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Posted Date: 8 August 2023

doi: 10.20944/preprints202308.0681.v1

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Circular Approach to Finished Tanned Leather: Regeneration by Cryogenic Technology

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Abstract: Finished tanned leather are usually covered by a thin polymeric layer. This layer has the scope to change the morphological aspect of the last leather layer, as well as to improve the impermeabilization properties. Often, the finished product is refused by the final client and tanneries must restore significant quantity of materials. Therefore, it is very important to remove this finished polymeric layer, to recover the underneath tanned leather and to predispose it to a new finishing. The bonding between the polymeric film and leather is so strong that, today, only a blade shaving process can perform this separation at the expenses of also removing a layer of tanned leather and consequently reduce the leather thickness. Here, a novel separation method was developed, based on the significant difference in the dilation properties between the tanned hide and the polymeric film at low temperature. The use of cryogenic fluids, in particular the direct application of liquid nitrogen, can freeze the polymeric layer under the glass transition temperature and then inducing a brittle behaviour. The result is an easy separation without any alteration of the tanned leather layer. Thus, the process here developed, allows the reuse of the tanned leather towards a new life in the respect of the circular economy principles.

Keywords: recycle; circular economy; cryogenic removal

1. Introduction

Tanned leather is an important material and versatile material with a lot of different applications, like in clothing, footwear, home furnitures and car upholstery sectors [1]. Form the environmental point of view tanned leather nobiltate a waste from the meat food chain that cannot be avoided, the animal hide [2]. Accordingly, until humans will continue to eat meat, the leather market will continue. Moreover, the tanning process induces unsurpassed durability properties to the final product justifing the success of the leather industries since the beginning of the human history. However, such a durability is obtained at the expense of the use of several chemicals and at least 20 L of water per kilogram of raw hide [3]. In conclusion, when considering the traditional factors affecting the Life Cycle Assessment of the tanned leather, the impact of the animal growth is significantly higher than that of the successive industrial processing of the raw hide to obtain the finished tanned leather [4][5].

Additionally, the leather processing industry is a very conservative sector. Progress were traditionally made in sustaing the market demand instead of in reducing the environmental impacts [6]. By chance, things are rapidly changing and the demand for more environmentally sustainable products is pushing this industry to innovative. Examples are the introduction of green tanning agents, to reduce the amount of some unavoidable chemicals and planning their substitution in the near future, and last but not least to reduce the amount of polluted waste water [7][8][9]. Focussing the attention on tannery wastes, main ones are scraps and wastewaters. The formers are difficult to be recycled and mainly are incinerited or landfilled [10]. These scaps represent the 60% of all raw material weight [11]. Very often they are not only the cutting edges used to select the leather core where the defects are substantially absent, but they represent the whole piece if the client does not accept the final quality. Unfortunately, the respect of the promised leather quality can be assessed

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only when the whole process (tanning and finishing) ins complete [12][13][14]. Accordingly, the problem generated by these scraps is not "only" environmental but it has also an economic relevance. If a finished leather becomes waste, all the energies and chemicals used to do that become negative voices [15].

It is then clear that is of paramount relevance to try to recover at least the whole finished leathers. The finished layer is made by a mixture of resins and dyes [16][17] and usually this layer produces visual and handy effects that are designed for the final costumer, typically a fashion firm. For this reason, a finished leathewr that does not pass the acceptance parameters difficultly could be sold to a different costumer.

A possible recovery process is based on removing the finished layer in a way that the tanned leather underneath could be refinished again [18][19]. Unfortunately, the finished layer us strongly adehrent to the tanned leather, and the only possible recycling chance requires the removal of this very adeherent finished layer.

This operation can be industrially performed by blade shaving it and to reconduce the leather to the "crust" status, ready to another time for the finishing step. Unfortunately at the expenses of also removing a layer of tanned leather and consequently to reduce the leather thickness.

In conclusion, there is space to develop a new recovery process where the delaminations proceeds avoiding the blade shaving and where the leather crust properties are preserved [20]. The solution here proposed is the cryogenic delamination. In facts, tanned leather and polymeric finished layer have different dilatation properties at low temperature. Leather generally could resist in hard conditions preserving its structure, because the complex collagen matrix has a large quantity of strong covalent bonds [21]. Moreover, the tanning agents improves this resistance in terms of bonds between different collagen chains. On the contrary, the finished layer is a polymeric cover whose structure is different depending by the used recipe. In general these polymers are polyurethanes and/or polyacrylates. These polymers have a glass transition temperature significantly higher than that of leather. Thus, if they are frozen below that point their mechanical behaviour shifts from elastic to brittle. Immediately cracks appear leading to the layer detachment from the leather.

As cryogenic fluids, because its commercial availability, preference goes to liquid nitrogen, whose operating temperature approaches -200°C. However, it is not necessary to reach these temperatures. The -80°C of CO_2 dry ice are also sufficient [22]. Here, it is preferably its use in the form of CO_2 snow, applying the same apparatuses adopted for paints removal from metal surfaces by CO_2 ice blasting [23].

In this work, being the process conditions very easy to be replied, the attention will be focussed on assessing the quality of the delaminated leather and in particular on assessing the finished layer removal effectivity.

