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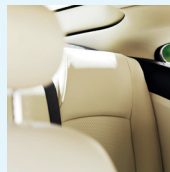


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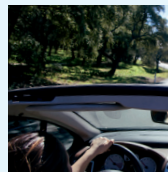
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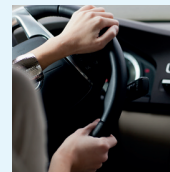
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Study on the Degreasing of Sheep Skin Using Subcritical Fluid Extraction

by

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Abstract

Degreasing is one of the important processes for the production of leather and fur. This study aimed to develop a degreasing method using subcritical n-pentane. Sheep skin was chosen as raw skin for this investigation. The best possible combination of degreasing parameters was found using single factor experiment and response surface methodology. The effects of temperature and pressure on the degreasing efficiency were evaluated further with histological analysis. The results showed that the optimum degreasing parameters were a degreasing time of 58 min, pressure of 0.45 MPa, temperature of 41.0°C and thus yielded a degreasing rate of 52.46% theoretically and 51.46% experimentally. Histological sections showed that the degreasing effect of subcritical n-pentane was quite significant and the lipid droplets around the hair follicles were dramatically reduced. It has been proven that subcritical n-pentane degreasing is an effective technique for sheep skin degreasing.

Introduction

Wool sheep skins have a fat layer in the grain-corium junction. The structure is in the form of large lipocytes, closely associated in a mass, which can act as a barrier to the penetration of aqueous reagents. Also, there is sebaceous grease in the wool follicles. The natural fat content of different animals is variable, breed-dependent, and may range from 3 to 50% of the skin weight.¹ In the processing of lambskin or sheepskin into fur, it is significant that the grease should be removed from the sheepskin to allow chemical penetration and uniform reactions through the skin cross section and to avoid odor problems if the fat turns rancid.² Organic solvent degreasing has remarkable degreasing effect, but this approach produces a considerable increase of environmental pollution, by emission of volatile and semi-volatile organic compounds, and may present problems in the biological treatment plants for waste water.³ In the traditional degreasing process in aqueous medium, fats are emulsified in the presence of an anionic or nonionic surfactant and solvent (light petroleum rich in hexane). A single stage is not sufficient to obtain high efficiency and consequently this operation is time demanding. Another disadvantage of the process lies in the pollution of the environment. Effluents contain high pollutant loads that are only partially, or not at all, recycled. The extracted

fat is not recovered.⁴ The use of enzymes for degreasing poses several advantages such as elimination of organic solvents and surfactants, improved fat dispersion, production of waterproof and low-fogging leathers and possible recovery of valuable by-products. However, the disadvantages are that the lipase does not remove all types of fats in the same way that solvents do and the process cost is slightly escalated.⁵ Therefore, it is extremely urgent to seek new degreasing methods which are efficient, environmentally-friendly, energy-saving and clean. Subcritical fluid extraction (SFE), also called pressurized low polarity fluid extraction, is one of the most popular techniques and widely used in the extraction of oil and natural products.⁶⁻⁸ While subcritical extraction was utilized in the lipid extraction industry, it has the advantages of a mild operational temperature which is as low as 30°C-45°C, products extracted free from solvent residues, relatively lower operation pressure, lower operating cost and lower equipment investment, shorter extraction time, environmental compatibility, good selectivity, one step from the extraction to the separation and avoidance of residual solvents compared with supercritical extraction.^{9,10} SFE is rapidly emerging as a powerful means of extraction of solid samples, especially seed oil. It can be considered a technological revolution in the extraction industry.¹¹ In addition, when degreasing of sheep skin for fur-making following the soaking procedure, the rehydrated sheepskin is vulnerable and its denaturation temperature is 60°C,¹ the temperature of degreasing should be controlled lower than the denaturation temperature. So, it is possible to apply subcritical fluid extraction system to sheep skin degreasing under a mild temperature as low as 35°C-45°C. Till now, the application of subcritical solvents in fur processing for degreasing has not been reported. Different subcritical fluids have been used in SFE, such as CO₂,¹² n-butane,¹³ n-propane¹⁴ and n-hexane.¹⁵ Among them, n-pentane is used as the subcritical fluid mainly because it needs lower critical pressures and temperatures and it has excellent dissolving power for lipophilic compound. Also, this extractant has a low boiling point, is inexpensive, colorless, and a clean solvent that leaves no residue in the product. In summary, subcritical fluid is widely used in oil extraction and has the advantages of environmental protection and no solvent residue. The purpose of degreasing is to remove fat in sheep skin, so subcritical fluid extraction is theoretically an effective method for the degreasing of sheep skin. This study has sought to develop a degreasing method with subcritical n-pentane.

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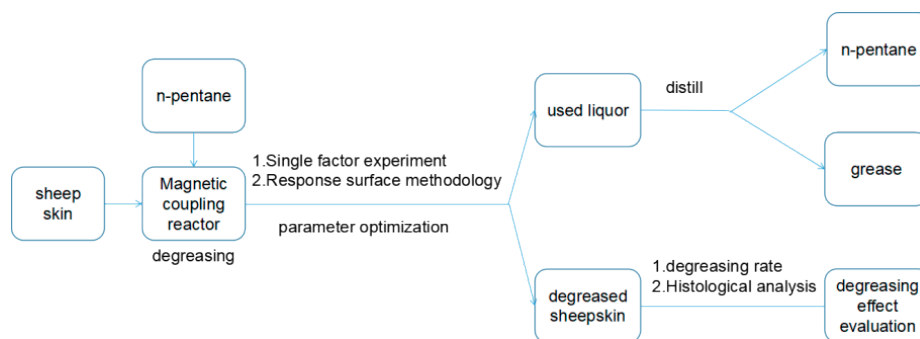


Figure 1. The sheep skin degreasing procedure with subcritical n-pentane.

Experimental

Materials & Instruments

N-Pentane was purchased from Jinshan Chemical Reagent Co., Ltd (Chengdu, China). Sheep skin is native of Chengdu. Magnetic coupling reactor was purchased from Weihai Huixin Chemical Machinery Co., Ltd. LEICA CM1950 freezing microtome and CX41 RF microscopes were purchased from Leica- (Germany).

Experiment Procedure

The subcritical n-pentane degreasing procedure for the sheepskin is illustrated in Figure 1.

Sample Preparation

After the salted fresh sheepskins had been soaked and then fleshed, they were cut into pieces in the size about 4cm ×4cm for degreasing treatment further. 100g pelt samples were weighed for each experiment.

Degreasing with Subcritical n-Pentane Extraction

Subcritical n-pentane extraction degreasing was carried out using a laboratory scale unit named Magnetic coupling reactor. For each

degreasing, prepared skin samples were added into the reactor, and n-pentane was added. The ratios of skin sample to n-pentane varied according to the experimental design described in Table I and Table II. The degreasing was performed at different temperatures, pressures, and times, as shown in Table I and Table II. The factors effecting degreasing were optimized with single factor experiment and response surface methodology (RSM). At the end of degreasing, the subcritical n-pentane containing the lipid was transferred to a separator, the solvent was collected by reduction vaporization, the degreated oil was collected for further study. The degreated skin was collected for the degreasing effect evaluation and thermal stability analysis.

Single Factor Experiment Design of Subcritical n-Pentane Degreasing Process

The main factors affecting the degreasing effect of subcritical n-pentane include treatment temperature, time, pressure and solid-liquid ratio. In order to study the influence of these technological parameters on the degreasing effect, this study was conducted according to the single-factor experimental design (Table I and Table II).

Table II shows the variation range of factor A, B, C and D.

Table I
Single factor experiment scheme

Experimental scheme	Reaction time /min	Degreasing temperature /°C	Degreasing pressure /MPa	Solid-liquid ratio /(g/ml)
1	A	39.5	0.5	1:7
2	60	B	0.5	1:7
3	60	40.5	C	1:7
4	60	40.5	0.4	D

Table II
Factor table for single factor experiment

Experimental factor	A: Reaction time /min	B: Degreasing temperature /°C	C: Degreasing pressure /MPa	D: Solid-liquid ratio /(g/ml)
Variable range	30	38.5	0.2	1:3
	40	39.5	0.3	1:5
	50	40.5	0.4	1:7
	60	41.5	0.5	1:9
	70	42.5	0.6	1:11

Table III

Response surface experiment level and coding

Level NO.	Factors		
	Degreasing time X_1/min	Degreasing temperature $X_2/^\circ\text{C}$	Degreasing pressure X_3/MPa
-1	50	39.5	0.3
0	60	40.5	0.4
+1	70	41.5	0.5

Optimization Design of Subcritical n-Pentane

Degreasing Process by RSM

The single factor experiment found that the degreasing temperature, degreasing time and degreasing pressure have significant influence on the degreasing effect. The process was optimized according to Box-Behnken design.¹⁶ The designed response surface experimental scheme was shown in the Table III.

The second-order polynomial equation¹⁷ was used to establish a predictive model of the degreasing ratio:

$$Y = \beta_0 + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} X_i X_j$$

where Y represents the degreasing ratio; β_0 , β_i , β_{ii} and β_{ij} are the constant term, linear term, quadratic term and interaction term coefficients of the fitting formula respectively; X_i and X_j represent the coded values of each factor level, namely, reaction temperature, time and pressure.

Characterization of Degreasing Effect

Degreasing Rate

The oil content in the sheep skin before and after being degreased was determined by Soxhlet extraction and the test process was carried out in accordance with the ISO 4048:2018 (Determination of matter soluble in dichloromethane and free fatty acid content).¹⁸

The degreasing rate was calculated by the following formula:

$$Y = \frac{X_0 - X_1}{X_0} \times 100\%$$

Where Y is degreasing rate, X_0 and X_1 respectively represents the oil content of sheepskin determined before and after degreasing.

Histological Analysis of Degreased Skin

In order to characterize the degreasing effect, the sheepskins before and after being degreased were treated with the section and stain method described in the published paper¹⁹ then observed with bio-optical microscope.

Results & Discussion

Effect of Degreasing

The results of single factor experiments show that degreasing pressure, degreasing time and degreasing temperature have significant influence on the degreasing effect of subcritical n-pentane. The optimal degreasing temperature is 40.5°C, degreasing time 60 min and degreasing pressure 0.40 MPa. The effect of the ratio of solid to liquid on the degreasing effect is not obvious which results about 0.8% difference of degreasing rate.

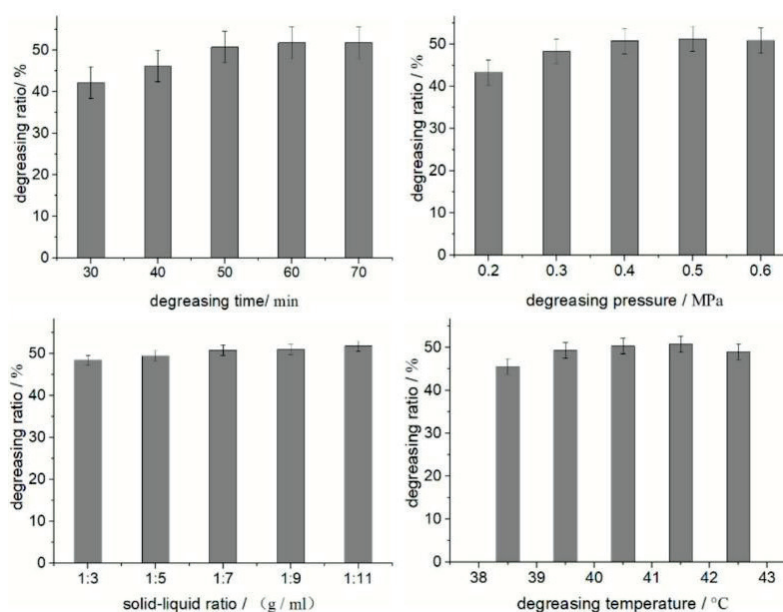


Figure 2. Single factor results

Table IV

Experimental scheme of response surface methodology and response value of degreasing rate

Level NO.	Independent variable factor			Y degreasing rate (%)	
	Time X_1 (min)	Temperature X_2 (°C)	Pressure X_3 (MPa)	Experimental value	Predicted value
1	-1	1	0	52.8075	52.28
2	0	-1	-1	51.5114	51.28
3	1	-1	0	49.9567	50.49
4	1	1	0	52.3995	52.08
5	1	0	1	49.9050	49.99
6	0	0	0	52.0733	51.81
7	0	1	-1	49.7490	50.36
8	-1	-1	0	50.8181	51.14
9	0	-1	1	50.2329	49.62
10	0	0	0	51.7019	51.81
11	0	0	0	51.8267	51.81
12	0	0	0	51.8075	51.81
13	0	0	0	51.6568	51.81
14	-1	0	1	50.6343	50.93
15	-1	0	-1	49.8857	49.80
16	1	0	-1	50.1800	49.88
17	0	1	1	53.0314	53.26

Optimization of Subcritical N-Pentane Degreasing Process by RSM

Multiple regression analysis is performed on the experimental data in Table IV to obtain the fitting regression equation:

$$Y = 51.81 - 0.21X_1 + 0.68X_2 + 0.31X_3 + 0.11X_1X_2 - 0.26X_1X_3 + 1.14X_2X_3 - 0.65X_1^2 + 0.33X_2^2 - 1.01X_3^2$$

Where Y represents defatted ratio: X_1 , X_2 and X_3 is degreasing temperature, degreasing time and degreasing pressure respectively.

Table V

Analysis of variance of regression model of subcritical n-pentane degreasing rate

Source of variance	Coefficient	Sum of squares	Df	Mean square	F value	Prob>F
Model		17.03	9	1.89	6.88	0.0094
X_1 - time	-0.21	0.36	1	0.36	1.32	0.2884
X_2 - temperature	0.68	3.74	1	3.74	13.58	0.0078
X_3 - pressure	0.31	0.77	1	0.77	2.79	0.1389
X_1X_2	0.11	0.051	1	0.051	0.19	0.6786
X_1X_3	-0.26	0.26	1	0.26	0.95	0.3617
X_2X_3	1.14	5.20	1	5.20	18.90	0.0034
X_1^2	-0.65	1.77	1	1.77	6.44	0.0388
X_2^2	0.33	0.46	1	0.46	1.68	0.2364
X_3^2	-1.01	4.32	1	4.32	15.71	0.0054
Residual		1.93	7	0.28		
Lack of fit		1.82	3	0.61	23.19	0.0054
Pure error		0.10	4	0.026		
Correlation total		18.95	16			
R-Square	0.8984					
C.V.%	1.02					

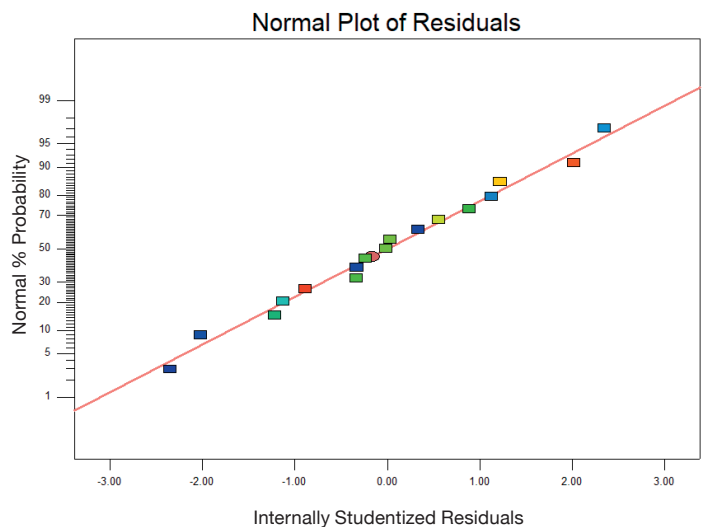


Figure 3. Residuals

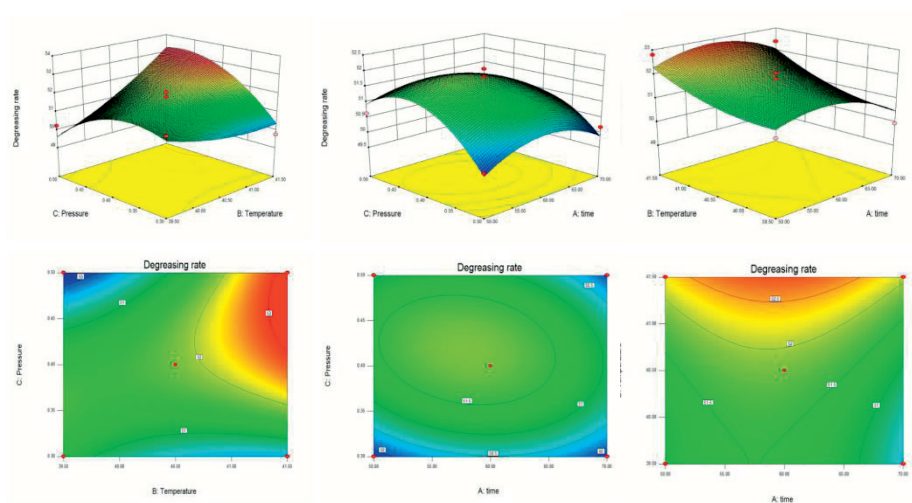


Figure 4. Response surface graph and contour map

From the variance data, it can be seen that the regression model equation $F=6.88$ for the subcritical n-pentane degreasing rate, $\text{Prob} > F < 0.05$, the residual distribution probability is roughly in a straight line, indicating that the fitting model has high fitting accuracy and good fitness. The determination coefficient (R^2) of this model is 0.8984, very close to 1, and the coefficient of variation (C.V.) is $1.02\% < 5\%$, indicating that the better the correlation between the experimental value and the predicted value,²⁰ the response surface equation model is used for subsequent process optimization. The F value of X_2 , the primary term of degreasing temperature, is 13.58; the F value of X_3^2 , the secondary term of degreasing pressure, is 15.71; and $\text{Prob} > F < 0.01$, indicating that degreasing temperature and degreasing pressure have a significant impact on the degreasing effect of subcritical n-pentane.²¹

The interaction between degreasing time and pressure has a significant effect on the degreasing efficiency of subcritical n-pentane. The design-expert 10 software (made by Stat-Ease Inc. which is located in Minneapolis, USA) is used for calculation and analysis, and the optimal process parameters are obtained as follows: degreasing

time 58 min, degreasing temperature 41°C , degreasing pressure 0.45MPa . The degreasing rate of subcritical n-pentane under this process condition is $51.46 \pm 1.90\%$. Therefore, the response surface model has a good fitting degree and the optimized parameters for the subcritical degreasing process are reliable.

