pomegranate peel tanned leather, the tensile strength and percentage of elongation²⁰ and tear load²¹ of the leather were determined. Samples for the tests were taken in accordance with ISO 2418²² standard. The samples were conditioned according to the ISO 2419²³ standard and their thicknesses were measured according to the ISO 2589¹⁸ standard. For both tests, 3

parallel and 3 perpendicular samples were taken, and the test results were given as the mean value.

Results and Discussion

Extraction Yield and Tannin Content of Pomegranate Peel: During the extraction of plant materials, water-soluble/insoluble non-tannin matters (such as sugars, salts, flavones, gallic acid, other acids, etc.) also pass into the extract as well as tannins. Looking from the viewpoint of the tanning process, although non-tannin matters do not have tanning properties, their presence in the tanning bath may affect the character of produced leather. The tannin/non-tannin and soluble/insoluble matter contents of pomegranate peel extract are given in Figure 1. The extraction yield was determined to be 44.5(±0.2)%.

Gurler¹² reported that the pomegranate peels, which were supplied from a company as a ready extract, contain 37.2% tannin and 72.1% total soluble matter and El Maujahed et al.² reported that 38.2% of extraction yield was obtained from the extraction of pomegranate peels with distilled water in 1:10 ratio for 12 hours at 100°C in the dark ambient by use of ethanol as an additive.

According to the results, it was seen that the extraction yields and tannin contents differ in pomegranate peels. Many factors such as harvest time, supplied region and extraction conditions can be effective for this variation.

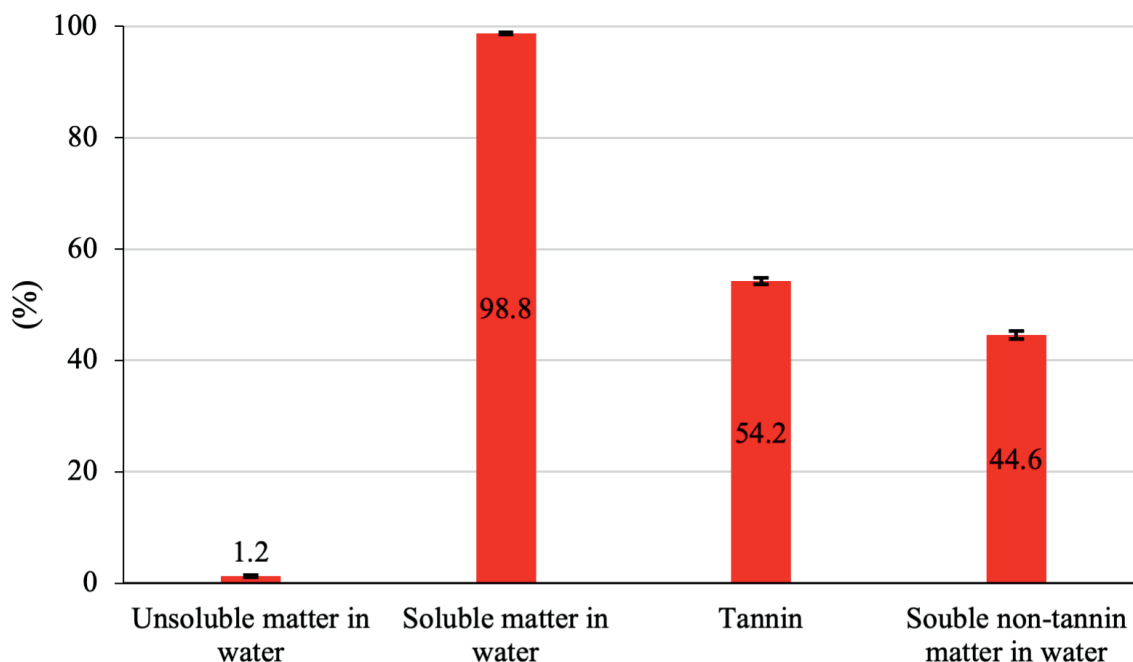


Figure 1. Tannin/non-tannin and soluble/non-soluble matter contents of pomegranate peel extract.

Table II
Comparison of commercially available tannins and tannin sources

Tannin	Tannin Type	Part of Plant	% Tannin in extract	% Tannin content in plant part
Mimosa	Condensed	Bark	70	36
Qubracho	Condensed	Wood	70	21
Chestnut	Hydrolysable	Wood	75	10
Olive	Hydrolysable	Leaf	28	10
Pomegranate	Hydrolysable	Peel	54	24
Sumach	Hydrolysable	Leaf	50	20
Tara	Hydrolysable	Pods	50	40
Gambier	Condensed	Leaf	50	25

In Table II, a comparison of commercially available tannins and tannin sources are given above (since there are various types of plants and different plant species having various amounts of tannin contents even for a type of tannin, in this table are approximate values).