2. Materials and Methods

Materials:

The cryogenic delamination was done on different kinds of finished leather. They were three samples of commercial leather, with three kinds of colour and finished layer, for a method versatility demonstration. They were all tanned by chromium, because it was the most common strategy [24]. This choice was done to discover if the new potential recycling system that was descripted below, was suitable for ordinary leather. They had distinct characteristics, reported on **Table 1**:

Table 1. This table reports main general characteristics of leather samples.

Sample	Thickness before (b) and after (a) (mm)	Look	Color	Photo before	Photo after

Entry 1	1,64 (b) 1,54 (a)	Full hand	black		
Entry 2	1,56 (b) 1,36 (a)	Compact touch	brown		
Entry 3	1,29 (b) 1,11 (a)	Soft hand	Light brown		

They were analysed by some techniques, for a better characterization of samples and comparison with products.

Cryogenic delamination

For a lab-scale reproduction of this new method, cutted leather pieces were prepared in different dimensions, from 1cm x 1cm to more. Then, they were soaked in liquid nitrogen batch, conserved in a Dewar vessel. Samples become completely frozen in five seconds to one minute, depending on the size. It happened generally when the usual change of nitrogen state, while liquid is in contact with other hotter, will decrease dramatically. In this state, leather was really contracted and, more than collagenic crust, mainly the polymer layer. So, it started to be possible the finished layer delamination, helped by a tweezer and a slow folding action of operator to samples. This step was done very carefully and patiently; in fact, there are some process issues to pay attention. The polymeric layer is so thin and very fragile, it costed long time for the elimination. At the same time, the collagenic crust is also (less) contracted and if it will be fast and strongly bent, the breaking risk of the biological substrate, could be real. For these reasons this was a researching process, to be improved by a continue nitrogen flux that will freeze and remove without a leather conformation changing. In any case, this is a demonstration of the different polymeric layer answer to the cryogenic condition. Of course, when a sample was starting to be defrost a lot, it was important to restart a new batch. After that, some new samples were analysed:

- The polymeric layer removed, to know and characterize which compound is it.
- The resulting crust leather, to be sure of all polymeric removal and the quality maintenance.
- The original sample for a better comparison.

Analysis

Solubility: The aim was a valuation of the polymeric layer solubility, to analyse and characterize it in wet condition. Different experiments were done on *Sample 1*, in vials, with a 5mm x 5mm of this layer already removed from leather. The black one was chosen, for its strong and hard layer. If there was a partial dissolution, the insoluble part was tested with other potential solvents. If there was a solvent that could solubilized the finished layer of *Sample 1*, this was tried with the others. After putting inside glass vials the pieces, 3ml of solvent were added and they were corked and agitated for 8 hours at room temperature. The solvents tried were: distilled water, dimethyl sulfoxide (DMSO) (Honeywell, Muskegon, USA), tetrahydrofuran (THF) (Sigma-Aldrich, St. Louis, USA), chloroform (Carlo Erba Reagents, Val de Reuil, France), acetonitrile (Carlo Erba Reagents, Val de Reuil, France), ethanol (Sigma-Aldrich, St. Louis, USA), methyl tert-butyl ether (Sigma-Aldrich, St. Louis, USA), n-hexane 99% (Carlo Erba Reagents, Val de Reuil, France), dichloromethane (DCM) (Sigma-Aldrich, St. Louis, USA), cyclohexanone (Carlo Erba Reagents, Val de Reuil, France), acetone (Carlo Erba Reagents, Val de Reuil, France), toluene (Fisher Scientific, Loughborough, UK), butanone (Fulka Chemie, Buchs, Switzerland), methyl acetate (Fisher Scientific, Loughborough, UK), ethylene glycol (Carlo Erba Reagents, Val de Reuil, France), dimethyl sulfide (DMS) (Sigma-Aldrich, St. Louis, USA), dioxane (ThermoFisher, Kandel, Germany) and dimethylformamide (DMF) (Sigma-Aldrich, St. Louis, USA). DMF was also tried at 100°C for 3 days. When something was solubilized and something not, thanks to the mixture of various analogous polymers with different substituents, what remains insoluble was tried to pick up and resolve in another solvent.

Spectroscopy*:* Fourier Transformed InfraRed (FTIR) was analysed polymeric layers, on the external and internal face. The spectra were acquired with a Nicolet iS 10 FT-IR spectrometer, equipped with ATR Smart iTR module and a zinc selenide crystal. 64 scans were collected at 4 cm^{-1} resolution. The aim was the characterization of polymeric layer.

Microscopy*:* Scanning Electron Microscope (SEM) images were acquired by Zeiss Evo50, with EDS Bruker Quantax 200 6/30 probe instrumentation, used after complete freeze-drying of the samples. SEM analysis was done on the surface, below and sideway of collagen crust of *Sample 1*, to be sure of the polymer removal and to know the leather state, before and after the treatment [25].

Tensile strength and elongation behaviour: a reproduction of UNI EN ISO 3376:2020 [26], for an evaluation of mechanical properties, before and after removal. Universal dynamometer Instron mod. 5900R-4505 was used, with a load cell of 5 kN and an uncertainty of 0,3N. The samples were used in a different conformation respect the normative, like strips, for a prior study of them. For a tensile strength determination, the machine ran until the sample was break, this is the maximum force value. At the same time another value could be recorded: the elongation at maximum force. These values are expressed:

$$T_n = \frac{Fmax}{w \text{ x } t} \tag{1}$$

where Fmax, W, t and T_n are the measure force as described above, the sample width and thickness (both expressed in mm) and the tensile strength. The sample elongation E_{max} was evaluated as follow:

$$E_{max} = \frac{L2 - L0}{L0} \text{ x } 100 \tag{2}$$

Being L_2 and L_0 are the final and the initial length of the sample.