The Effect of Degreasing Temperature and Pressure on the Grease left in the Subcritical N-Pentane Degreased Skin

Figure 5 shows histological micrographs of blank specimens and degreased skins treated with n-pentane at different temperatures. Similarly, the reddish brown particles are lipid droplets and the pink structures are fibrous tissue such as fibrin. The histological sections in Figure 5-a shows a slight decrease in granular lipid droplets in the two groups compared with the blank histological sections, and only a small part of the lipid glands became empty. When the degreasing temperature rises to 40.5°C and 42.5°C , more lipid glands become empty in the histological sections of the skin, and the lipid droplets in the lipid glands become less. Therefore, when the degreasing temperature of subcritical n-pentane rises above 40.5°C , the lipid droplets around the hair follicles decrease significantly.

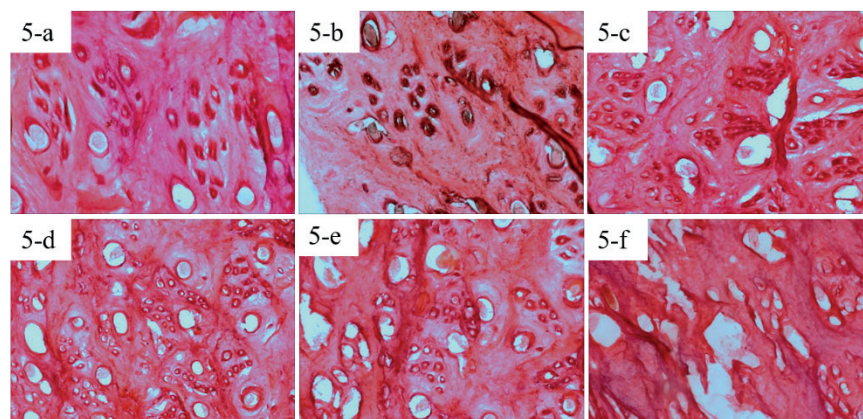


Figure 5. Histological photomicrographs of degreased skin under different temperature (a, b, c, d, e, and f indicate blank samples and degreasing temperatures of 38.5° , 39.5° , 40.5° , 41.5° , and 42.5°C , respectively)

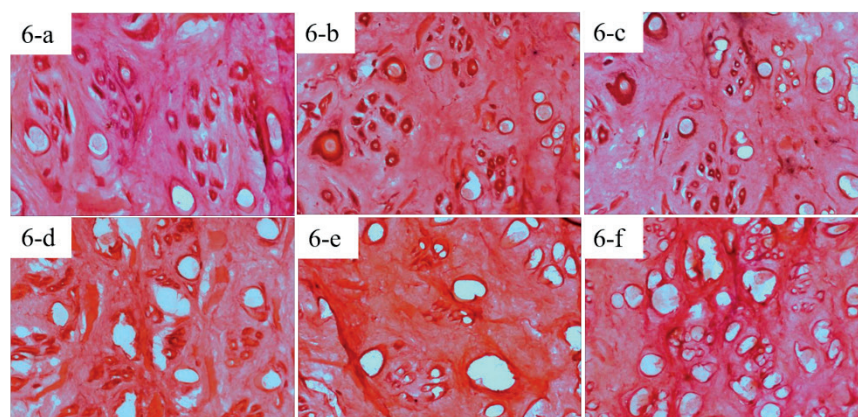


Figure 6. Histological photomicrographs of degreasing skin under different pressure (a, b, c, d, e, and f indicate blank samples and degreasing pressures of 0.2, 0.3, 0.4, 0.5, and 0.6 MPa, respectively)

Figure 6 shows histological micrographs of blank specimens and degreased sheep skin treated with n-pentane at different pressures. Reddish brown granular material is stained lipid cells, and fibrous tissue structures such as collagen fibers are stained red or pink. As can be seen from the blank histological sections shown in Figure 6, there are many groups of granular lipid droplets around the hair follicles in the skin before being degreased. When the degreasing pressure is 0.2MPa and 0.3MPa, after subcritical n-pentane treatment, the granular lipid droplets in the skin showed a slight decrease. From the histological section diagrams of 0.4, 0.5 and 0.6MPa, it can be seen that the gradual increase of the degreasing pressure, the granular lipid droplets in the degreased skin showed a significant decrease. It indicates that when the degreasing pressure rises above 0.4MPa, the degreasing effect of subcritical n-pentane extraction is very significant.

Conclusion

A degreasing method using subcritical n-pentane extraction has been developed. The optimized degreasing parameters were obtained as follows: time 58 min, temperature 41°C, pressure 0.45 MPa according to single factor experiment and response surface methodology. The degreasing rate was 52.46% theoretically and 51.46% experimentally under the optimal degreasing parameters. Histological micrographs showed that the lipid droplets around the hair follicle were significantly reduced in the degreased sheep skin. The result indicated that degreasing of sheep skin with subcritical n-pentane is efficiency, and the operation condition is mild.

Acknowledgement

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Thermal Characterization and Pyrolysis of Waste Leather Treated with CoCl_2 And MnCl_2

by

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Abstract

Leather tanned with different agents was pyrolyzed in the presence of CoCl_2 and MnCl_2 catalysts. A bovine leather sample tanned with two inorganic tanning agents (chromium and titanium salts) and two organic tanning agents (glutaraldehyde and methylacrylic resin) has been used in this study. The samples were soaked in solutions of CoCl_2 or MnCl_2 of known concentration. The influence on decomposition temperature and the resultant pyrolysis compounds has been evaluated by using thermogravimetric analysis (TG/DTG) and flash pyrolysis (Py-GC/MS). A multivariate analysis has been applied to the pyrolysis products obtained confirming the effect of the catalyst treatment on leather, specifically on samples tanned with organic agents. According to the results, CoCl_2 (higher Lewis acidity) shows a greater influence than the MnCl_2 (lower Lewis acidity). The results indicate that the presence of chlorides affects the nature of the pyrolysis products, increasing the yield of the aromatic compounds in all the samples, thus improving the added-value of the volatiles. These catalysts reduced slightly the decomposition temperature.

Introduction

Nowadays waste valorization is of great interest due to the environmental problems derived from waste disposal. Many landfills around the world are reaching their maximum waste level because of the large volume of disposed waste. On average, 427 kg of waste are landfilled in the EU-27 per inhabitant per year.¹ While there is an obvious need to minimize the generation of wastes; improvement in technologies for valorizing them will play an important role in mitigating the environmental problems in addition to increasing the economic benefit in the case of industrial wastes. Turning industrial waste into a resource is one key to drive the economy towards a more circular model.

One of the industrial wastes that have been proven to be suitable for waste valorization is leather. Tanning processes generate significant volumes of by-products that can be treated and valorized in many cases.^{2,3} One way for the recovery of leather waste is pyrolysis

treatment. Pyrolysis of leather wastes has been discussed in the literature, although it has not been studied in depth. Early studies found in this area were made in 1982 by Muralidhara et al.⁴ Later, Caballero et al.,⁵ Yilmaz et al.,⁶ and Oliveira et al.⁷ studied different aspects of leather pyrolysis such as thermal decomposition kinetics, pyrolysis in fixed bed reactor and production of activated coal, respectively.

Later, our research group carried out the thermal characterization of leather wastes with different tanning agents,⁸ investigated the suitability of using a sodium hydroxide solution as a modifier for a pyrolytic process,⁹ analyzed the composition of the gases and the liquids obtained in flash and slow pyrolysis of chrome tanned leather waste and the estimation of the calorific values of the different pyrolytic fractions,¹⁰ characterized commercially available leathers in order to obtain information about their composition, characteristics and origin¹¹ and developed a kinetic model for chrome tanned leather untreated and treated with NaOH under different conditions.¹²

More recently, two more references have been found, studying the pyrolysis of chromed tanned leather waste.^{13,14}

The pyrolysis allows the valorization of wastes from an energy point of view or as source of added value products. Catalytic pyrolysis is a similar process but improves the waste valorization by reducing the temperature of the decomposition process or increasing the yield of any interesting product.

The effect of pyrolysis by catalyst salts on the decomposition of different lignocellulosic biomass waste has been widely studied. It is known that transition metal ion chlorides are highly active in pyrolysis of different materials. Some papers can be found in the literature related to the study of the catalytic effect of different chlorides on pyrolysis of biomass type materials such as almond shell,^{15,16} cellulose,^{17,18} lignite,¹⁹ wood^{20,21,22} or algae²³ and polymeric type materials like PVC,²⁴ polyethylene,^{25,26} polycarbonate,²⁷ PUR foam²⁸ or oil-slime.²⁹ But there are no papers published about the catalytic effect of metal chlorides on leather pyrolysis.

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Cobalt(II) and manganese (II) chlorides changed the pyrolysis behavior of almond shells.¹⁵ When the pyrolysis was carried out in a fluidized bed reactor the products obtained also varied in the presence of both catalysts. The results revealed a decrease in the yield of gas phase while the yield of liquid was kept constant. The effect of pre-soaking treatment produced a considerable variation in the composition of the pyrolytic liquid phase, increasing the percentage of furfural and decreasing the percentage of acetic acid. Thermal behavior of almond shell is also modified by CoCl_2 .¹⁶ Most of the processes take place at lower temperature in the presence of CoCl_2 and there is an increase in the evolution of hydrogen, 2-furaldehyde and chloromethane. However, Khelfa et al.¹⁷ showed that impregnation of MnCl_2 had an insignificant impact on lignin pyrolysis.

The catalytic effect of cobalt chloride on lignite pyrolysis has also been studied, together with other metal chlorides.¹⁹ While the results showed no significant variation in the decomposition temperature of lignite, the effect of chloride on the yield of the liquid fraction is a noteworthy aspect. Specifically, in the case of soaking pre-treatment with CoCl_2 the liquid fraction increases 15% to 38% when the lignite is impregnated with 15% of CoCl_2 . Some of the major components of the liquid phase, such as phenolic compounds, aliphatic, aromatic and carboxylic groups, increased by 150%, 83%, 100% and 200% respectively with the soaking treatment.

Wan et al.²⁰ evaluated the effects of different catalysts on product selectivity of microwave-assisted pyrolysis of corn stover and Aspen wood. Cobalt chloride was one of the catalysts studied. They concluded that the catalysts used increased the bio-oil yield, varying also the other fractional yields in different ways, and GC-MS results showed that the use of the catalysts significantly reduces the number of compounds in the bio-oil. Meanwhile, Özbay et al.²¹ studied the catalytic pyrolysis of waste melamine coated chipboard in a fixed-bed reactor at different temperatures in the absence and presence of catalysts. Lewis acids (metal chlorides), bases and basic salts were used as catalysts. They found that the oil produced by Lewis acids contained aldehydes while these compounds could not be observed in the other conditions.

In recent studies, Eibner et al.²² found that anhydrous sugar yields were strongly influenced by the presence of metal salt catalyst in pyrolysis of eucalyptus wood. Seven metals – Ce, Mn, Fe, Co, Ni, Cu and Zn - were selected and impregnated using nitrate salts. Cobalt and manganese were found to inhibit levoglucosan formation while they highly favored the LAC (1-hydroxy-(1R)-3,6-dioxabicyclo[3.2.1]octan-2-one) yield.

Moreover, Chalov et al.²⁹ demonstrated that the highest conversion of oil-slime into gaseous and liquid products was observed in the presence of iron subgroup metal chlorides, especially CoCl_2 . They also studied the influence of a cobalt chloride solution of 5 w % on

the thermal stability of oil-slime by TGA. The results show that the use of cobalt chloride increases the degradation rate, which means that the process is faster at the same temperature settings.

The present paper is focused on studying the influence of cobalt chloride and manganese chloride on the pyrolysis of leather tanned with four different tanning agents with the aim of learning how these catalysts can affect the decomposition of this type of wastes. Catalyst CoCl_2 has been selected because, according to the literature, it is one of the most effective catalysts on lignocellulosic materials. In the case of MnCl_2 , it has been selected because of its lower Lewis acidity than that of CoCl_2 at a constant chloride counter anion. Differences in the catalysts' acidity level are only due to differences in the cations (size and electronegativity). Thermogravimetric analysis and flash pyrolysis of samples in a pyro-probe device were carried out to determine the catalytic effect of these metal chlorides on leather pyrolysis. Afterwards, multivariate statistical analysis techniques were used for the pyrolytic data treatment, allowing us to perform the comparison and analysis of the results in a more objective way.

Materials and Experimental Equipment

Materials

The experiments were carried out on bovine leather tanned with four different tanning agents. Two of them were inorganic tanning agents (chromium (III) and titanium (IV) salts) and the other two were organic tanning agents (glutaraldehyde and methylacrylic polymer). The proximate and ultimate analysis of the original samples can be found elsewhere.⁸

In order to prepare the solutions of the metal chlorides, powdered manganese chloride (MnCl_2) with purity greater than 99% and powdered cobalt chloride (CoCl_2) with purity greater than 98%, both from Sigma-Aldrich, were used. Solutions were prepared just before their use.

Thermobalance

Thermogravimetric analysis was carried out in a TGA/SDTA 851 Mettler-Toledo thermo-balance in a nitrogen atmosphere with a flow rate of 50 ml min^{-1} . The temperature of the sample was measured with an R type thermocouple. The temperature values used were those recorded by the probe of the device, located under the crucible, and not the programmed values.

Pyroprobe connected online with a Gas Chromatograph (Py-GC/MS)

For the flash pyrolysis of the samples, a pyroprobe 5250 device was used. The capillary sample tube was automatically introduced into the center of a platinum resistor, which was heated up in an inert atmosphere. The products generated in pyrolysis were analyzed by using gas chromatograph (HP-6890N) with a capillary column HP-5MS, provided with a mass spectrometry detector (HP-5973 MSD).

Experimental Procedure

Thermobalance

The temperature range selected for the study was 25° to 800°C with a nominal heating rate of 10°C min⁻¹. The amount of sample analyzed was around 7-8 mg, taken as two cylindrical portions of 2 mm diameter. The tanned leathers were approximately 2 mm thick.

All the tests were carried out in duplicate to evaluate the repeatability of the test. It was found to be good as the curves overlapped and the mean absolute difference between duplicates ranged between 0.1 % and 0.9 % of weight loss in TG curves and 0.0001 % s⁻¹ - 0.001 % s⁻¹ in DTG curves

At the start of the study, the equipment was calibrated using indium and aluminum standards; later periodic checks were made to ensure that the equipment remained according to the calibration specifications.

Pyroprobe connected online with a Gas Chromatograph (Py-GC/MS)

The amount of sample pyrolyzed in each experiment was approximately 150 µg, introduced into a quartz capillary tube. The capillary was automatically introduced into the center of a platinum resistor, which was heated in an inert atmosphere. The parameters used in this process were nominal heating rate, 20°C ms⁻¹; pyrolysis time, 20 s; and process temperature of 500°C.

The resultant pyrolysis products were rapidly removed from the reaction zone (quartz capillary surrounded by the resistor) using a flow of helium, through a transfer line at a temperature of 280°C until introduced into the gas chromatograph provided with a

mass spectrometry detector for analysis. The volatile compounds generated were analyzed using an HP-5MS (30-m-long and 0.250 mm internal diameter) capillary column. The conditions used for the analysis were T_{initial} = 37°C, T_{final} = 320°C, heating rate = 12°C min⁻¹, and t_{total} = 33.5 min. The qualitative analysis of the chromatogram obtained was carried out using the mass spectra commercial libraries WILEY275 and NIST02.