Tanning properties of pomegranate peel: The shrinkage temperatures and thicknesses of intact pelt and the leather treated with pomegranate peels are given in Table III. From the results, it was clearly seen that tanning with pomegranate peels resulted in a remarkable increase in shrinkage temperature (26.8°C) and filling coefficient (57.1%) comparing with the intact pelt. From the evaluation of the shrinkage temperature and filling coefficient results, it was deduced that pomegranate peel tannin has an effective tanning ability.

Pomegranate peel extract solutions at different ratios (15, 20, 30%) were used in tanning process of garment leathers by Gurler¹² and it was stated that the highest shrinkage temperature was obtained

to be 79°C with 15% of pomegranate peel. However, controversially, it was also specified that as the amount of used pomegranate peel extract increased, the shrinkage temperature decreased to 74°C.

Color of tanned leather: Leathers tanned with vegetable tannins possess the characteristic color of the tannins used. This type of leather is either not dyed through or dyed in pastel or dark tones, arbitrarily. For this reason, it is important to determine the final color of leather tanned with pomegranate peel. Table IV shows the L, a, b values obtained from color measurements of the tanned leather. From the examination of the data, it was seen that the color of the leather tanned with pomegranate peel is predominantly in yellow tones and contains a slight reddish tone.

Mechanical properties of tanned leather: Physical test results of leather tanned with pomegranate peel are given in Table V. It can be obviously seen that the obtained tensile (20.1 N/mm²) and

Table III

Thickness and shrinkage temperature values of intact pelt and tanned leather

	Thickness (mm)	Shrinkage temperature (°C)
Intact pelt	0.7(±0.5)	41.7(±0.6)
Tanned leather	1.1(±0.4)	68.5(±0.7)

Table IV

Color measurement values of leather tanned with pomegranate peel

L	a	b
75.7(±0.6)	3.2(±0.3)	28.3(±0.7)

Lightness/brightness (L=0 black, L=100 white), red/green color (+a red, -a green) and yellow/blue color (+b yellow, -b blue).

Table V

Mechanical properties of leather tanned with pomegranate peel

Tensile Strength (N/mm ²)	Elongation at break (%)	Tear Strength	
		Max. Force (N)	Thickness (mm)
20.1(±2.9)	71.2(±5.4)	32.0(±1.5)	0.7(±0.02)

tear (45.7 N/mm) strengths met the acceptable quality standards recommended by United Nations Industrial Development Organization (UNIDO)²⁴ for vegetable tanned upholstery leathers (<2 mm of thickness, 10 N/mm² for tensile strength and 15 N/mm for tear strength). In addition, the obtained values also met the quality requirements for garments leathers recommended by UNIDO²⁴ regardless of the tanning method (min. tensile strength of 12 N/mm² and min. tear strength of 20 N/mm).

In literature, related to the mechanical properties of the leathers tanned with pomegranate peel; Gurler¹² reported that the highest tensile and tear strength values of pomegranate peels tanned leathers were found to be 6.3 N/mm² and 17.4 N/mm, respectively.

Conclusion

In this study, the tanning ability of pomegranate peel tannin and its possible utilization as a main tanning agent in leather industry were investigated. For this purpose, after determining the tannin content of the pomegranate peels, a basic tanning process was applied using 30% of ground pomegranate peel powder (containing 7.2% active tannin matter considering the determined tannin content). Considering the filling coefficient (which is also a sign of fiber isolation), shrinkage temperature and physical properties of the tanned leather, it was concluded that pomegranate peels (containing remarkable polyphenolic compounds) which arise from as a waste in fruit juice enterprises can be utilized as a new source of vegetable tanning agent.

In case of using ground pomegranate peel powder instead of extraction product, it is crucial to determine the tannin content of pomegranate peels, since the tannin content of pomegranate peels may change more or less on account of different harvest times, in order to accurately calculate required amount of tannin to be used in tanning process according to different types of vegetable tanned leather articles.

However, it is necessary to emphasize here that tanning with increasing amounts of pomegranate peel powder bearing higher amounts of active tanning matters i.e. 11-15% (which is generally required for different types of vegetable tanned leather articles) will result in much better tanning performance and leather characteristics.

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