Thermal analyses: They were done for a determination of different behaviour to heating condition of polymer, crust leather and sample [27].

- Differential Scanning Calorimetry: DSC was done on 5mg of every sample, that were heated and cooled between − 60 and 180 °C for four times. The heating rate was of 20 °C/min in a suitable sample holder. The instrument was Mettler Toledo Polymer DSC. It allowed to know an exactly transition temperature.
- Thermal Gravimetric Analysis-Thermal Mechanical Analysis: TGA-TMA samples were heated from 30-900°C, at heating rate of 10 °C/min. The instrument was PerkinElmer STA 6000. Two analyses were coupled and in the analysis was possible to see the weight decrease and the temperature paths.

3. Results and discussion

Cryogenic removal

In base on the principle revealed before, the contraction of polymeric layer permits an easy separation of it form the underside leather. This is possible due to the different glass transition temperature between the two substances and a very efficient resistance of leather.

A representative sketch of the principle of this process is illustrated in **Figure 1**.

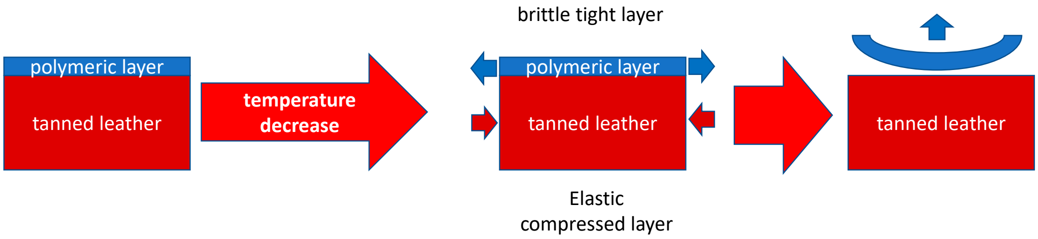

Figure 1. Schematic illustration of the cryogenic delamination process.

This is done immersing the sample into liquid nitrogen [28]. Some other techniques were tried, like cotton immersion and application on leather (to avoid the possible leather damages) or nitrogen spilling on the leather surface [29] but the first one rests the most efficient. Another possibility could be the ΔT extremization, by the nitrogen affixation on a 40°C leather samples, to check if polymer will be removed in less time on a hotter support. Anyway, all these methods weren't useful and fast as the first.

An example of the frozen leather aspect is illustrated in **Figure 2**, where the cracks produced by different contraction are evidenced.

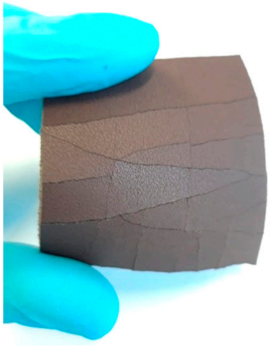

Figure 2. finished layer break due to N_2 liquid and slow folding.

One of the main advantage of this idea is about the aswer to thickness, it has remained the same in case of leather, with only a difference of tenths of millimetres. These data demonstated the high innovation and quality of this method, much better than the shaving recycle system. Also, in **Table 1**, the cryogenic polymer removal, was easily observable. It allowed to know which was the best way, to discover some interest effects about this method.

Dissolution

For analysing the chemical properties of these layers, as molecular structure (NMR) or polymeric status (GPC), it was important to find a good solvent for them. It also permits to separate some components with liquid chromatography and permits to know the mixture composition, very important for some properties. Infact, the contracting temperature (T_c) depends by compounds; if these substances have a particular T_c, it could be applicated a better temperature control for the cryogenic remotion.

Common solvents were tried, used during the finishing step in tanning industries [30]: cyclohexanone, acetone, butanone, methyl acetate, ethylene glycol and dioxane. Ethanol was used, to represent alcohols commonly used in the same field said before. Common diluent was tried to apply, normally used in the finishing polymer mixture in tanning industry, n-hexane. Methyl tert-butyl ether was tried to represent ethers commonly used in the same field said before. Solvents, normally used in deuterated form for nuclear magnetic resonance (NMR) analysis to know the exact structures, were tried: distilled water, DMSO, DCM, and chloroform [31]. THF, normally used in Gel Permeation Chromatography (GPC) analysis to know and characterize different polymers, was tried.

Acetonitrile, generally used in high permeation liquid chromatography (HPLC), was tried. Toluene, to check the non-polar solvent dissolution activity, was tried. DMS, to know the polymers behaviour with useful or reactive substances [32], were tried and finally DMF: generally used for polyurethanes dissolution [33]. All these compounds didn't dissolute completely the polymeric layer, like it could be seen on **Table 2**:

Table 2. solubility in different solvents of several samples.