Chloride Treatment Process

For the CoCl₂ and MnCl₂ soaking process, a circular test-piece of leather, of 34 mm diameter, was immersed in 10 ml of water-based solution with a known chloride concentration resulting in a ratio of the liquid phase to the solid phase of 8 ml g⁻¹. Concentration of chloride solutions was 5% and a soaking time of 100 min were used.

The leather was dried under controlled temperature and relative humidity conditions for 48 h and stored in a desiccator before use.

Multivariate Analysis

The IBM SPSS 19.0 for Windows software was used in this study for data analysis and evaluation. The principal component analysis (PCA) was applied to analyze the interrelationships among a large number of variables (in our case the selected compounds). A cluster analysis was also performed which allows the grouping of cases or variable of a data file according to the likeness of similarity between them.

Results and Discussion

Thermogravimetric Study

Treated samples were subjected to a thermogravimetric analysis to assess the effect of both chlorides in the decomposition temperature of the samples.

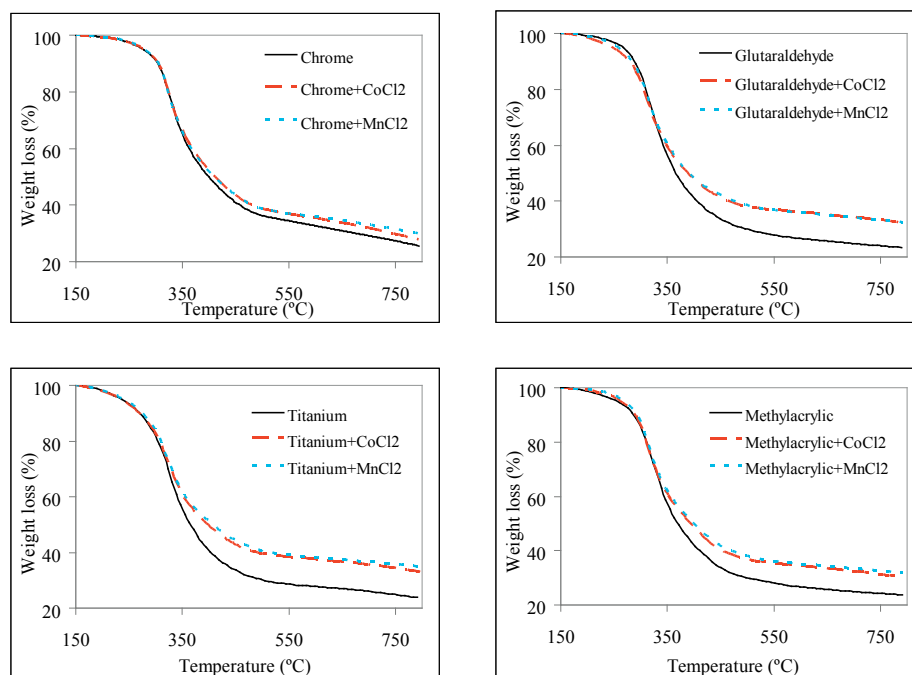


Figure 1. TG curves of treated and untreated samples

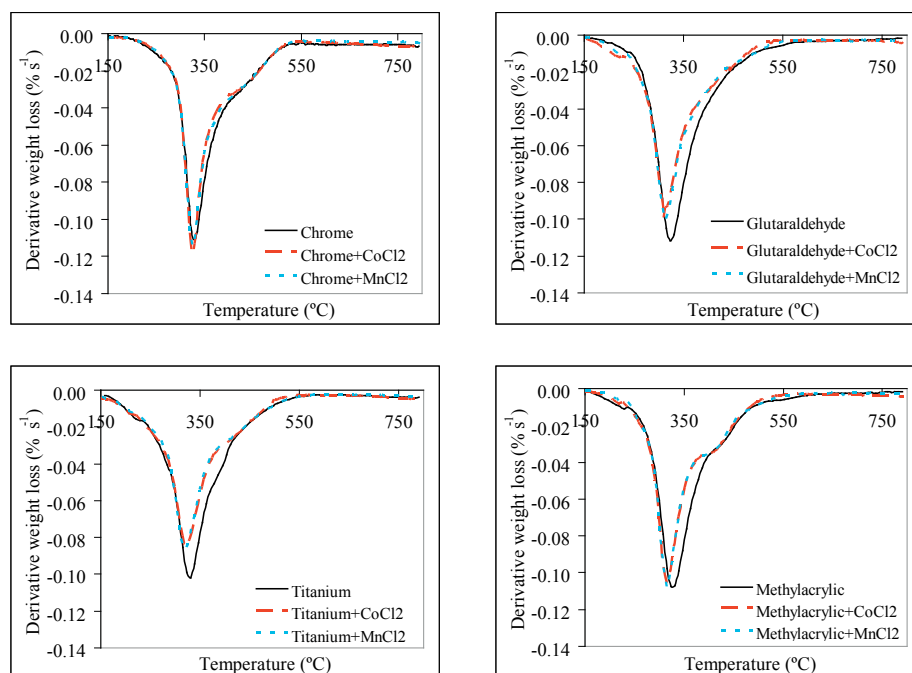


Figure 2. DTG curves of treated and untreated samples

Figures 1 and 2 show the TG and DTG curves, respectively, obtained for each of the four leather samples studied (chrome, glutaraldehyde, titanium and methylacrylic polymer as tanning agents), before and after the chloride soaking treatment process.

In general, graphs show that chloride soaking treatment slightly affects the decomposition pattern of all samples. In TG graphs it can be observed that the treatment influences on the final residue and the main decomposition step of the samples. In all four types of leather, chloride treated samples show greater final residue than original samples. A subsequent determination of the ash content in studied leather samples indicates that the increase in the ash content is similar to the increase of mass percentage due to the respective chloride uptake. Besides, both chlorides show similar variation of the final residue.

The influence on the main decomposition step is more apparent in the DTG graphs where the main peak shifts slightly to lower temperatures

with respect to the curves corresponding to untreated samples. Table I shows the temperature for maximum decomposition rate of the samples. This table shows the average value of duplicated tests.

In all samples, the main decomposition temperature decreases, with a difference in temperature that ranges from about 4°C in the case of chrome tanned leather to 8°C in the case of titanium tanned leather. A decrease in temperature was also reported by Chalov et al.²⁹ by working on thermal decomposition of oil-slime, where the use of cobalt chloride decreased the thermal stability of the sample resulting in the decrease of the temperature of the maximum rate of weight loss, from 465°C to 440°C. A decrease in the thermal decomposition temperature implies a higher energy efficiency of the process. In general, for all four types of leathers, behavior of samples treated with manganese chloride is very similar to the samples treated with cobalt chloride since curves overlap. No significant differences can be observed between results obtained with both chlorides.

Table I

Temperatures for maximum decomposition rate of leather tanned with different tanning agents before and after chloride soaking treatment

Tanning agent	T _{original sample} (°C)	T _{CoCl2 sample} (°C)	ΔT (°C)	T _{MnCl2 sample} (°C)	ΔT (°C)
Chrome	330.7	326.5	-4.2	326.6	-4.1
Glutaraldehyde	320.5	313.6	-6.8	314.1	-6.3
Titanium	326.7	319.4	-7.3	318.7	-8.0
Methylacrylic	323.2	316.5	-6.7	315.9	-7.3

The sample less influenced by the treatment is chrome tanned leather where curves with and without chlorides almost overlapped, the final residue is quite similar, and the temperature of the main decomposition peak only shifts about 4°C. Parallel works of this research group show that chrome is the tanning agent that modifies most the collagen structure, since chromium salts form the more stable bonds with collagen due to their fixation to lateral collagen strands by coordinate covalent bonds, thus, chromium prevents any other agent from varying the thermal decomposition of chrome tanned leather.

Methylacrylic and titanium tanned leathers are the most influenced samples since small shoulder at around 400°C appears better defined after the chloride treatments. Previous studies on thermal decomposition of leather¹¹ indicated that two parallel reactions can

explain the main decomposition peak and the shoulder at around 400°C. The fact that the shoulder is more visible in chloride treated samples can be explained by a higher effect of chlorides in only one of the processes, in this case the main decomposition step, resulting in a higher separation and better definition of both peaks.

Flash pyrolysis in a Py-GC/MS system

Flash pyrolysis of samples generated a great distribution of products. Figure 3 shows details of the pyrogram obtained for each of the samples studied. The abundance of each peak has been normalized by the value of the maximum peak. Significant differences in peak distribution have been marked on the graphs.

Since there was a linear relationship between the total area of the pyrogram and the amount of sample pyrolyzed, all peaks detected

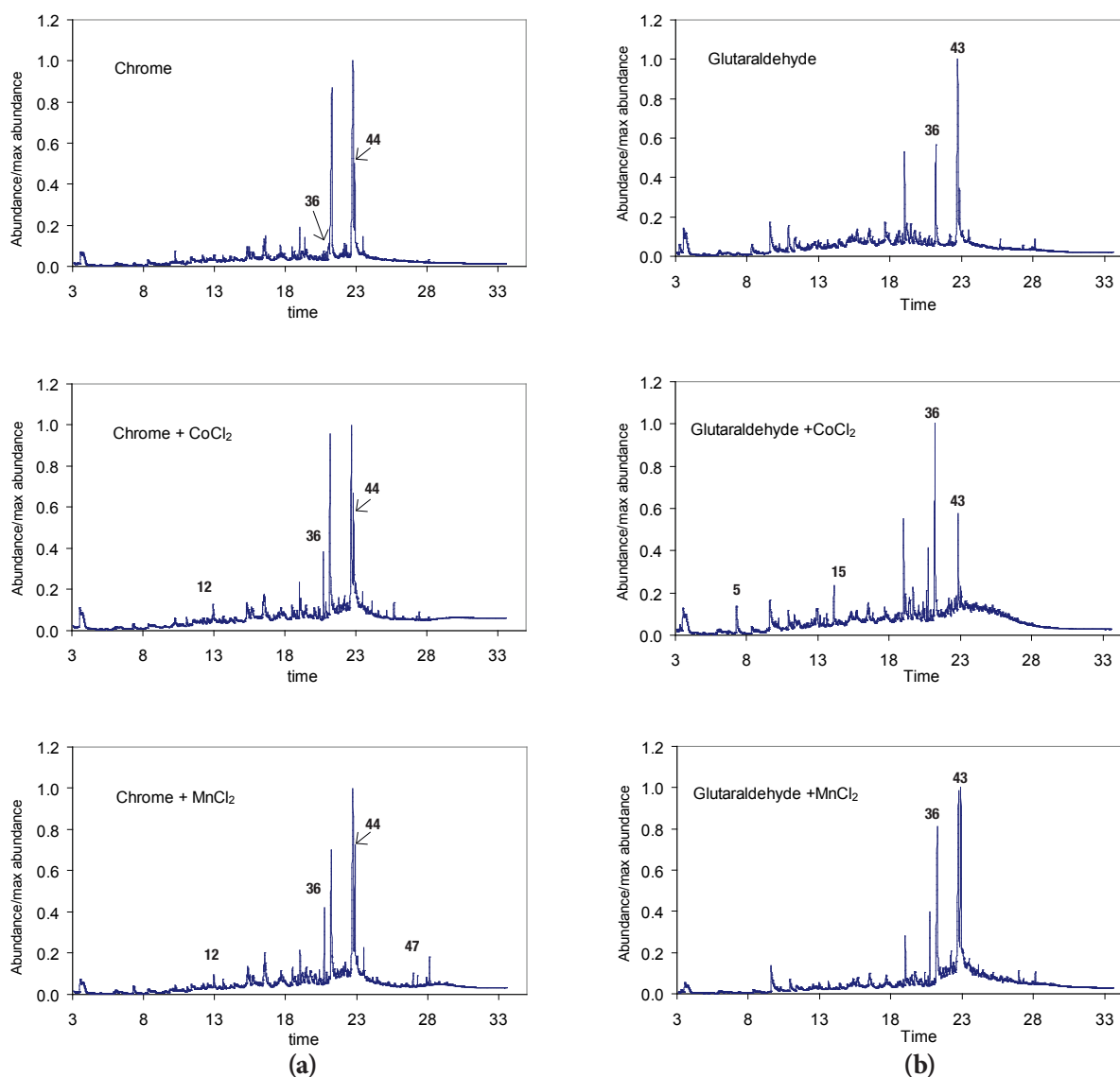


Figure 3. GC-MS chromatograms of tanned samples:
(a) chrome tanned leather, (b) glutaraldehyde tanned leather.

(5) Styrene, (12) 2,5-Pyrrolidinedione-3-methyl, (15) nonanoic acid, (36) Benzene (1-methyldodecyl), (43) 9-octadecenoic, (44) Octadecanoic acid; (47) Cholesta-3,5-diene.

were normalized with regard to the total area of the chromatogram. Similar to the data processing carried out in previous studies,^{8,9} all peaks in each pyrogram were integrated. Chromatographic peaks with a relative area higher than 0.5%, in at least one of the samples, were selected and identified. Tests were done by duplicate and the mean area of duplicates was calculated. The addition of all peaks goes from 84% of the total chromatogram in chrome tanned leather to 60% in methylacrylic tanned leather treated with MnCl_2 . Table II shows the list of compounds identified according to this criterion, together with their area percentage in each sample. The values reported correspond to the average value of the experiments in duplicate. The relative error is around 20%, which is a usual value in this type of experiments. The highest values correspond to the smallest peak areas.

Table II shows the presence of a great number of nitrogen containing compounds, similarly to the results reported previously on pyrolysis of untreated samples and samples treated with sodium hydroxide.⁷ The number of these compounds reaches over one third of the detected compounds which is not usual in other biomass. These compounds are derived from the amide/amine groups of leather collagen. The greater area percentage are observed in long chain acids, like hexadecanoic acid (#40), 9-octadecenoic acid (#43) and octadecanoic acid (#44), probably from the fatliquoring step of leather manufacturing. Phenol (#7) is observed in a high area percentage in samples with organic tanning agents while it is hardly obtained in samples with inorganic tanning agents, as it was observed in previous studies of different types of tanned leather.⁸ It is also noteworthy the identification of a derivative of cholesterol (cholest-3,5diene #47) in some of the samples.

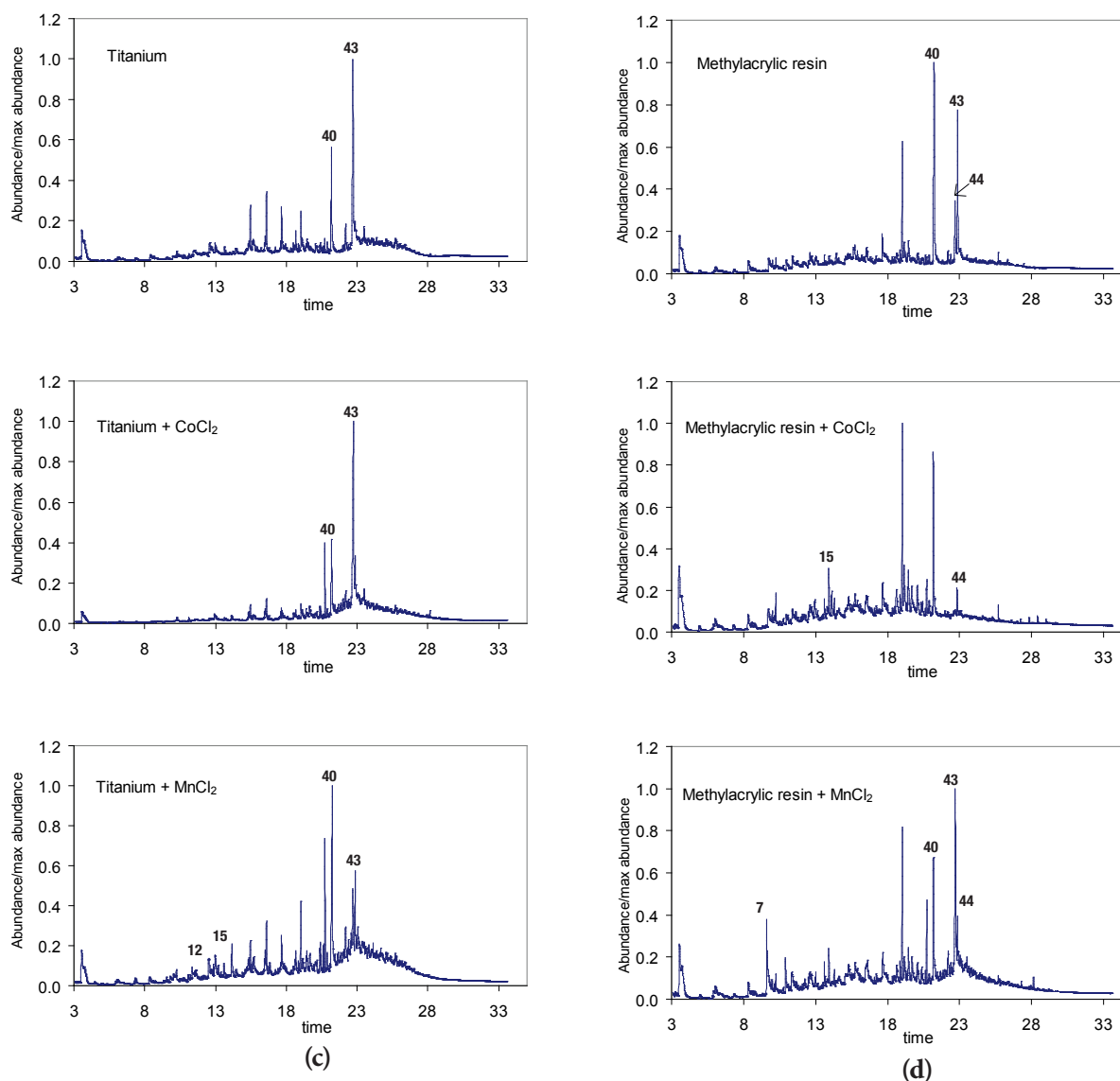


Figure 3 (continued). GC-MS chromatograms of tanned sample:
(c) titanium tanned leather; (d) methylacrylic resin tanned leather.