Sample	Solvent	Dissolution activity
Sample 1 finished layer	Distilled water	Negative
	DMSO	Partially
	THF	Negative
	Chloroform	Polymer separation
	Acetonitrile	Negative
	Ethanol	Negative
	n-hexane	Negative
	DCM	Negative
	Cyclohexanone	Polymer separation
	Acetone	Negative
	Methyl tert-butyl ether	Negative
	Toluene	Negative
	Butanone	Negative
	Methyl acetate	Negative
	Ethylene glycol	Negative
	DMS	Negative
	Dioxane	Negative
	DMF	Partially
Sample 1 uncolored finished layer	THF	Negative
	Acetone	Negative
	Acetonitrile	Negative
	Methanol	Negative
	Distiller water	Negative
	Toluene	Negative
	DCM	Negative
	DMF (100°C)	Negative
	Dioxane	Negative
Sample 2 finished layer	DMSO	Partially
Sample 3 finished layer	DMSO	Negative

DMSO and DMF were the only solvents that could dissolute certainly one layer (the colored) and only in two samples (not in *sample 3*). After that, some lipophilic and hydrophilic common solvents were tried, to check which direction must be followed. But, also in these cases, there weren't exhaustive results. It could be possible that PU were particularly substituted and functionalized, so they weren't reactive like the simplest and normal forms [34]. The polymers separation seen in **Figure 3**, by cyclohexanone and chloroform, permitted to analyze better the uncolored layer, without the presence of the colored one. Furthermore, thanks to these solvents, samples were prepare for other analysis. The uncolored finished layer was tested with, mainly, solvents seemed unactive. Them were used because, if the uncoloured part was dissolved, it become undetectable on the colored finished layer of *sample 1*.

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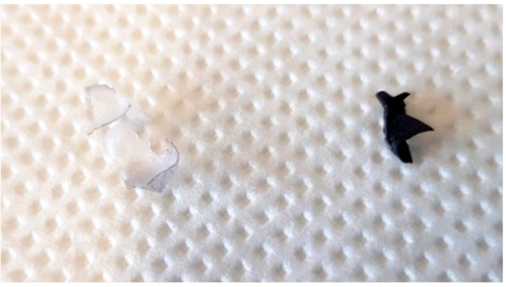


Figure 3. separation of polymeric finished layers.

After this first assay, it was decided to analyse samples in solid state, thanks to the poor solubility.

FTIR

In case of infrared spectroscopy, it was used for the identification of the polymeric layer. The finished layers of all three main *samples* and the separated pieces of *sample 1* were analyzed; they belonged to the same polymer family: polyurethanes (PU). In fact, the substance that was made up, was possible to determine, with a good approximation. This was done by the amount of infrared radiation absorbed analysis, or transmitted, by a sample.

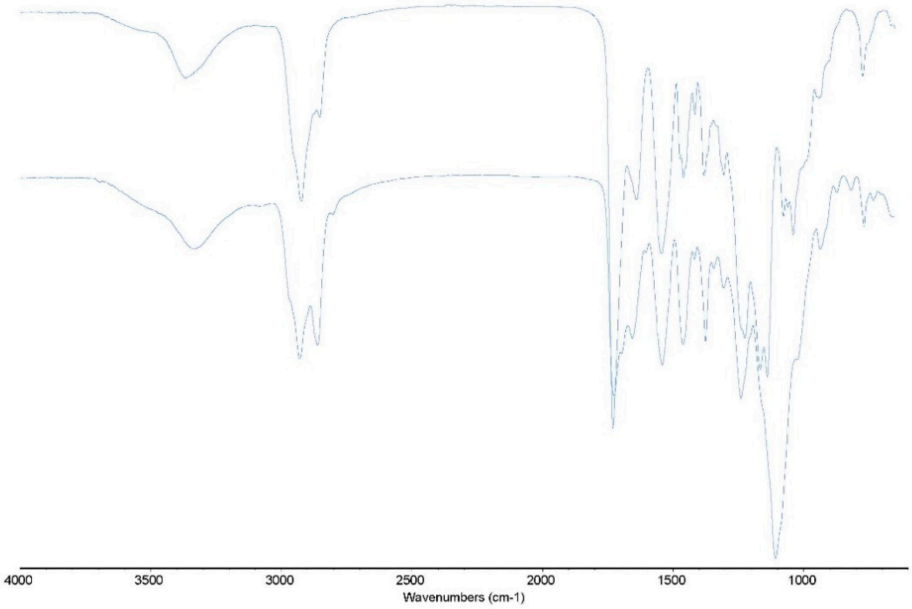


Figure 4. FTIR representative spectra, here it is showed the case of *sample* 1, on the top outside finished layer and down the underside leather layer.

There were some differences in substituents, in quantity of CO and NH isocyanides. It confirmed the mixture of different polymers and the variety of them in similar *samples*. Where they were a mixture of several substances, the general characterization, became more complex. Fortunately, the resulting spectra were very similar. In particular: at 3300-3500 cm^{-1} there was the normal NH stretching of amines, at 2850-3000 cm^{-1} there was the usual CH stretching of alkanes, at 1630-1750 there was the ordinary CO stretching of amides and esters, at 1500-1690 cm^{-1} there was the classic NH scissoring of amines and amides, at 1350-1440 cm^{-1} there was the usual CH deformation of alkanes, at 1000-1300 there was the common CO stretching of esters, at 1000-1250 cm^{-1} there was the ordinary CN stretching of amines, at 720-725 cm^{-1} there was CH rocking of alkanes and at 660-900 cm^{-1} there was the ordinary NH wagging of amines. It has to bring in mind that 900-600 cm^{-1} area is the fingerprints, characteristic area of everly particular compound. All these signals represented functional groups of polyurethanes. An overlapping of the polymer species spectrum with a general PU (aliphatic PU from amine exended polyesther ATR ZnSe) in **Figure 5** was also done, to be sure of in case of uncolored finished layer. It confirmed the polymeric main structure, so these spectra were compared to find more characteristics of analyzed polymers. An accurate spectra analyses, arrived from a peak interpretation and a comparison with polymer libraries reveals that the outside layer, coloured and soluble on DMSO and DMF, was PU with aliphatic chains. The inside layer in front of leather, maybe the uncoloured, insoluble and shiny one was mainly ether-based PU [35].

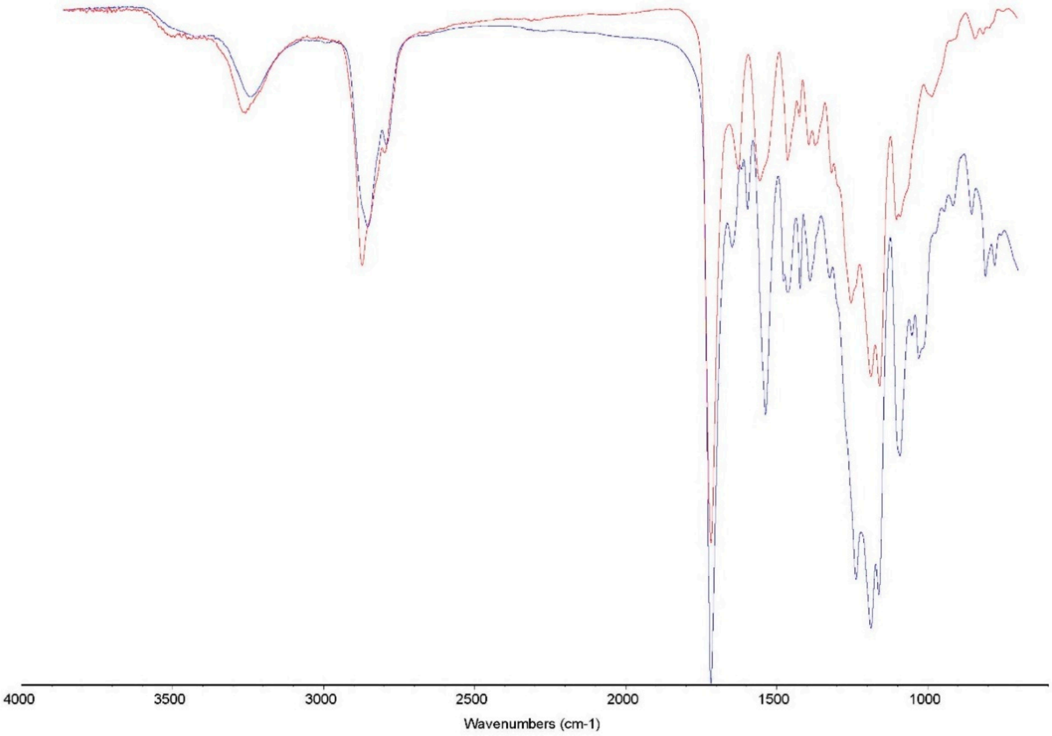


Figure 5. uncolored layer (blue, down line) and a classic polyurethane (red, upper line) overlay.

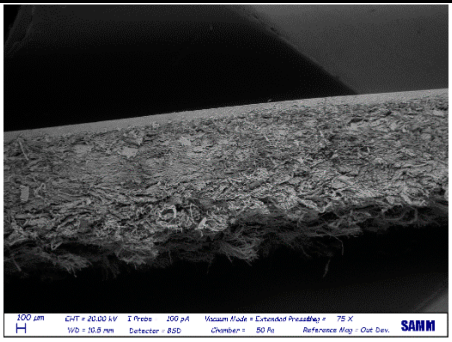
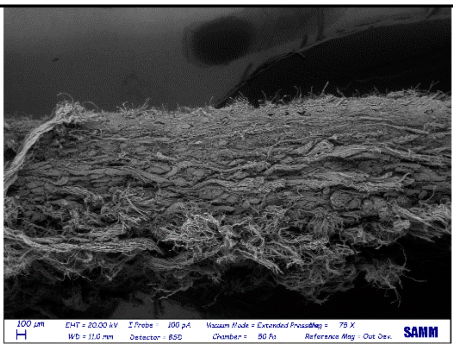
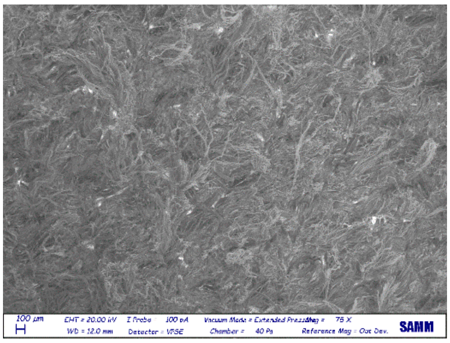
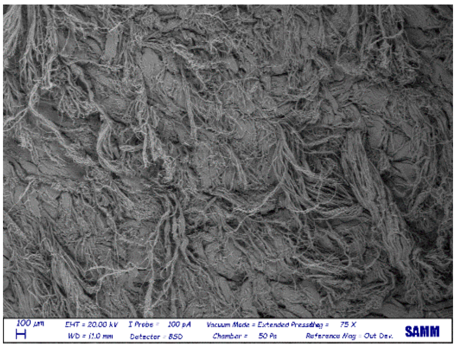
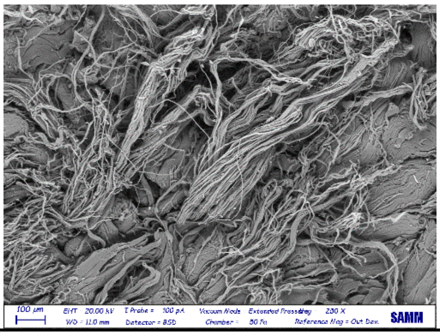
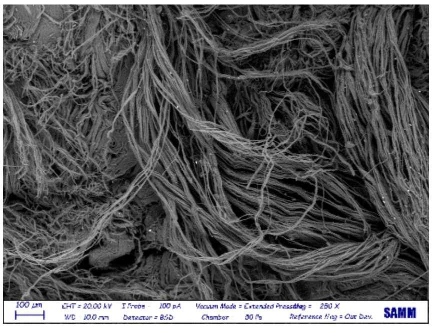
These results confirmed also that the polyurethane used is functionalized and different from the normal one and it could permit an explatation of why it was so difficult to dissolve these layers. Also, generally in the finishing step, leather surface changes some characteristics thanks to not only one product, but more and usually they are a mixed products [36]. Another interest confirmation, is the completely absence of collagen [37]. It was an important result to exclude the leather damages or cryogenic substrate removal. This was a further confirmation of method effectiveness and validation.