(12) 2,5-Pyrrolidinedione-3-methyl, (15) nonanoic acid, (40) hexadecanoic acid,
(43) 9-octadecenoic, (44) Octadecanoic acid.

Table II
Area percentage of identified compounds

Peak #	Group #	Name	Match Quality*	Ti	TiCoCl ₂	TiMnCl ₂	Res	ResCoCl ₂	ResMnCl ₂
1	i	Pyridine	b	0.134	0.119	0.783	0.195	0.236	0.185
2	i	1H-Pyrrole	b	3.288	2.584	4.327	4.496	6.799	5.355
3	iii	Toluene	b	4.187	3.520	2.649	5.933	6.880	5.394
4	i	1H-Pyrrole, 3-methyl-	b	0.521	0.487	0.748	0.900	1.483	1.399
5	iii	Styrene	a	0.280	0.299	0.581	0.574	0.486	0.275
6	i	1H-Pyrrole, 2-ethyl-	b	0.616	0.463	0.893	1.484	1.756	1.294
7	ii	Phenol	a	0.136	0.150	0.422	1.865	2.924	6.539
8	i	Pyridine, 2,5-dimethyl-	d	---	---	---	0.469	0.993	0.545
9	ii	Phenol, 2-methyl-	a	---	---	---	0.879	1.486	2.486
10	ii	Phenol, 4-methyl-	a	1.215	0.469	0.648	1.173	0.921	1.496
11	iv	1H-Pyrrole-2-carbonitrile	d	0.327	2.380	2.326	0.979	1.278	0.861
12	vii	Octanoic acid and 2,5-Pyrrolidinedione-3-methyl	b	0.592	0.732	2.923	0.629	1.223	0.259
13	iii	Benzenepropanenitrile	b	0.679	0.447	0.638	0.587	0.922	1.527
14	vi	Cyclopentane, 1,2,3-trimethyl-, (1.alpha.,2.alpha.,3.beta.)-	d	---	---	---	0.694	1.215	1.247
15	v	Nonanoic acid	b	---	0.683	2.783	0.224	1.860	0.238
16	i	Indole/indolizine	b	---	---	---	1.153	0.459	0.243
17	vi	Tetradecene, (E)-	b	0.447	0.715	0.929	---	---	---
18	vi	Tetradecane	a	1.696	0.658	0.956	---	---	---
19	iv	4-Pyridinol, 3-amino-2,6-dimethyl-	d	0.672	0.655	0.840	1.282	0.714	0.734
20	vi	Cyclopentane, decyl-	c	1.142	0.767	0.575	0.843	0.913	0.927
21	vii	Phthalamide (=1-H-isoindole-1.3(2H)-dione)	a	---	---	---	---	---	---
22	vi	Pentadecane	a	2.414	1.155	1.618	---	---	---
23	vii	2-Hydroxy-5-methylcyclohepta-2,4,6-trien-1-one	b	---	---	---	1.630	1.956	1.239
24	vi	Hexadecane	d	2.275	0.897	1.432	---	---	---
25	ii	Acetic acid, phenyl ester	d	0.417	0.548	0.798	0.565	1.724	1.232
26	vi	Heptadecene	a	0.844	0.416	0.733	---	---	---
27	i	6-Methyl-2,2'-bipyridine 1-oxide	d	2.296	3.312	3.979	5.118	8.846	5.217
28		Unknown 1		0.662	1.932	0.814	---	---	---
29	vii	1H-Pyrrolo[1,2-a][1,4]diazepine-1,5(2H)-dione, hexahydro	d	---	---	---	1.595	3.662	1.565
30	v	Tetradecanoic acid	a	0.488	0.869	0.599	---	---	---
31	vii	3-Phenyl-1H-pyrazole-4-carbaldehyde	d	0.626	0.692	1.372	1.273	2.574	1.658
32	vii	1,4-diaza-2,5-dioxobicyclo[4.3.1]nonane	b	0.533	1.839	1.459	0.366	1.593	1.283
33	vii	2-Hydroxy-3,5,5-trimethyl-cyclohex-2-enone	d	0.489	0.576	0.752	0.743	1.742	1.354
34	vi	1-Nonadecene	a	0.665	0.650	1.199	---	---	---
35	iv	Pentadecanenitrile	a	0.456	0.250	0.819	0.412	0.418	0.370
36	iii	Benzene, (1-methyldodecyl)-	c	0.616	3.612	4.562	0.538	1.395	2.428
37	iii	8,9-Dihydro-7H-cyclopenta[1,4]naphthylene	b	0.689	0.724	0.745	0.521	0.424	0.587
38	v	Z-7-Hexadecenoic acid	a	0.288	0.399	0.192	---	---	---
39	vii	3,9-diazatricyclo[7.3.(3,7)]dodecan-2,8-dione	d	3.796	2.819	4.256	2.816	7.958	3.415
40	v	Hexadecanoic acid	a	7.186	6.577	9.932	18.248	---	3.415
41	vi	1-octadecene	b	0.349	0.444	0.275	0.261	0.239	0.158
42	iv	Oleanitrile	a	2.585	2.597	2.941	0.714	0.216	1.565
43	v	9-Octadecenoic acid (Z)-	a	27.937	23.329	4.487	7.213	0.195	1.538
44	v	Octadecanoic acid	a	2.770	2.882	3.536	1.649	1.239	1.375
45	iv	Hexadecanamide	d	0.212	0.269	0.566	0.391	0.164	0.198
46	vi	Dodecane, 1-cyclopentyl-4-(3-cyclopentylpropyl)-	d	0.589	0.613	0.580	0.143	---	0.218
47	vi	Cholesta-3,5-diene	a	0.158	0.437	---	---	---	0.454
Total area percentage				75	73	71	69	67	60

* Identification quality: (a) ≥ 95 %, (b) 90-94 %, (c) 80-89 %, (d) 50-79 %.

By observing Table II, the significant differences pointed out in pyrograms of Figure 3 among samples untreated and treated with chlorides appear clearly. In all samples, the compounds benzene, (1-methyldodecyl)- (#36) increased significantly its percentage of area with both chloride treatments. In chrome tanned leather also the yield of hexadecanamide (#45) showed a great increase with the treatment the same as cholesta-3,5-diene (#47) with manganese

chloride. In titanium tanned leather it is noticeable the presence of nonanoic acid (#15) in treated samples, even with an area percentage greater than 2 % in samples treated with manganese chloride, while in the original sample it is not detected, and also the 1H-Pyrrole-2-carbonitrile (#11) presents a significant increase in the presence of chlorides. Similarly to titanium tanned leather, glutaraldehyde and methylacrylic tanned leather also show a very high increase in

Table II (continued)
Area percentage of identified compounds

Peak #	Group #	Name	Match Quality*	Cr	CrCoCl ₂	CrMnCl ₂	Glut	GlutCoCl ₂	GlutMnCl ₂
1	i	Pyridine	b	0.176	0.136	0.162	1.876	0.632	0.359
2	i	1H-Pyrrole	b	2.329	2.270	2.325	3.296	2.786	1.695
3	iii	Toluene	b	3.838	3.415	3.219	4.644	4.669	3.435
4	i	1H-Pyrrole, 3-methyl-	b	0.655	0.534	0.672	0.748	0.545	0.392
5	iii	Styrene	a	0.377	0.549	0.736	0.357	0.714	0.338
6	i	1H-Pyrrole, 2-ethyl-	b	0.862	0.578	0.578	1.377	0.777	0.636
7	ii	Phenol	a	0.150	0.122	0.119	4.729	4.325	4.267
8	i	Pyridine, 2,5-dimethyl-	d	0.883	0.628	0.387	0.594	0.427	0.242
9	ii	Phenol, 2-methyl-	a	---	---	---	2.643	2.295	1.516
10	ii	Phenol, 4-methyl-	a	0.643	0.232	0.311	1.870	0.443	0.717
11	iv	1H-Pyrrole-2-carbonitrile	d	---	---	---	0.245	0.375	0.347
12	vii	Octanoic acid and 2,5-Pyrrolidinedione-3-methyl	b	0.942	1.363	1.364	0.326	2.413	0.343
13	iii	Benzenepropanenitrile	b	0.431	0.475	0.677	0.428	0.680	0.773
14	vi	Cyclopentane, 1,2,3-trimethyl-, (1.alpha.,2.alpha.,3.beta.)-	d	---	---	---	---	---	---
15	v	Nonanoic acid	b	---	---	---	0.172	2.736	0.216
16	i	Indole/indolizine	b	0.267	0.262	0.174	0.383	0.392	0.538
17	vi	Tetradecene, (E)-	b	0.739	1.743	1.352	0.258	0.345	0.267
18	vi	Tetradecane	a	0.245	0.358	0.357	0.118	0.124	0.112
19	iv	4-Pyridinol, 3-amino-2,6-dimethyl-	d	0.790	0.539	0.898	0.961	0.698	0.834
20	vi	Cyclopentane, decyl-	c	0.463	0.547	0.779	0.641	1.815	0.920
21	vii	Phthalamide (=1-H-isoindole-1,3(2H)-dione)	a	1.355	1.148	2.174	0.836	0.512	0.348
22	vi	Pentadecane	a	0.836	0.726	0.635	0.589	0.154	0.293
23	vii	2-Hydroxy-5-methylcyclohepta-2,4,6-trien-1-one	b	---	---	---	1.538	0.939	0.799
24	vi	Hexadecane	d	0.926	0.548	0.572	---	---	---
25	ii	Acetic acid, phenyl ester	d	0.198	0.278	0.473	0.973	0.613	0.423
26	vi	Heptadecene	a	0.455	0.328	0.280	0.353	0.372	0.166
27	i	6-Methyl-2,2'-bipyridine 1-oxide	d	1.987	2.148	2.282	5.949	5.460	3.715
28		Unknown 1	---	---	---	---	---	---	---
29	vii	1H-Pyrrolo[1,2-a][1,4]diazepine-1,5(2H)-dione, hexahydro	d	1.534	1.187	1.213	1.715	2.722	0.753
30	v	Tetradecanoic acid	a	0.725	0.771	0.528	0.245	1.374	0.316
31	vii	3-Phenyl-1H-pyrazole-4-carbaldehyde	d	1.730	1.523	1.181	1.578	1.396	1.618
32	vii	1,4-diaza-2,5-dioxobicyclo[4.3.1]nonane	b	1.124	0.622	2.667	1.622	3.412	2.682
33	vii	2-Hydroxy-3,5,5-trimethyl-cyclohex-2-enone	d	0.976	0.914	0.972	1.798	0.922	0.657
34	vi	1-Nonadecene	a	0.163	0.284	0.252	0.488	0.394	0.284
35	iv	Pentadecanenitrile	a	0.268	0.168	0.219	0.278	1.256	0.430
36	iii	Benzene, (1-methyldodecyl)-	c	0.483	2.888	2.993	0.647	2.842	2.770
37	iii	8,9-Dihydro-7H-cyclopenta[1,2-b]naphthylene	b	0.988	0.816	0.746	0.382	0.546	0.224
38	v	Z-7-Hexadecenoic acid	a	1.388	0.473	0.218	0.129	0.258	0.339
39	vii	3,9-diazatricyclo[7.3.(3,7)]dodecan-2,8-dione	d	6.953	1.664	5.117	4.885	8.452	7.888
40	v	Hexadecanoic acid	a	12.293	7.192	7.874	4.885	8.452	7.888
41	vi	1-octadecene	b	0.516	1.336	0.697	0.595	0.488	1.727
42	iv	Oleanitrile	a	---	0.162	0.276	0.391	0.434	0.574
43	v	9-Octadecenoic acid (Z)-	a	28.467	19.569	19.633	19.875	0.125	17.753
44	v	Octadecanoic acid	a	5.363	7.827	9.267	3.932	5.238	11.372
45	iv	Hexadecanamide	d	0.585	1.567	1.666	0.567	0.777	0.647
46	vi	Dodecane, 1-cyclopentyl-4-(3-cyclopentylpropyl)-	d	0.525	0.833	0.844	0.358	---	0.179
47	vi	Cholesta-3,5-diene	a	0.237	0.646	1.259	0.485	---	0.598
Total area percentage				84	69	78	81	74	82

* Identification quality: (a) $\geq 95\%$, (b) 90-94 %, (c) 80-89 %, (d) 50-79 %.

the percentage of nonanoic acid in the presence of cobalt chloride, going from 0.17 in the original glutaraldehyde sample and 0.22 in the original methylacrylic sample to 2.7 and 1.86 in the respective treated sample. In both samples is also noteworthy the decrease of 9-octadecenoic acid (#43), going from 19.88 in the original glutaraldehyde leather and 7.21 in the methylacrylic leather to 0.13 and 1.20 in the respective samples treated with CoCl₂. Another

significant decrease is also observed in methylacrylic tanned leather in the case of hexadecanoic acid (#40), which is not detectable in the sample treated with CoCl₂.

For an easier analysis of results, the compounds were grouped according to their principal functional group. Table III shows the percentage of identified compounds classified according to their main

Table III
Classification and area percentage of identified compounds

Group #	Group name	Ti	TiCoCl ₂	TiMnCl ₂	Res	ResCoCl ₂	ResMnCl ₂
i	Heterocyclic Aromatic Compounds (HAC)	6.855	6.965	10.729	13.816	20.571	14.239
ii	Phenols	1.769	1.166	1.868	4.482	7.055	11.753
iii	Aromatics	6.451	8.601	9.176	8.154	10.107	10.210
iv	Nitriles, amines and amides	4.252	6.150	7.492	3.779	2.790	3.729
v	Acids	38.668	34.739	21.528	27.333	3.293	6.566
vi	Alkanes and alkenes	10.578	6.752	8.296	1.942	2.368	3.005
vii	Ketones and aldehydes	6.036	6.658	10.763	9.052	20.707	10.774

Group #	Group name	Cr	CrCoCl ₂	CrMnCl ₂	Glut	GlutCoCl ₂	GlutMnCl ₂
i	Heterocyclic Aromatic Compounds (HAC)	7.160	6.555	6.580	14.223	11.019	7.576
ii	Phenols	0.991	0.633	0.903	10.215	7.676	6.924
iii	Aromatics	6.117	8.144	8.371	6.457	9.450	7.540
iv	Nitriles, amines and amides	1.644	2.436	3.060	2.443	3.538	2.831
v	Acids	48.236	35.832	37.520	29.239	18.183	37.883
vi	Alkanes and alkenes	5.104	7.349	7.027	3.886	3.693	4.546
vii	Ketones and aldehydes	14.613	8.419	14.688	14.297	20.767	15.088

functional group. Seven groups were established: (i) heterocyclic aromatic compounds, which includes pyrrole and pyridine; (ii) phenols, which refers to phenol derivatives; (iii) aromatics; (iv) nitriles, amides and amines, including nitrile derivatives; (v) acids; (vi) aliphatics, including alkanes and alkenes; and (vii) ketones and aldehydes.

In Table III it can be observed that the main group in the original samples is the acids, which area percentage decreases with the chloride treatment in almost all the leather samples, only the glutaraldehyde leather treated with MnCl₂ experiments exhibit an increase. This decrease is more pronounced in the methylacrylic sample reaching a decrease of around 35 % of the value in the original sample. This reduction is mainly due to the significant decrease in the amount of 9-octadecenoic acid (#43) commented on previously, although other acids, like nonanoic acid (#15), experiment an increase with the treatment. On the other hand, chloride treatment increases the aromatics area percentage in all leather samples, mainly due to the significant increase in the yield of benzene (1-methyldodecyl)- (#36) and the slight decrease of other aromatics like toluene. The

group formed by heterocyclic aromatic compounds decreases its yield in chrome and glutaraldehyde tanned samples, while the area percentage increases in titanium and methylacrylic samples. The area percentage of phenolic derivatives decreases in the chrome, glutaraldehyde and titanium samples while increases significantly in methylacrylic sample, mainly due to the increase of phenol (#7) in this sample. The group formed by ketones and aldehydes decreases slightly with the CoCl₂ treatment in the chrome sample while it experiences an increase in the other samples, the same as the MnCl₂ treatment. These results in the group of aldehydes are consistent with the ones reported by Özbay et al.²⁰ who concluded that Lewis acids favored the formation of aldehydes.

In order to perform a deeper comparative study among the twelve samples (four original samples and the same ones after the CoCl₂ and MnCl₂ treatments), a multivariate statistical analysis was developed. In this way, the Principal Component Analysis (PCA) and the hierarchical cluster was carried out in such a way that the chromatograms were transformed into a matrix with 24 rows (i.e. including the two replicates of each one of the twelve samples

Table IV
Principal component analysis (PCA). Total variance explained.

Component	Total variance explained								
	Initial eigenvalues ^a			Sum of square loadings extraction			Sum of square loadings rotation		
	Total	% variance	% cumulative	Total	% variance	% cumulative	Total	% variance	% cumulative
1	107.036	65.106	65.106	107.036	65.106	65.106	24.343	14.807	14.807
2	28.354	17.247	82.353	28.354	17.247	82.353	49.670	30.212	45.020
3	10.765	6.548	88.901	10.765	6.548	88.901	56.521	34.380	79.399
4	7.429	4.519	93.420	7.429	4.519	93.420	23.051	14.021	93.420

^a Extraction method: Principal component analysis

studied) and 47 columns (significant compounds identified with a relative area higher than 0.5%, in at least one of the samples). The PCA gave 4 principal components that could account for the 93.4% of the variance which can be interpreted as an acceptable percentage. Table IV shows, in individual and cumulative percentages, the total proportion of explained variance for each factor, for both rotated (Varimax rotation) and non-rotated solutions. Figure 4 represents the dendrogram obtained from the analysis of the hierarchical clusters, which shows the results of a complete comparison among the samples studied.

The dendrogram in Fig. 4 shows that the experiments are reproducible (first cluster on the dendrogram). In general, organic tanning shows better reproducibility than inorganic tanning. The last cluster is formed by the addition of two main groups, the first upper half of the diagram is comprised by all samples with organic tanning (glutaraldehyde and methylacrylic) original and chloride treated samples, and the lower half is comprised by the samples with inorganic tanning (Ti, Cr), original and chloride treated. This classification is consistent with the results reported by Marcilla et al.⁸ where in a third level of the hierarchical cluster, mineral tannings were grouped as well as the organic tannings. This observation can indicate that the treatment is not so strong to mask the inherent characteristics of leather due to type of tanning, contrary to what happened with an alkaline treatment with NaOH reported by Marcilla et al.⁹ where the alkaline treatment made the pyrolysis products of all treated samples more similar between them than those of the corresponding untreated samples.

Within the group of the inorganic tanning, certain symmetry is observed in the behavior of both chrome and titanium tanned

samples. In these leathers, chloride treated samples are grouped first in a second level, and then they are grouped with their respective sample without any treatment in a third level. This observation indicates that chlorides have some influence on leather and it is similar for both cobalt and manganese chloride. The last level of this group is formed by the addition of all chrome tanned samples with all titanium tanned samples. Relating these results with those observed in Table II, it can be seen that chloride treated samples have similar area percentage of identified compounds for both chlorides, but they differ from the original leather in benzene, (1-methyldodecyl)- (#36), 7-hexadecenoic acid (#38), 9-octadecenoic acid (#43) and hexadecanamide (#45) for chrome tanned samples, and nonanoic acid (#15), 6-methyl-2,2'-bipyridine 1-oxide (#27), 1,4 diaza-2,5-dioxobicyclo [4.3]nonane (#32) and benzene, (1-methyldodecyl)- for titanium tanned samples, what justifies such clustering.

This symmetry in behavior is not observed between samples within the group of the organic tanning. More differences in the order of sample clustering are shown in dendrogram. In relation to glutaraldehyde samples, untreated leather and leather treated with MnCl₂ are grouped first in a second level, unlike inorganic tanned samples. In methylacrylic samples, the second level is formed by the group of leather treated with both chlorides, but then, untreated methylacrylic sample is added to the previous glutaraldehyde group, instead of being added to its respective group of treated samples as it is observed in inorganic tanned samples. The last addition in the cluster is the glutaraldehyde sample treated with CoCl₂, which appears quite far away from the sample treated with MnCl₂ and the sample without treatment. This clustering order can be explained by a higher influence of the chloride treatment in the organic tanned samples, especially in the case of the glutaraldehyde sample treated with CoCl₂.

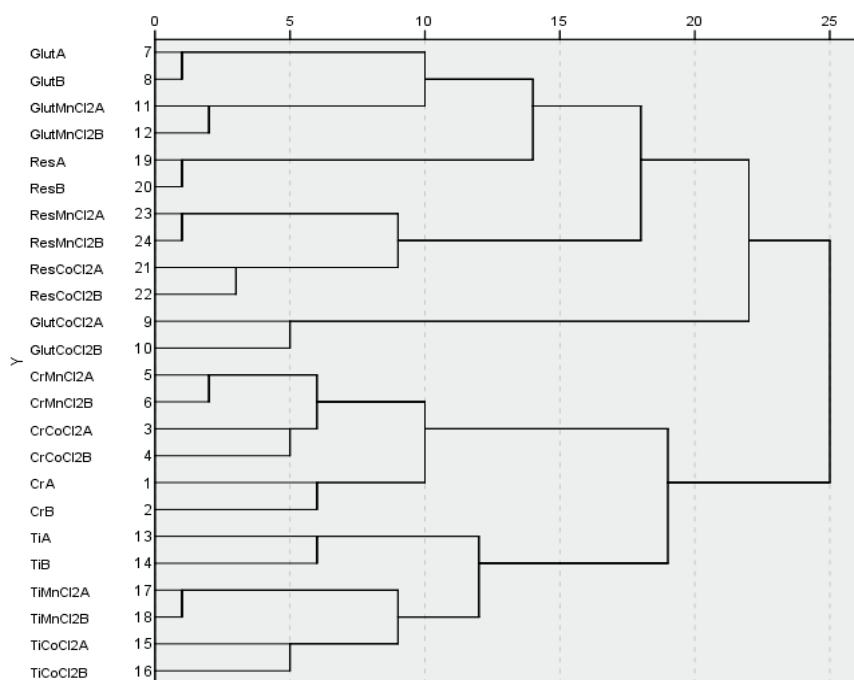


Figure 4. Dendrogram obtained from the analysis of the hierarchical clusters

By relating the results observed in dendrogram of Figure 4 with the compounds of Table II, we have pointed out previously that glutaraldehyde sample treated with CoCl_2 shows a significant increase in the amount of nonanoic acid (#15) and a significant decrease in the amount acid 9-octadecenoic (#43) in relation with the amount obtained in the original glutaraldehyde sample and the sample treated with MnCl_2 . It can also be observed that five compounds (peaks #15, 27, 29, 31 and 39) show different behavior in methylacrylic leather treated with CoCl_2 with respect to the untreated leather and the leather treated with MnCl_2 , which would explain the clustering order of this sample in dendrogram.

Conclusions

Pyrolysis technology does not reduce the amount of waste generated in a process but allows its disposal and valorization by converting it into a source of energy or added-value products. The study of the catalytic pyrolysis is interesting since the presence of a catalyst can improve the benefits of the pyrolysis by reducing the process temperature and/or increasing the yield of certain interesting products.

In this paper, the catalytic effect of CoCl_2 and MnCl_2 on the pyrolysis of different tanned leather samples has been studied. The results indicate that these salts clearly influenced the nature of the products obtained and slightly modified the operating temperature. Thus, the thermogravimetric study shows a slight decrease in the temperature of maximum decomposition rate, ranging from 4°C to 8°C. Chrome tanned leather was less affected by the catalysts' soaking treatment because chrome has already modified most of the thermal behavior of collagen.

The study of volatile products obtained after flash pyrolysis shows that the influence level of the chlorides on the products obtained depends on the tanning agent in the sample. It was found that the percentage of acid compounds detected decreased with the chloride treatment, with a particular marked decrease of 9-octadecenoic acid. On the contrary, the percentage of aromatics (important products in the chemical industry) increased in all samples after the chloride treatment, with specially marked increases for benzene (1-methyldodecyl)-. The methylacrylic tanned leather gave a significant increase in phenol yield (essential for production of many polymers and chemical products) with the chloride treatment. This behavior was not observed with other leather samples. Finally, the group formed by ketones and aldehydes (remarkable products in chemical industry) also increased in all samples, except for the chrome sample treated with CoCl_2 .

A multivariate statistical analysis confirmed that the inorganic tanning agents (chromium and titanium salts) produced such significant modifications to the leather structure that prevented/minimized posterior alterations, being less sensitive to the chloride treatment than the organic agents (glutaraldehyde and methylacrylic polymer).

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Biodegradability Study of Footwear Soling Materials in Simulated Compost Environment

by

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Abstract

Aim of the present study is to investigate the biodegradability and decomposing properties of footwear soling materials by standard biodegradability test method. Biodegradability tests were performed by aerobic exposure of the selected six soling materials to the soil matrix and measuring the degradation and decomposition occurred with time. All soling materials were characterized for physical and physicochemical properties such as weight loss, hardness, density, tensile strength, abrasion resistance, thermal and morphological properties before and after exposing to the simulated compost environment. In the present study, the end-of-life nature of footwear soling materials currently used by the footwear industries are explored, which will further emphasize the importance of development and use of biodegradable materials in the footwear manufacturing.

Introduction

The global environment is increasingly deteriorating as a result of the socio-economic activities. Recently protection of the environment has become a global issue. Environmental sustainability refers to the synchronised conquest of environmental, social, and economic balance. Leather product industry occupied a prominent position in the world's economy but also it is accountable for the respective environmental consequences.¹⁻³

The global market value of leather goods was worth approximately 239.78 billion U.S. dollars⁴ whereas the global leather footwear market size was valued at USD 166.53 billion in 2018 and is expected to grow with a CAGR of 2.8% from 2019 to 2025.⁵ Depending upon the fashion forecast the utilization of number of pairs of footwear per person in every country is increasing nowadays. Being an essential commodity in today's world, worldwide footwear consumption had reached 24.2 billion pairs in 2018, raised by 2.7% over 2017 and this figure continues to rise.⁶ Now India is the second largest producer of footwear globally accounting for 13% of global footwear production of 16 billion pairs.⁷ India produces 2065 million pairs of

different categories of footwear which includes leather footwear of 909 million pairs, leather shoe uppers of 100 million pairs and non-leather footwear of 1056 million pairs.⁸

Undoubtedly, synthetic polymer materials play very important roles in our daily lives. Synthetic polymeric materials in footwear are increasingly replacing the natural ones. For example, polymeric materials such as polyurethane (PU), ethylene vinyl acetate (EVA), thermoplastic rubber (TPR), and thermoplastic polyurethane (TPU) are slowly replacing the natural materials, leather and natural rubber (NR), as shoe sole materials.⁹ Although extensive research has been performed on biodegradable plastics, the critical processing methods and high cost limited their application in many industries including footwear industry.¹⁰⁻¹³ Irrespective of the material used for making footwear, shoes are simply thrown away to the open environment without knowing the adverse effect they may cause in future. This creates an enormous amount of post-consumer shoe wastes that is currently being disposed in landfill sites around the universe that creates soil and water contamination. This may lead to various health issues in future. So, research and development on preparing biodegradable materials suitable for footwear application have become emergent need of the society.¹⁴ It is well known that leather is degradable.¹⁵⁻¹⁷ However, Pantazi et. al. found that the biodegradation capacity of vegetable-tanned leather is higher than the chrome-tanned leather while that of synthetic leather is very low as required by EN ISO 13432:2002.¹⁸ So in the present study, leather has been chosen to identify the leather shoe soles end-of-behavior in the specific compost environment and also as one of the control biodegradable material to compare with the plastics. The aim of the present study is to investigate the biodegradability and decomposing properties of different types of present day footwear soling materials by standard biodegradability test (soil burial) method (ASTM D5998) while exposing the sample materials to simulated compost environment.¹⁹ The physico-chemical and mechanical properties of these footwear materials are analyzed before and after exposure to the simulated compost environment. Properties such as weight loss, hardness, density, tensile strength and abrasion resistance are studied. Characterizations such as infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), differential scanning

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calorimetry (DSC) and scanning electron microscopy (SEM) are performed. The results of this study will add knowledge about the polymeric materials that are used currently in footwear making and help to minimize the adverse effect to the environment by making necessary changes in the footwear manufacturing.

Materials

Total six different types of footwear soling materials such as vegetable tanned leather (LA), natural rubber (NR), ethylene vinyl acetate (EVA), polyurethane (PU), thermoplastic rubber (TPR) and thermoplastic polyurethane (TPU) were chosen and collected from the domestic market. Roughing process was done for all soling materials by using surface roughing machine to expose the basic soling material and also to maintain the uniform surface. By using clicking machine and standard dies, samples were cut into two different shapes (rectangular and dumbbell). Each sample specimen was marked with specimen number and sample code. Before conducting the biodegradability test, the samples were conditioned in the laboratory climatic conditions as per the ISO 2419 standard (temperature: $20^{\circ} \pm 2^{\circ}\text{C}$ and relative humidity: $65\% \pm 5\%$), for a period of 48 hours.

Compost Composition

The composition of the compost (dry weight) (Figure 1) per 5000 g was 2040g of cow dung, 570g of sawdust, 790g of newspaper and computer paper, 100g of white bread, 390g of shredded leaves, 960g of food waste (dry milk, potato, carrot, onion, pumpkin, tomato and other vegetables), and 150g of urea.²⁰

Methods

Soil is an extremely species-rich source of inoculum for evaluation of the biodegradability of plastics in the environment. The natural and fertile soil was collected from the surface layers of CLRI garden.

A laboratory mixture of equal parts (by weight) of soil samples obtained from at least three diverse locations, an agricultural field, a forest and a pasture or meadow was made. Soil from multiple and diverse locations were collected to maximize the biodiversity. To avoid significant perturbations of the microbial population, soils that have been exposed to pollutants were rejected. Preferably, the soil was used as fresh as from the field to assure active microbial content. The soil was sieved to less than 2-mm particle size, and obvious plant materials, stones, or other inert materials were also removed. The soil was stored in a sealed container at $4^{\circ} \pm 1^{\circ}\text{C}$ for one month. The moisture content of the soil was determined with moisture balance equipment. The compost was prepared by maintaining a particular ratio of component as described earlier. Open pots of 4L volume made up of clay were filled with the mixtures of compost and soil in 1:25 ratio, according to the standard test method ASTM D5998. The moisture content of the mixture was determined by following the equation $[(\text{Weight of fresh solids} - \text{Weight of dry solids} / \text{Weight of fresh solids}) * 100]$ as per the method of APHA-AWWA-WPCF 2540D and G respectively (as described in the method ASTM D5998). The percentage moisture content of compost and soil was $28.4\% \pm 1.5\%$ and $92.2\% \pm 2.1\%$ respectively. The moisture content of the soil mixture was maintained by spraying water at regular time intervals (250 mL/day). The degradation study of the samples was carried out at ambient temperature, between 30° - 40°C . Six empty pots of same specification were used, each for a particular soling material. 25% of the composting pot was filled with the mixture of soil and compost; and the specimens were placed in a cyclic order one after another. The pot was then filled with the mixture of soil and compost covering the sample specimens, until 4 cm down from the edge of the pot, as shown in Figure 2. Each pot containing nine specimens of a particular sample and filled with soil-compost mixture, was buried uncovered under the field in CLRI garden. The samples (three specimens for each sample of soling material) were removed manually from the pot after 30, 60 and 90 days, rinsed thoroughly with distilled water, dried to a constant weight at ambient temperature (30° - 40°C) and subjected to physicochemical,

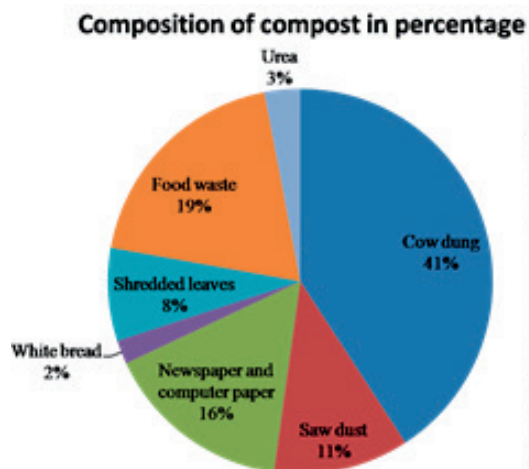


Figure 1. Compost composition and prepared compost.



Figure 2. Step-wise procedure for the placement of samples and filling of the pot with soil - compost mixture (i) clay pot for composting, (ii) 25% filled pot, (iii) placement of sample specimens, and (iv) covering of the sample specimens with soil - compost mixture.

morphological and thermal characterizations. The sole samples before exposure to the simulated compost environment are designated as BD and those after exposure are designated as AD.