SEM

Despite directly by a visual analysis, it could be possible to see if leather turned in crust state; for a better comprehension, this kind of microscopy was done [38]. This analysis was done for a better visual of top, down and side of leather: before and after finished layer remotion. Them reveals an important leather surface modification, a witness of an high changing on the collagen fibres status. It permitted to observe the collagen fibers disposition and confirmed the completely polymer removal (**Table 3**).

Table 3. SEM images, before and after nitrogen treatment collagen status.

Sample	Before	After

leather side		
leather top		
leather down		

These fibers changed status, from more compact and tidier to free and messy. Normally, with the polymeric layer, these are more orderly and bonded. If this part will be removed, these become more free and superficially untied, ready to a new finishing treatment, centring perfectly the objective of this innovative recycling method [39]. This could demonstrate the complete polymer removal. In fact the finished layer deposition is the step that could start to take a correct disposition, according with fashion and customer taste.

A possible problem could be the modification of all leather layers in case of stability and collagen disposition, maybe for the contact with very low temperature. But a reassurance about that arrived from SEM images “leather down”, In particular the collagen fibers not directly interested of remotion. It permitted to demonstrate if there could be a leather modification, after this treatment at -200°C. With a careful observation, collagen fibers stayed in similar disposition and conformation, without any particular changes.

So, these images demonstrated the innovative capacity of this new removal method and differentiated it from the others partial disruptive methods to recycle leather [40].

Tensile strength according to UNI EN ISO 3376:2020

This normative was applied to check if there were differentiations in terms of qualities on leather and permitted to be sure about the crust leather resistance, after nitrogen treatment. Samples were compared with and without treatment and generally, leather with finished layer had more resistance than without. The polymers structure reinforcement thanks the more contribute. At the same time, these results were expected to be really like the normal resistance values. So, it could be possible to demonstrate the good resistance of leather, also after nitrogen treatment.

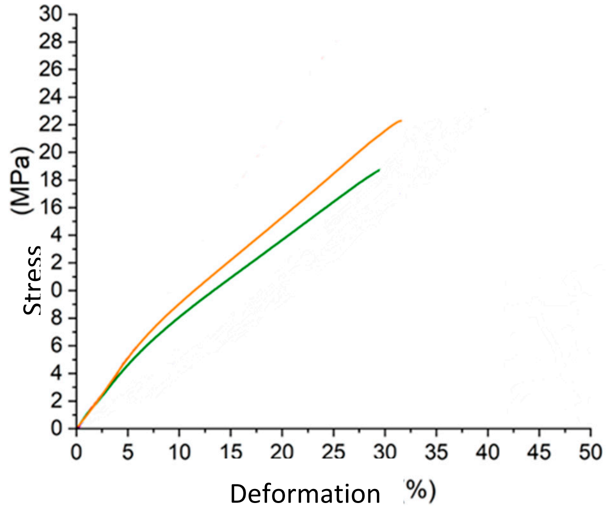


Figure 6. stress/deformation chart obtained by tensile tests at 23°C. As representative case, it was used *sample 2*, green line with finished layer and yellow line without by the application of cryogenic method.

Surprisingly, leather with this treatment not only remained with similar resistance, but in one case over three, it improved its strength characteristics (**Table 4**) [41]. This is because, generally, the finishing operations are done to take mainly some visual effects, touch effects and permeation resistance [42]. It is important and in base of which kind of polymers are applied, it could change lots characteristic quatities. So, the tensile resistance isn't the main discriminative characteristic in this kind of leather. Or to say better, it has already high resistance and a little decrease does not pay high attention. It could be due to the collagen fibres compression and less elasticity of polymers applied on this substrate. Anyway, these results were quite similar between the same sample, so these were a very positive answers for this new method. Interest was about the brown sample (*sample 2*) that apparently was like *sample 1,* but experimentally it had a stronger resistance and a different profile. Before there was a high stress resistance and after that the slop was less, remaining high. Another way to see these important results is **Table 4**.