Characterization

The weight of the samples were measured using an analytical balance. The weight loss of the samples after exposure to simulated compost environment was measured following the below equation,

$$\% \text{ weight loss} = [(W_b - W_a) / W_b] \times 100$$

where,

W_b = weight of the initial sample before exposure to compost environment, and

W_a = weight of the sample after exposure to compost environment for time t .

All the physical properties were measured by standard SATRA test methods as per the recommendations for shoe soles. Hardness is defined as the resistance of a material against deformation, particularly permanent deformation, indentation or scratching. There are two most common test methods for hardness i.e., Rockwell and Durometer. The hardness numbers derived from any of these tests are numbers without units. The Rockwell is generally used for hard plastics whereas for softer materials, Durometer is used. The Durometer is used to determine the relative hardness of the soft material. The test method is based on the penetration of a specific indenter forced into the material under specific condition. There are two types of Durometer which are commonly used, type A and D, i.e. Shore A and Shore D. The basic difference is according to the shape and dimension of the indenter. Type A is used for soft materials while type D is for relatively harder materials. Hardness is a major characteristic of any outsole, midsole or foam foot bed as it relates with ease of flexing and cushioning effect. The hardness of the sole samples were characterized by Durometer hardness tester (SATRA TM 205). The density of all materials was measured by SATRA TM 134 except leather. In this method, the density or specific gravity

is measured by measuring their volume displacement in water. For solid structured, soling materials most accurate method to determine volume is by adapting Archimedes' principle i.e. the weight in air, weight in water method. This method requires an analytical balance that has facilities for hanging samples above the weighing pan and for supporting a beaker with water above the pan. Density is calculated as follows.

A = weight in air, g

B = weight of sinker in water, g

C = weight of sample + sinker in water, g

D = $(C - B)$ weight in water, g

E = $(A - D)$ volume of water displaced, cc

F = (A/E) density, g / cc

The density of leather and cellular materials was measured using SATRA TM 68. As leather and cellular materials absorb water, it is not recommended for volume displacement method. The dimensions of the test specimen were measured and their volume was calculated. The mass of the specimen was then measured and the average density determined. Three circular test specimens were cut from the sole, patterns were removed and the surfaces were made flat and smooth so as to have an adequate degree of accuracy. Diameter was measured using Vernier calipers and thickness using dial gauge. Density was calculated using the following formula.

For circular specimen,

$$\text{density, g / cc} = M / (3.14 \times r^2 \times h)$$

where,

M = mass of the specimen in g;

h = height or thickness of the circular specimen in cm ;

r = radius of the circular specimen in cm.

The tensile strength was determined using INSTRON model 3369 equipped with 1kN load and the jaws separating speed of 500 mm/min (SATRA TM 137). The sample length and the width between the

clamps were 20 mm and 6 mm respectively. Thickness at the normal position is measured using dial gauge and width using Vernier calipers. System generated value was recorded and average value reported.

$$\text{Tensile strength, Mpa} = F / (T \times W)$$

where

F = force in Newtons.

T = thickness in mm;

W = width in mm.

The abrasion resistance of leather was determined by reciprocating method (SATRA TM 84). All other material's abrasion resistance was determined by rotating drum method (SATRA TM 174). A moving carriage is fitted to the equipment to hold the test specimen applying a force of 10N over the test specimen. It has a mechanism of automatically lifting the holder after 84 revolutions or 40 meters, so that the test specimen is prevented from contact with the abradant. The specimen was abraded along the length of a cylinder so that it traverses a helical contact path with the abrasive. The mass loss of the test specimen and its density were measured and volume loss calculated.

$$\text{Relative volume loss, mm}^3 = 200 \times T_n / \text{Density} \times 0.5 \times (C_n + C_{n+1})$$

where

T_n = mass loss of the test specimen,

C_n & C_{n+1} are two successive mass loss of the standard rubber piece.

The attenuated total reflectance-infrared spectroscopy (ATR-FTIR) data was collected using JASCO FTIR-4200 by non-destructive technique to measure the wavenumber dependent transmission of sample between the range of 4000–600 cm^{-1} at 25°C with a resolution of 4 cm^{-1} and 32 scans. The background spectra were collected for the air and subtracted from the sample spectra. Thermal analysis was carried out using TA Instruments Q200 Differential Scanning Calorimeter (DSC), USA in the temperature range from -70°C to

300°C at a heating rate of 10 °C/min under nitrogen atmosphere. Prior to the measurement, the sample was sealed in aluminum pan before cooling to -70°C and equilibrated at that temperature before heating up to 300°C. The system generated graph is used to analyze the thermal characteristics of the materials tested. Thermo Gravimetric Analysis (TGA) was carried out by using TA Q50 in the temperature range from room temperature to 800°C at a heating rate of 20°C/min under nitrogen atmosphere. The system generated graph was then used for analysis. To study the morphological characteristics of samples before and after the biodegradability test, samples were scanned in FEI-Quanta 200 scanning electron microscope (SEM). The SEM instrument was operated at 5kV. Prior to scanning, the samples were sputter coated with a thin layer of gold. An incident electron beam is raster-scanned across the sample's surface, and the scattered electrons from the sample are gathered to collect an image of the surface. The electrons interact with the atoms that contain the sample producing signals that reveal information about the sample's topography.

Results and Discussion

Physical Properties

Weight loss

The biodegradation studies of the different soling materials in same composting environment showed different outcomes. The aerobic exposure of the soling material shows that the weight of the leather sole gradually decreases during the period of the study (30 to 90 days), due to decomposition of leather sole. In natural rubber (NR) sole, there is no loss in weight for first 60 days whereas after 90 days, there is some weight loss (1.5%) noted in the sole. In case of EVA, PU, TPR and TPU soles, there is no change in weight for first 60 days of study, but after 90 days, there is slight weight loss of less than 0.4% observed, which may be because of some physical changes due to exposure to the compost/wet environment. After 90 days, the percentage weight loss recorded for LA, NR, EVA, PU, TPR and TPU is 26.14, 1.48, 0.38, 0.01, 0.22 and 0.22 respectively (Figure 3a).

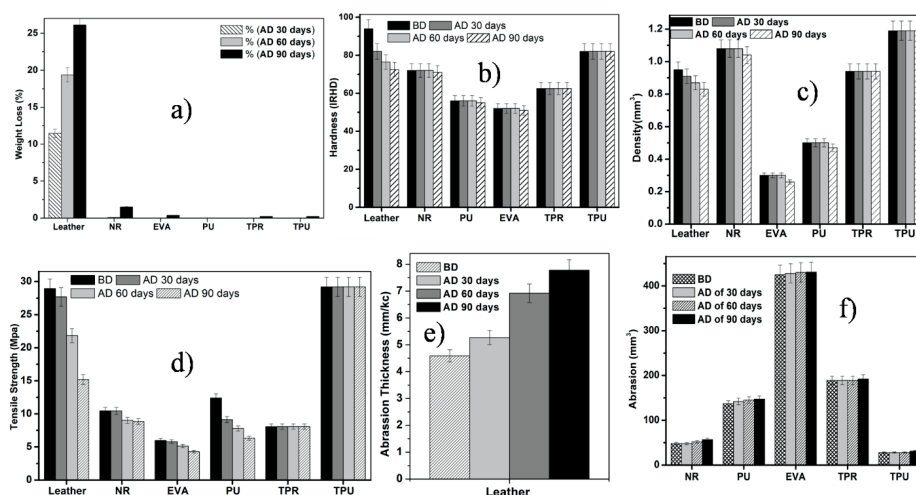


Figure 3. Physical characterization of the sole samples before (BD) and after (AD) 30, 60 and 90 days of exposure to the simulated compost environment a) Weight Loss, b) Hardness, c) Density, d) Tensile Strength, e) Abrasion Resistance of Leather, and f) Abrasion Resistance of all other samples.

Hardness

The hardness values show that the hardness of the leather sole also gradually decreased from 30 to 90 days, due to decomposition of the leather sole. Although in NR, PU and EVA soles there was no difference in hardness for first 60 days, the hardness reduced slightly after 90 days. In case of TPU and TPR soles, there was no change in hardness for first 60 days. Even after 90 days, there was no significant change found, which may be due to the strong resistance towards degradation (Figure 3b).

Density

The density of the leather sole also gradually decreases from the original sample during 30 to 90 days of exposure to simulated compost environment. In case of NR, PU and EVA soles, during the first 60 days, there is no change in density. But after 90 days, there is a significant change of density due to weight loss of the sole. In case of TPR and TPU soles, there is no change in density during the period of 90 days, which is in good agreement with other physicochemical characterization (Figure 3c).

Tensile Strength

The tensile strength of the leather and PU sole gradually and significantly decreases with the increase in time of exposure to the compost environment from 30 to 90 days. This is due to decomposition of the leather sole and hydrolysis of the ester bonds in PU. The tensile strength of EVA and NR also decrease gradually during 60 to 90 days which may be due to the deterioration of product quality but it is unaffected in case of TPR and TPU even after 90 days which shows the strong resistance to degradation (Figure 3d).

Abrasion Resistance

The abrasion of the leather sole gradually increases with the increase in time of exposure to the compost environment from 30 to 90 days, as a result of decomposition of the leather sole (Figure 3e). The abrasion of PU sole and EVA increased gradually which may be due to the atmospheric effect on properties. But this doesn't affect the soles such as NR, TPR, and TPU on first 30 days. Although after 60 days, there is no change in TPR and TPU but insignificant changes are noticed in NR. After 90 days very little increase in abrasion is observed in these samples which may be due to aging of the samples in the compost environment (Figure 3f).

ATR-FTIR Measurement

To investigate the chemical changes in the soling material due to their exposure to the simulated compost environment, the ATR-FTIR spectroscopy was performed for all the soling material samples before and after the experiments (Figure 4).

Leather

Basic IR peaks (cm^{-1}) were detected in leather sample as it is for a typical leather containing additives. The protein is detected by bands at 3307 cm^{-1} due to $-\text{NH}$. After 90 days burial of the leather sample, the formation of the aldehyde is identified by the presence of the new

peaks at 1725 cm^{-1} , 2932 cm^{-1} and a small shoulder at 2844 cm^{-1} . These new peaks at 2932 cm^{-1} and 2844 cm^{-1} correspond to the asymmetric and symmetric stretching of the $-\text{CH}$ group respectively.²¹ Also, the new peak at 1727 cm^{-1} is due to the stretching of $>\text{C}=\text{O}$ group. The formation of new peaks indicates the formation of the aldehyde group due to initial decomposition of the leather samples. Another new peak at 1207 cm^{-1} corresponds to $-\text{CH}$ stretching. The peaks observed at 3325 cm^{-1} , 1610 cm^{-1} and 1066 cm^{-1} are corresponding to $-\text{NH}$ stretching, bending and outer plane bending respectively, which further confirms that the protein structure is still remaining even after 90 days. Hence the decomposition of the protein as a part of biodegradation was just started but not completed which is in good agreement with SEM analysis as well as physical characterization (Figure 4a).

Natural Rubber

After 90 days burial of the rubber sample, the formation of the aldehyde is identified by the presence of the new small peak at 1725 cm^{-1} , due to the stretching of $>\text{C}=\text{O}$ group. The formation of small new peak after 90 days indicates the starting of biodegradation process for the rubber samples and formation of aldehyde group (Figure 4b). It is well known that natural rubber is a biodegradable material.²²

EVA

In the ATR-FTIR spectra of EVA, the absorption peaks at 2914 cm^{-1} and 2849 cm^{-1} are attributed to the symmetric and asymmetric stretching vibration of ethylene, respectively. The peak at 1458 cm^{-1} represents the deformation vibration and the peak at 721 cm^{-1} represent the rocking vibration of ethylene group. The flexural vibration of methyl group is represented by the peak at 1365 cm^{-1} . Characteristic absorption peaks of vinyl acetate groups are observed at 1735 , 1238 and 1015 cm^{-1} that corresponds to stretching vibration of $\text{C}=\text{O}$ band, asymmetrical stretching vibration of $\text{C}-\text{O}$ band and symmetric stretching vibration of $\text{C}-\text{O}-\text{C}$ band, respectively. All the characteristic bands of EVA present even after 90 days of exposure to simulated compost environment but there is a bizarre change in the ATR-IR spectra.^{23,24} As EVA sole are generally microporous cellular material, there may be soil contamination in the gaseous foam structure. The sharp peak at around 3334 cm^{-1} and a broad peak at around 1120 cm^{-1} may be attributed due to the presence of the composted-soil (organic soil) contamination in the void phase of the foam material.²⁵ The soil contamination was minimal which are in good agreement with physical, thermal and morphological properties (Figure 4c).

PU

The band of $-\text{NH}$ stretching at 3325 cm^{-1} and peak at 1588 cm^{-1} indicates the $-\text{NH}$ deformation. The stretching and bending vibrations of $-\text{NH}$ are found at 3314 and 1533 cm^{-1} , while the $\text{C}=\text{O}$ stretching frequency is noticed at 1720 cm^{-1} in spectrum.²⁶ The frequencies at 2953 cm^{-1} and 2862 cm^{-1} are corresponded to symmetric and asymmetric stretching vibration of $-\text{CH}_2$ group and its bending vibration is observed at 1402 cm^{-1} . There are no significant changes found in the

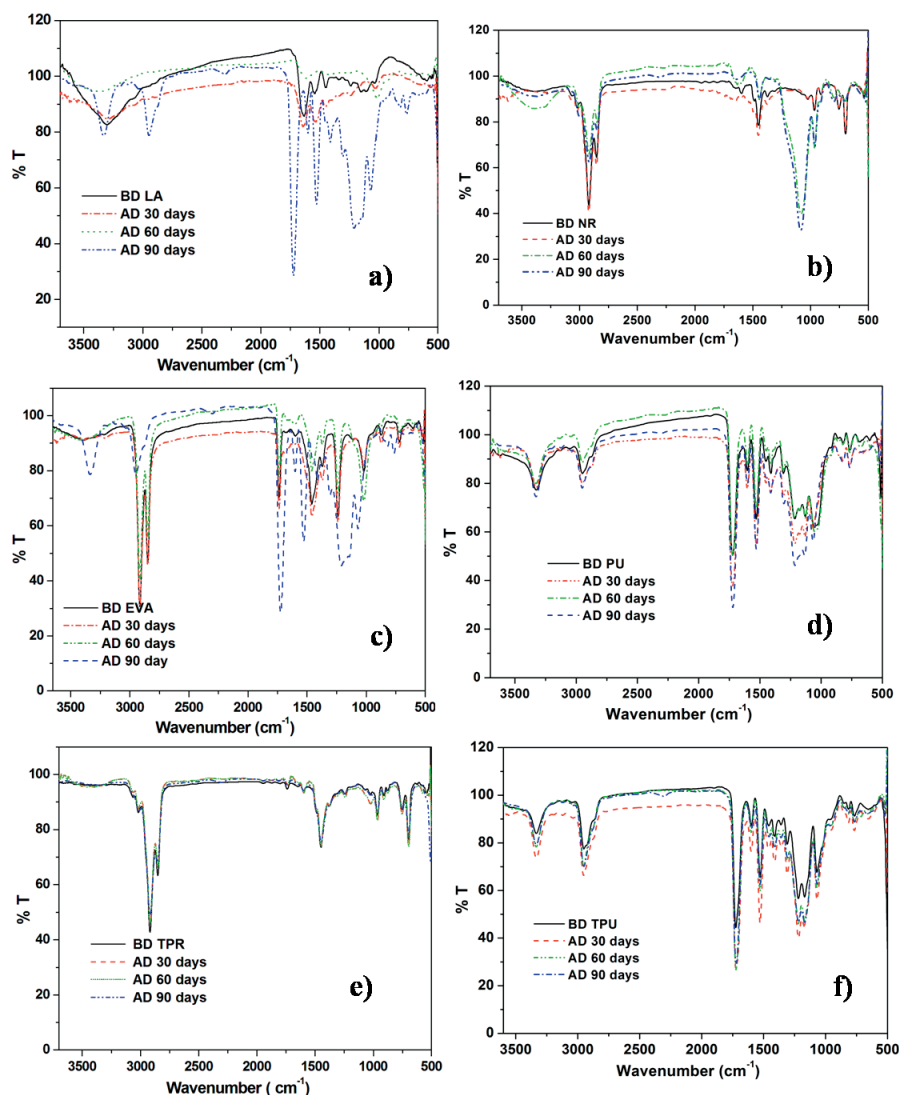


Figure 4. ATR-FTIR spectra of the sole samples before (BD), after (AD) 30, 60 and 90 days of exposure to the simulated compost environment.

>C=O region even after 90 days of exposure to simulated compost environment, which implies that PU soling materials are one of the very stable polymeric materials (Figure 4d).

TPR

Thermoplastic rubber shows typical absorption of styrene –C–H stretching at 3057 cm⁻¹, and butadiene =CH₂ and =CH stretching at 3010 cm⁻¹, –C–H asymmetric and symmetric stretching at 2917 and 2853 cm⁻¹ respectively, –C–H asymmetric bending at 1448 cm⁻¹, =CH in plane bending (twisting) at 1380 cm⁻¹, and =CH out of plane deformation (bending) of trans-1,4-C=C at 966 cm⁻¹. Hence there are no functional changes in the ATR-IR graph of TPR after 90 days of burial, which shows the stability of the material against the nature (Figure 4e).^{27,28}

TPU

The infra- red absorbance band of hydrogen bonded urethane carbonyl appears at lower wave numbers than that of the free

urethane carbonyl group.²¹ In the order of increasing wave numbers, two >C=O amide - I stretching bands are observed such as H-bonded carbonyl groups at 1600 cm⁻¹, and non H-bonded free carbonyl groups at 1723 cm⁻¹. The peak at 3336 cm⁻¹ indicates -N-H stretching of the urethane bond. The peaks at 2953 and 2866 cm⁻¹ correspond to symmetric and asymmetric stretching vibration of -CH₂ group and its bending vibration is noticed at 1463 cm⁻¹.^{29,30} The infra-red spectra of thermoplastic polyurethanes before and after exposure to simulated compost environment had no changes in the urethane >C=O stretching vibration in the amide -I region which is responsible for the biodegradation. Also, there are no significant structural changes in other regions. This corroborates the confirmation of the non-biodegradability and non-decomposing property of the TPU soling material even after 90 days of exposure to simulated compost environment, which are further confirmed by the TGA and DSC analysis (Figure 4f).

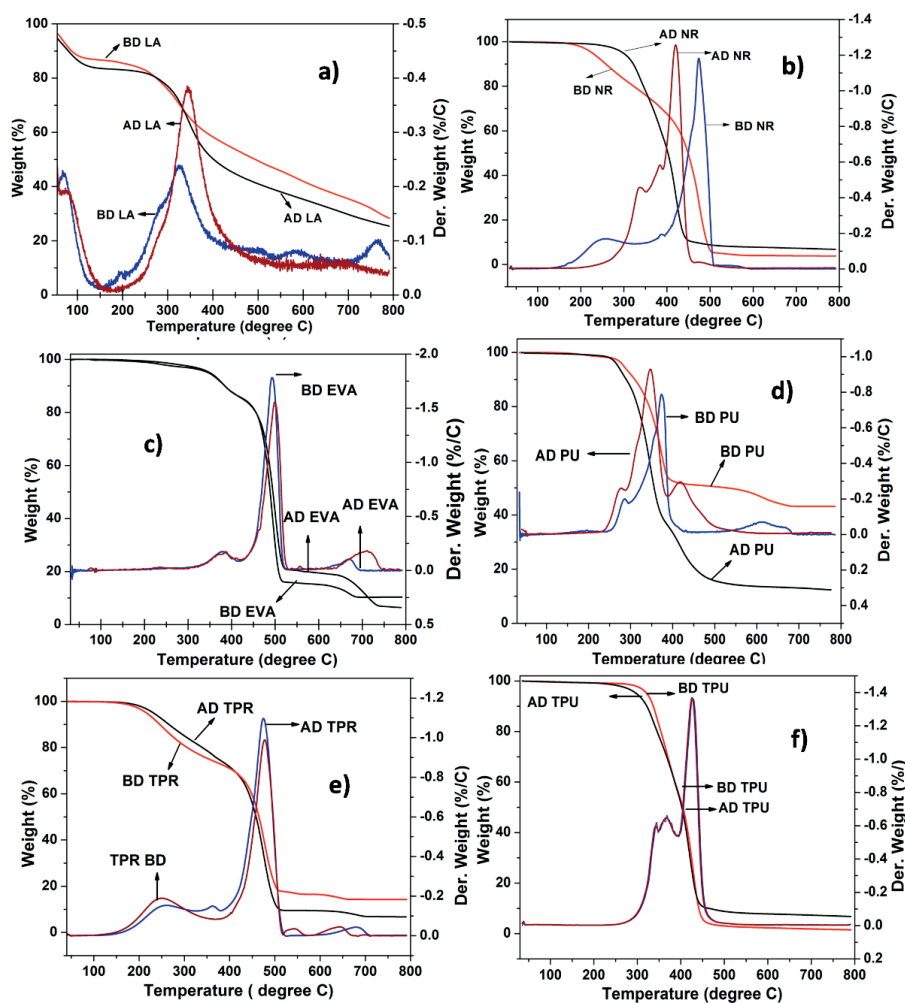


Figure 5. Thermogravimetric analysis of the sole samples before (BD) and after 90 days (AD) of exposure to the simulated compost environment.

Thermal Analysis (TGA and DSC)

The thermal characteristics of the leather samples show completely different behavior before and after the degradation study which is in good agreement with other physical characteristics.

The TGA pattern of both BD LA and AD LA are typical of vegetable tanned leather. Although no significant difference can be observed in the TGA pattern of BD LA and AD LA, few small but distinct peaks observed between 480° – 520°, 550° – 650° and 720° – 800°C in the DTG of BD LA show clear difference between these two samples. Both BD LA and AD LA show the first weight loss step below 150°C due to the evaporation of absorbed and bound water in the sample. The second major weight loss step between 250° – 400°C is primarily due to the decomposition of the collagen matrix.³¹ The small peaks observed in BD LA between 480° – 520°, 550° – 650°C provide significant hints on the complexity of the thermal decomposition of the collagen fibers, which are absent in the DTG of AD LA. The weight loss at high temperature range (600° – 800°C) in BD LA can be ascribed to the continuous pyrolysis of very stable residues, which can also be referred as passive pyrolysis region because of the very

low rate of mass loss. Nevertheless, percentage residue remained after 800°C for BD LA (28.3%) is higher than that for AD LA (25.4%). The additional weight loss and absence of DTG peaks between 480° – 520°C and 550° – 650°C in AD LA indicates degradation of some constituent of the leather after exposing them to the simulated compost environment for 90 days (Figure 5a).

The DSC curve of the leather samples before and after 90 days of exposure to simulated compost environment, display broad endothermic peak between 50 – 120°C. The thermal dehydration of the leather is observed as a broad endotherm centered at 75°C and 112°C for BD LA and AD LA respectively. The thermal denaturation of collagen matrix in leather³¹ is observed as a small endotherm at 170°C. Further, no peak is observed related to melting of the crystalline collagen zone embedded in the amorphous matrix.³¹ Due to decomposition, the crystallinity of the leather sample was lost although the collagen matrix has not degraded completely (Figure 6a).

Compared to all other polymeric soling materials, EVA samples before (BD) and after (AD) degradation show almost same trend in

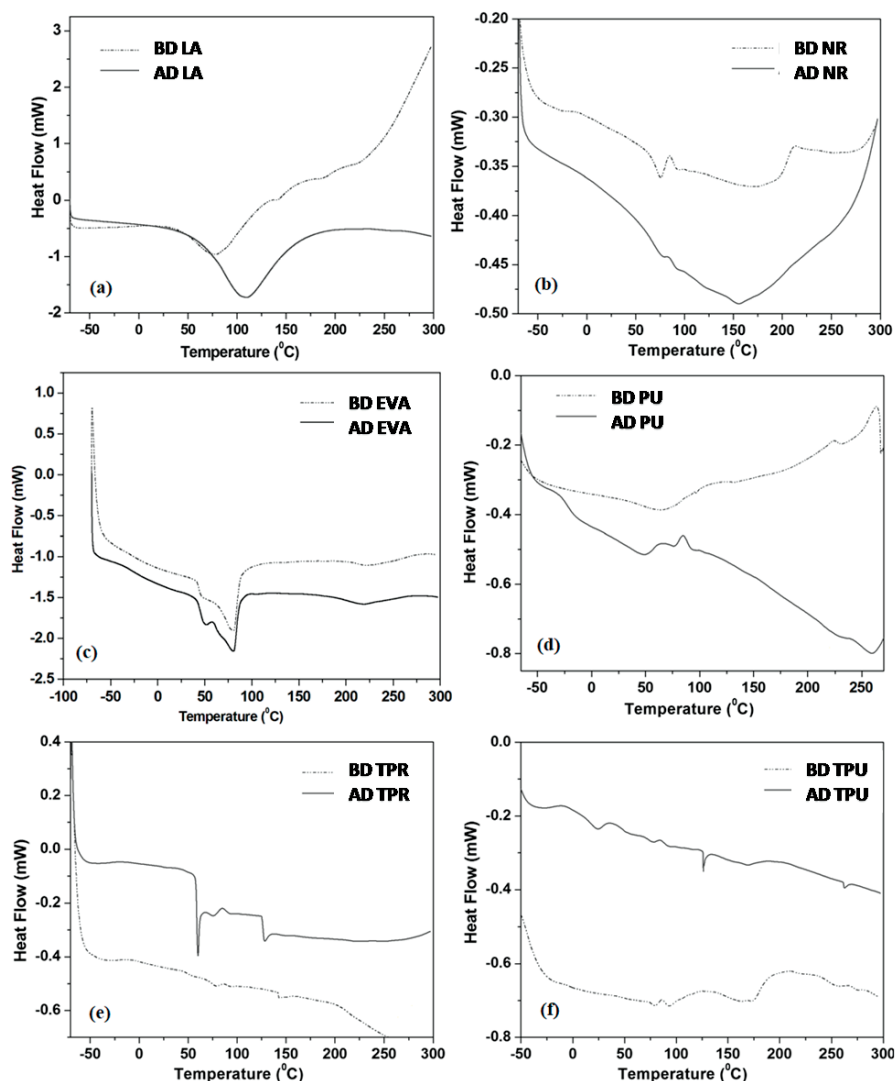


Figure 6. Differential scanning calorimetry of the sole samples before (BD) and after 90 days (AD) of exposure to the simulated compost environment.

both TGA (Figure 5 c) and DSC (Figure 6 c) studies, which is due to the high stability of the polymer backbone over aging in compost environment.

The TGA of AD PU shows a drastic weight loss as compared to the BD PU, which may be due to the hydrolysis of the ester bond that also results in poor physical properties (Figure 5d). The TGA of the TPU and TPR samples before and after exposing to degradation condition did not change, which proves that there is no alteration in the polymer content of these polymeric soling materials. This can be due to the fact that the presence of bulky rigid cyclic structures in these polymers might impede crystallization. This is in good agreement with other characterization results (Figure 5 e-f).

Although DSC shows that T_g remain same for before and after degradation samples of PU, TPR and TPU, but there is alteration in melting point which may be due to the soil contamination and also due to long exposure to compost/wet environment (Figure 6 d-f).

Morphological Analysis

The SEM images of the sole samples before and after exposure to simulated compost environment are shown in Figures 7 and 8. The surface morphology of the leather sole shows degradation/decomposition and opening of the fiber in the cross section on leather after 90 days (Figure 7d). The SEM images of PU, EVA, TPR, and TPU samples after 90 days of exposure to the simulated compost environment show significant physical and surface color change, which may be due to aging and water contamination on the soles. But there is no significant degradation/decomposition of any of these soles as shown in the SEM images (Figure 8), which is in agreement with the physical properties, ATR-FTIR and thermal analysis results. It is also seen that there are some cracks on the rubber sole samples, which may be due to the initiation of decomposition of natural rubber. This fact is also supported by the ATR-IR, mechanical and thermal characterization results.

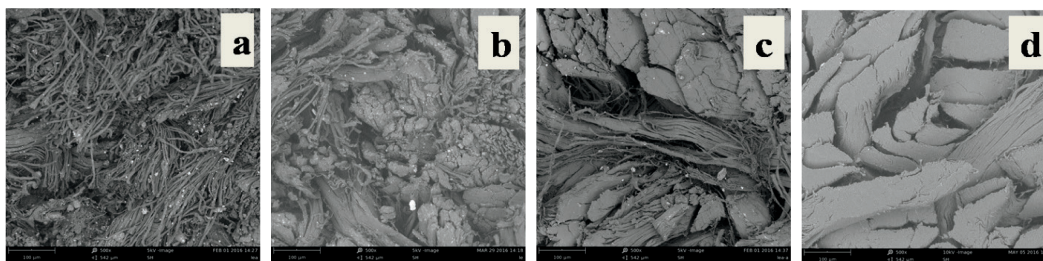


Figure 7. SEM images (100 μm scale) of the Leather sole samples a) before, b) after 30 days, c) after 60 days and d) after 90 days of exposure to the simulated compost environment.

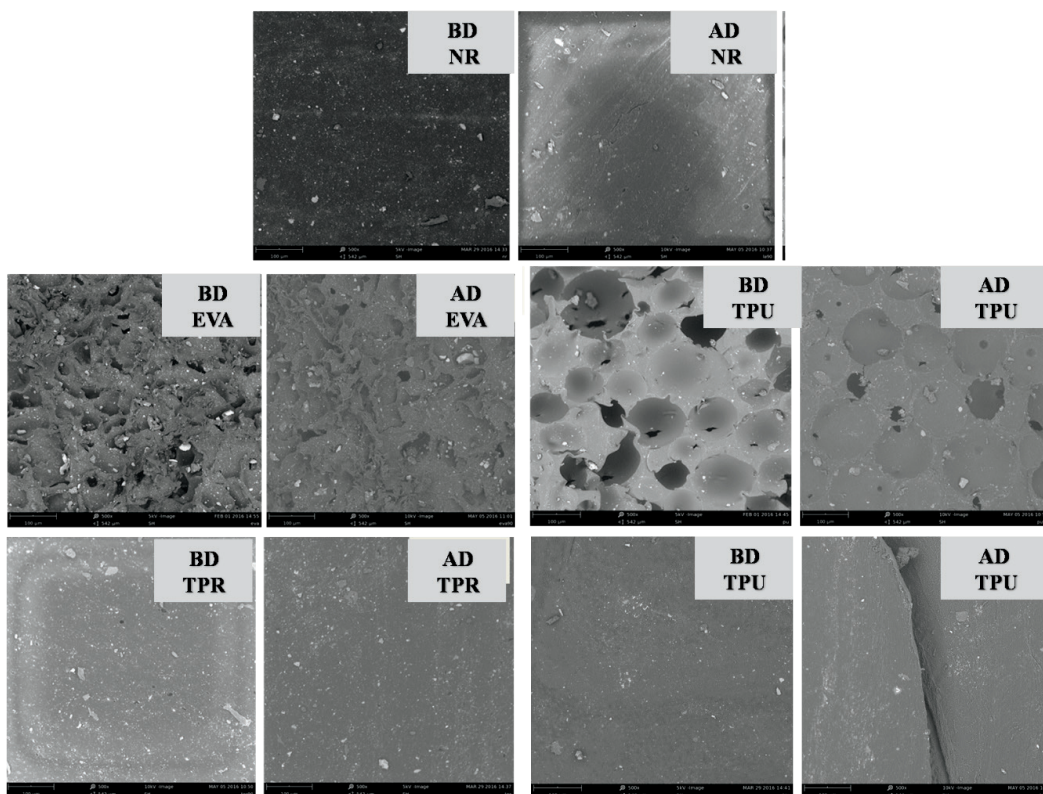


Figure 8. SEM images (100 μm scale) of the sole samples, before (BD) and after (AD) 90 days of exposure to the simulated compost environment.

Conclusions

Biodegradability and decomposing properties of the present-day footwear soling materials viz. LA, NR, PU, TPU, EVA, and TPR, were successfully investigated for a period up to 90 days and the results were compared. The weight loss recorded for the various sole samples were in the order, LA > NR > EVA > TPR > TPU > PU. The SEM images showed that the morphological characteristic of leather shoe sole (LA) was changed due to decomposition as an initiation of biodegradation. Post-degradation study of the LA and NR sole samples showed loss in weight that led to decrease in hardness and density. Further, for both the LA and NR, the tensile strength was highly reduced and the abrasion was increased. This implies that the biodegradation was started to occur in LA and NR soles. The structural conformation of LA obtained from

ATR-IR studied were in good agreement with the physical and thermal characterization results. The decomposition rate of LA sole sample was higher than the NR sole sample. In NR, along with physical properties, structural changes were also observed after 90 days of degradation study. PU and EVA sole samples showed significant changes in the physical properties, such as appearance, weight, tensile strength, hardness, density and abrasion resistance. However, no significant structural change was observed in the ATR-IR, SEM, TGA and DSC results. The TPR and TPU sole samples showed no change, except the abrasion value, which increased marginally due to soil penetration. The results proved that in terms of biodegradability, leather is the best footwear soling material and, TPR and TPU are the most stable among all the polymeric materials, till date.

The present study on the end-of-life nature of footwear materials currently used by footwear industry not only emphasized the importance of developing and using biodegradable materials in footwear manufacturing but also identified the stable polymeric soling materials, which will be helpful to establish the four 'R' system of waste management for environmental sustainability.

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Approaches Towards Tannery Modernization and Up-Gradation: Leather Industry 4.0: Multi-Disciplinary Approach

by

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Abstract

Analysis of various approaches for tannery modernization and up-gradation as leather industry 4.0 need to be analyzed keeping in view of significant advancements made in different disciplines of relevance to leather sector. Holistic views and plans for cleaner image with better environmental aspects are essential for the sustainable growth of the leather sector. In this paper, various plans and strategies for the next phase of tannery modernization denoted as TAN MOD 4.0 have been presented with the main objectives of near zero discharge of chemicals, waste minimization, value addition, productivity enhancement and safe & healthy environment in tannery. Different components such as basic up-gradation concepts, modern leather processing techniques and engineering inputs for leather sector such as process control systems, necessary automation tools and Internet of Things (IoT) are discussed.