Table 4. main values evaluated on tensile strength assay; the entries represented 1: blanck *sample 1*; 2: *sample 1* with cryogenic method; 3: blanck *sample 2*; 4: *sample 2* with cryogenic method; 5: *sample 3*; 6: *sample 3* with cryogenic method (with cryogenic method means without finished layer).

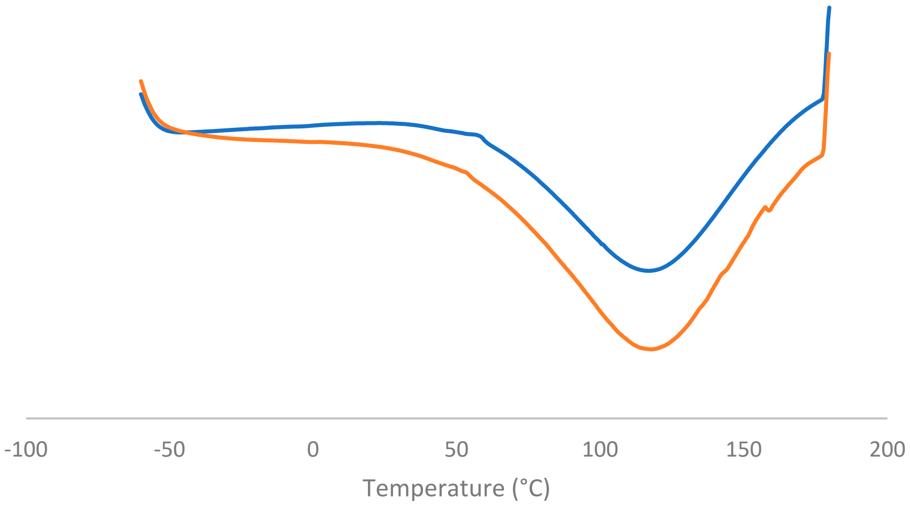
Entry	Deformation at maximum stress (%)	Maximum stress (MPa)
1	36.7	20.6
2	40.4	23.4
3	31.6	22.3
4	29.8	18.7
5	35.1	22.3
6	34.1	20.4

These results opened doors to the possible real affirmation of this new method, in terms of performances and results qualities. In fact, products had very high performances and it permitted to be the best substrate for another finishing step finally.

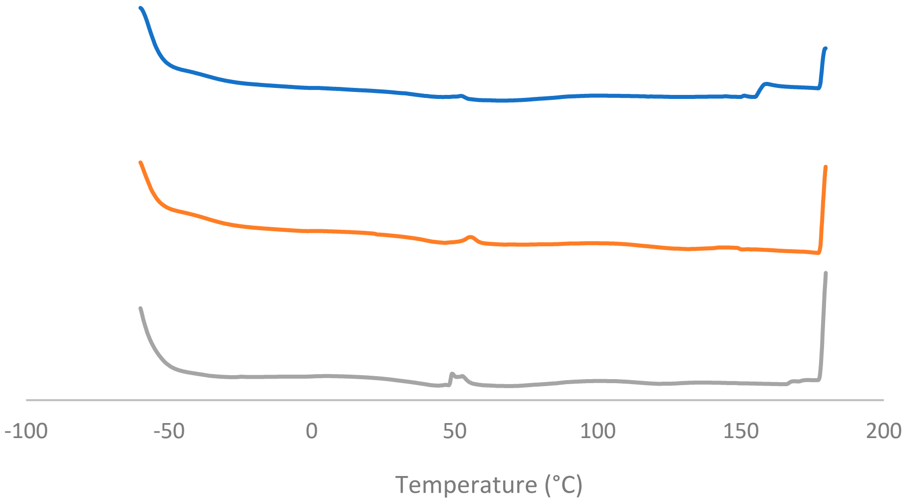
DSC

doi:10.20944/preprints202308.0681.v1

This kind of analysis was used to characterize and for a better understanding of thermal behavior of leather, after nitrogen method and polymeric layer [43]. It represented if there were differentiation in terms of exo and endothermic transformation, between -60 and 180°C. To be sure of that, two completely cycles (from cold to hot and from hot to cold) were done. It could confirm the results and said what was the materials attitude. The thermograms were grouped in terms of *samples*, charts were done like heat flow referred on temperature or time. In this article, it could be seen the black sample thermogram, (**Figure 7**) representative of the others samples.



(**a**)



(**b**)

Figure 7. DSC charts (temperature vs heat flow) : **a)** leather thermograms, from below: orange line was for *sample 1* without finished layer and blue line was for blanck *sample 1* and; **b**) it represented the overlay of all finished layers, from below, grey line for light brown (from *sample* 3), orange line for black (from *sample* 1) and blue line for brown (from *sample* 2).

From leather graphs, the first interesting phenomenon was about the great endothermic curve during the first heat cycle. It seems to correspond to water evaporation, an endothermal transformation that after the first cycle. But in reality it was a glass transition [44], assessable also in four cycle charts, thanks to the partial reversibilty of collagen; for this reason the third cycle was different from the first one. The profile was similar of all the kinds of leather, with a marked difference only on the relaxing trend. It was interest the exothermic curve at 60-80°C, maybe due to a possible mechanism that could happened only in case of leather plus polymer. The comparison of leather with and without finished layer, represented the protection polymer property to the heat flux. It was useful for a better determination of samples characteristics. At the same time, the changing on them after and before nitrogen, generally respected the normal thermal behaviour without so strong differences. It was a further confirmation, of the high qualities remaining inside treated leather. In **b** it was possible to see a regular thermal profile, without any great changes. The more defined and regular curve demonstrated: a similar physical status of all PU on leather and similarity on thermal characteristics in this range of temperature. The first endotermal curve, that represented the glass transition was around -50°C and the first exotermal curve that represented the cristallization process was around 50°C [45]. Anyway, the substantial difference of **b** with the others, attested another time the absence of leather with finished layer.