Introduction

In the growing technological advancements in various fields, leather industry also needs to have enhanced outlook. In this regard, the primary motivation of a framework for tannery modernization and up-gradation is to identify critical areas of weakness of the leather sector with reference to the context of global developments and prepare a strategic plan based on the strength of untapped opportunities.

The Indian leather industry is divided into three sectors as large, medium and small. It enjoys the strength of vast raw material (approx. 10% of global supply), rich expertise pool and unlimited human capital. Untapped potentials result from some weakness of the industry originating from resource-link-constraints. Industry suffers from un-clean image of environmental commitments, occupational health & safety of workers and global market quality. During recent years, global competition in leather and allied products trade are increasing. Lack of expertise ensuring high productivity and quality for cost leadership for low priced market segment, have

been identified as weakness. The industry also requires cleaner image and better environmental aspects. According to the above reasons, tannery up-gradation and modernization plans are essential for the sustainable growth of leather sector.

The following areas need to be upgraded and modernized:

- Tanning sector (wet processing & material handling)
- Occupational health and safety
- Pollution control
- Energy utilization

Tannery Modernization of Initial Phase

Tannery Modernization - Phase I has been carried out at CSIR-CLRI in 1990's under the LTM program.¹ Government of India had set up Leather Technology Mission (LTM) involving a grass root approach of taking technology to correct local deficiencies and to strengthen the ability of the cottage, rural and small scale sectors to cope with technological changes and integrate efficiently in the overall development of leather industry. This technology driven development grid for the Indian leather sector thus aims to augment raw material availability, upgrade technology, promote cleaner technologies and standardize quality and develop organizational and human skills in a significant measure to generate multiplier effects.

One of the work plan strategies of the Mission was to set up demonstration units for process control and cleaner tannery wet operations in a tannery to demonstrate the viable cleaner technologies in a number of commercial tanneries at various locations in India. Whereas, there are some un-filled gaps such as catering to Large as well as Medium Small Micro Enterprises (MSME) need to be analyzed. The small sectors (below 3000 Kg/day) of tannery also need to be considered in the present scenario. In addition, some of the relevant concepts of Tannery Modernization and Industry 4.0 also need to be considered for Leather sector.

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Industry 4.0

In the 21st century, Industry 4.0 incorporates cutting-edge technologies including additive manufacturing, robotics, artificial intelligence and other cognitive technologies, advanced materials, and augmented reality, according to the article “Industry 4.0 and Manufacturing Ecosystems” by Deloitte University Press.

The development of new technology has been a primary driver of the movement to Industry 4.0. Some of the programs first developed during the final stages of the 20th century, such as manufacturing execution systems, shop floor control and product life cycle management, were farsighted concepts that lacked the technology needed to make their complete implementation possible. Now, Industry 4.0 can help these programs reach their full potential and also connects the internet of things (IoT) with manufacturing techniques to enable systems to share information, analyze it and use it to guide intelligent actions.²

The Fourth Industrial Revolution (or Industry 4.0) is the ongoing automation of traditional manufacturing and industrial practices, using modern smart technology. Large-scale machine-to-machine communication (M2M) and IoT are integrated for increased automation, improved communication and self-monitoring, and production of smart machines that can analyze and diagnose issues without the need for human intervention.³

Considering the scenario of Industry 4.0 with relevant applicability to Leather sector and various aspects for the next level of Tannery Modernization as Tan-Mod 4.0 are presented in this paper.

Un-Filled Gaps in Tannery Modernization

- Wide Coverage also to Micro, Small and Medium sectors
- Wider coverage in entire country
- Skill development and training with regard to tannery modernization tools at worker level
- Realizing: mechanization is only a part of modernization and not the only goal
- Incorporating Environmental, Safety and Hygiene concepts at the tannery level

Tannery Modernization 4.0: Objectives

Various plans under Tannery Modernization are termed as TAN-MOD 4.0. In addition, TAN MOD 4.0 is focused not only for large scale units but would cater to MSME sector also. In this regard, programs on MSME for leather sector have also been studied and considered in TAN MOD 4.0. The small sectors (below 3000 Kgs/

day) of tannery also need to be taken care of in the present phase of implementation. Various plans are as follows:

- Process Optimization
- Improve Process Efficiency
- Better Design & Process Control
- Better Material Handling systems (lay out)
- Machinery up-gradation
- Energy audit: Use of non-conventional resources
- Primary treatment systems
- Environmental, Health and Safety
- Waste Minimization: Bye-product Utilization
- Better communication and information technology (IoT)

Present Plan under Tannery Modernization: TAN-MOD 4.0

The components for TAN-MOD 4.0 shall be broadly classified in to three categories (Fig. 1) as follows,

1. Basic Up-gradation concepts (BASICS)
2. Modern Leather processing techniques (LEAPRO)
3. Engineering for Leather Process (ENGG-LEAP)

The work elements for each component have been worked out as presented earlier in LERIG-2016.⁴ Various approaches for Tannery up-gradation and Modernization in Leather Sector TAN MOD 4.0 are presented as Sustainable solution (Fig. 2).

Some of the concepts envisaged under TAN-MOD 4.0 for leather sector shall comprise the following modules,

1. Lay-out Design and Facilities
2. Process control systems
3. Process Intensification tools
4. Odor abatement module
5. Occupational and Environmental Safety Module
6. Non-conventional Energy Module
7. Energy audit etc.

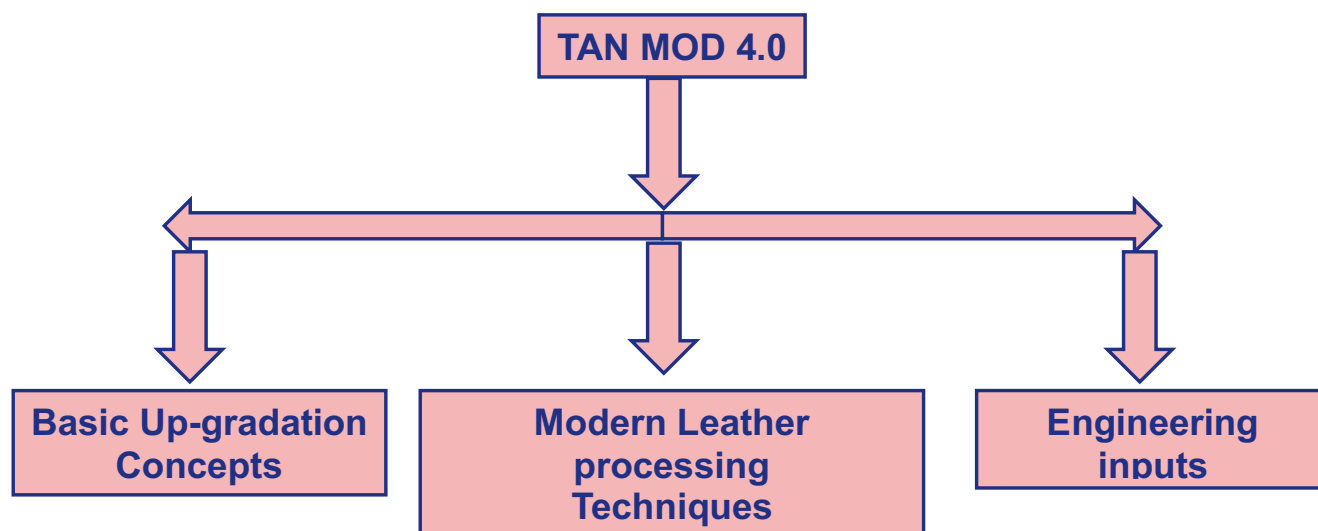


Figure.1. Schematic Plan for Tannery Modernization - TAN-MOD 4.0

The above components could cater to both more productivity as well as for emission control.

Benefits Envisaged from TAN MOD 4.0

- Near Zero discharge of chemicals – Pollution reduction at source (In-plant)
- Quality Consistency (95-100%)
- Water Minimization
- Waste Minimization (15-30%)
- Value addition for leather
- Productivity enhancement (25%-50%)
- Safe, Healthy Environment in Tannery

Basic Up-gradation concepts

- Basic Studies
 - Quality of chemicals
- Quantity & Quality of chemicals audit
- Quality/ Quantity of water
 - Hardness impairs quality of leather; TDS ↑
- Process vessels: Drums, Paddles or Pits
- Leather machinery

Quantity & quality of chemicals, leather process vessels and quality of machinery used for leather processing need to be selected properly and optimized for each unit operation.

Engineering for Leather Process (ENGG-LEAP)

- System for Recycle of spent liquors
 - Soak, Lime, Pickle, Chrome liquor recycling (RECYCLE)
- Process control systems⁵
- Process Intensification Tools: Near zero discharge of chemicals
- Energy audit & Solar energy for leather (ESOLAR)
- Tannery Odor control system
- Leather machinery up-gradation (LEAMAC)
- Tannery Lay-out up-gradation
- Scheduling and Sequencing
- Environmental, Health and Safety for Leather (EHSL)
- Better communication and information technology (IoT)
- R&D and Testing Centre

Various engineering for leather processing as shown above is necessary for waste minimization, optimal utilization of resources, energy control, and production management and for the safety of staff and environment. IoT could be used for online real time data transfer with regard to process parameters, process trouble shooting, product quality, inputs related to trade etc.

Materials storage facility

- Cold storage facility for preservation of raw skins/hides
- Wet-blue storage systems with automated water sprinklers
- Finished leather storage system with temperature and humidity controls
- Hazardous chemicals storage and dispensing facility (e.g. acids etc.)
- Leather specialty chemicals storage facility (fatliquors, dyes, syntans, etc.)

Since the materials under the process involves natural materials such as raw skins, hides and other intermediate goods, the storage of which become important with proper control of temperature, relative humidity etc. in order to avoid putrefaction

Materials Handling facility

- Trolley for raw skins/hides movement
- Electric forklift attached transport vehicles for raw skins/ limed pelts/wet-blue/dyed leather/finished leather etc.
- Bulk chemicals transport

Similarly, the materials handling systems are necessary in order to provide efficient and safe movement of materials from one yard to another or shifting within the same yard.

Modern leather processing techniques (LEAPRO)

- New eco-friendly pre-tanning technologies
 - Salt-less preservation
 - Enzymatic processes
- Novel eco-friendly / high-exhaust tanning process technologies
 - E.g. CLRI salt free tanning process
 - Float-less/ Float free tanning technologies
- New eco-friendly, high-exhaust post-tanning process technologies, REACH compliance
- New finishing methods
- Novel leather process recipes for high-end segments for value addition

In the growing demand for adopting Eco-benign processes and products and for compliance to environmental norms and achieving near zero discharge of chemicals (TDS, BOD, COD, Cr etc.), modern leather processing techniques (LEAPRO) become necessary. Various new eco-benign processes and products as developed become important.

Environmental, Health and Safety (EHS)

- Cleanliness and hygiene
- Occupational Health & Safety (OHS)
- Safety audit
- Personal protection equipment
- Inter-locking systems & trips
- Alarms
- Emergency management systems

Since leather processing involves various unit operations, types of raw materials which are biological in nature and use a range of chemicals starting from general bulk chemicals to specialty

chemicals and generation of liquid, solid and gaseous wastes, Environmental, Health and Safety (EHS) aspects become important in order to protect both the staff as well as environment.

Conclusions

Face lift and enhanced outlook as Leather Industry 4.0 through the concepts of leather, environmental and engineering sciences (in a broader sense) as multi-disciplinary approach are necessary in the growing environmental concern, market demand and economics. Various options for tannery modernization and up-gradation for leather sector have been discussed taking into consideration of advancements made in different areas of relevance to leather sector. Industry 4.0 with relevant applicability to leather sector and various aspects for the next level of tannery modernization as Tan-Mod 4.0 are presented in this paper. Plan for tannery modernization (TAN-MOD 4.0) has been discussed with main themes such as basic up-gradation concepts (BASICS), engineering for leather process (ENGG-LEAP), modern leather processing techniques (LEAPRO).

The main objectives and goals for this TAN-MOD 4.0 are to achieve near zero discharge of chemicals with pollution reduction at source (in-plant), waste minimization, value addition for leather, productivity enhancement and safe & healthy environment in tannery. Emphasis would be given for micro, small and medium sectors. Skill development and training program with regard to tannery modernization tools at worker levels are also essential and to improve EHS concepts.

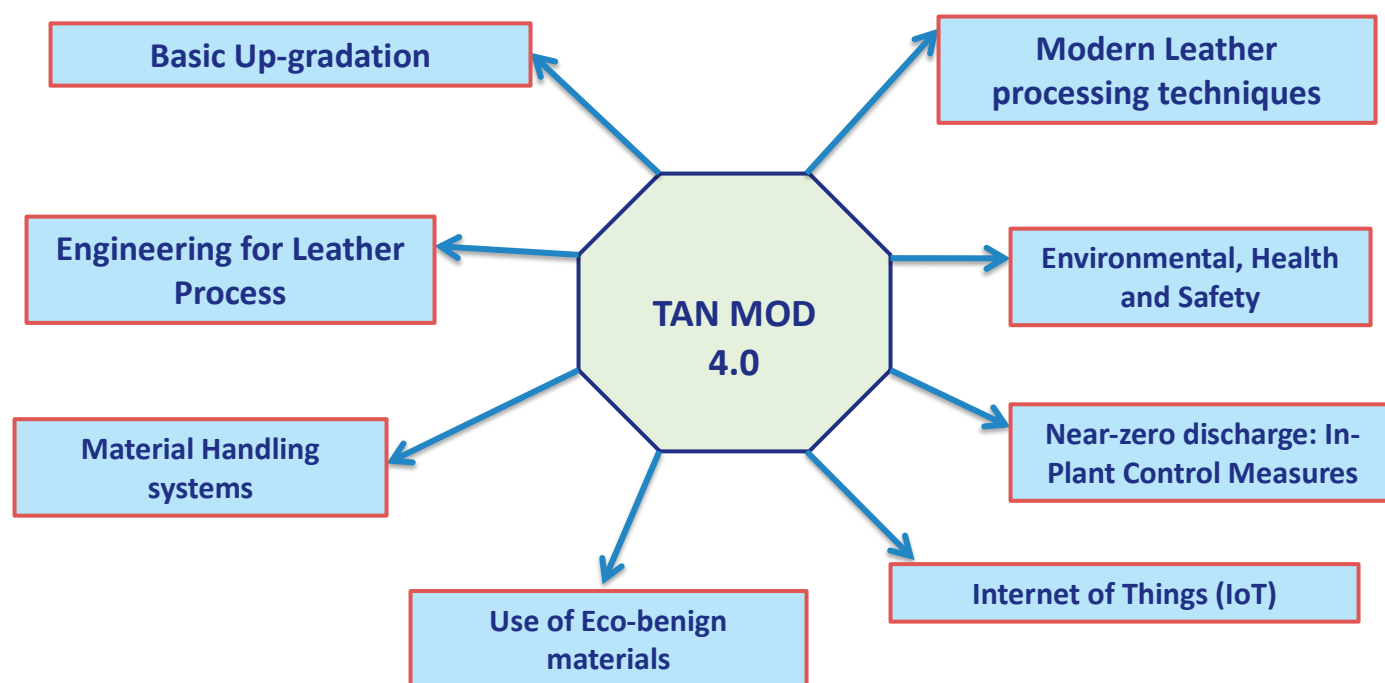


Figure 2. Approaches for Tannery up-gradation and Modernization in Leather Sector TAN MOD 4.0 as Sustainable solution.

Acknowledgements

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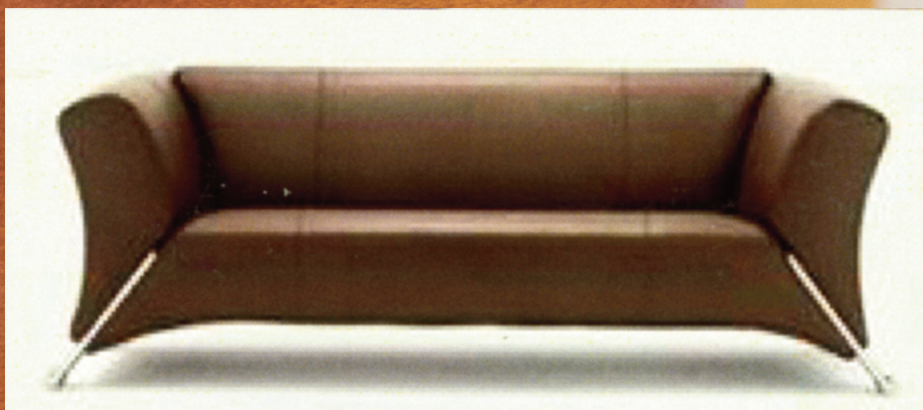
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Venkatasubramanian Sivakumar, see *JALCA* **113**, 72, 2018.

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