TGA-TMA

This analysis was done for a comparison with DSC, to know what happened at high temperature on substrate samples and to check if it was possible to do a weight loss analysis [46]. The behavior, was studied between 30 and 900°C. It permitted to have a complete panoramic of all the main characteristics of these materials, as well as better understand of polymeric role [47]. Results could be well explicated by *sample 1* thermogram (**Figure 8**).

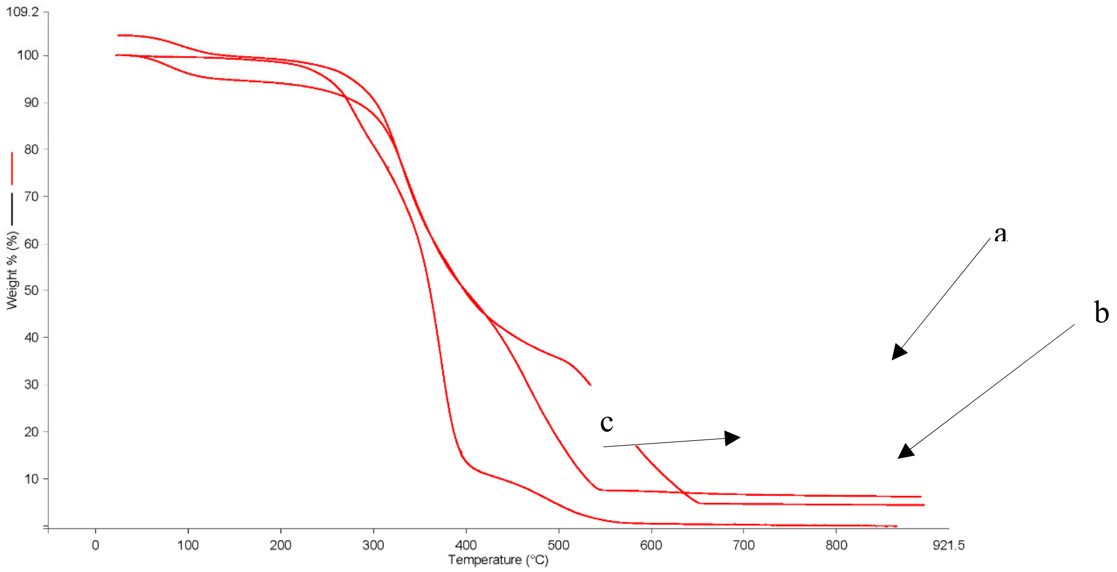


Figure 8. **a**) blank test *sample 1*; **b**) leather of *sample 1*; **c**) finished layer of *sample 1*.

It was possible to see similar transition peaks and weight loss range in **a** and **b**. At same time, there were high differences in **c**, with one main transition in a short temperature range. Unfortunately, the decomposition of polymer and leather started at the same temperature. For this reason, it wasn't possible to separate and quantify them by an isotherm. Another interest aspect was the protection of leather thanks to this polymeric layer at high temperature, in fact all three samples had represented this situation. A particular characteristic, like on tensile strength analysis, is the high resistance of *sample 2*. It wasn't thanks only to mechanical properties, but also in thermal qualities. temperature It happened some phenomena: in case of leather, the remaining weight is the inorganic part, chromium mainly (judging by the colour). Another is the indirectly leather weight diminution, in line with the DSC behaviour, to attest the undefined and different status of collagenic structures. Similar was the case of polymers. Another result that confirmed the DSC discussions, was the major temperature resistance of blank protected leather [48]. About polymers, they had all a similar behavior, they started a fast decomposition. For the cryogenic delamination method, TGA-TMA represented the possibility to attest the absence of leather in polymer, as in DSC. It was a useful analysis for a comparison of these techniques, for a thermal results validation and to have a complete idea of thermal behavior first and after nitrogen.

By all these analyses it was possible to check the potentialities of nitrogen finished layer removal method. It has to be better developed, but these data encourage this new principle, that could change the recycling field. Costs are the limiting factor, but with the unique versatility and the new improving leather value, it will be possible to be an important opportunity.

4. Conclusions

The global population grows up every day, but world has the same area. So, the only possibility to survive in good condition without a marked footprint, the chance to develop and improve human life, is a sustainable approach. It must pay attention to a lot of different things, that years ago weren't focalized. It has to improve value of many things that, for years and years before, were only considered wastes. But this is the better way to walk, for continuing to live together, according to Sustainable Development Goals (SDGs) of United Nations (UN). In this scenario, the article indicates one possible solution to take value, or for improving the leather scraps value. Maybe it could be seen like something not so important, compared the huge problems of environmental changes, carbon footprint etc... But all is connected and a reinforcement of circular economy in leather industry, could become an important brick for all other steps, for improving the sustainability of this sector. The use of liquid nitrogen for scraps revaluation rest a surprising solution and the primary resource could become easy to restore, in a closed system. Also, the machines that will use this technology will work in continuous and in common, like one per district. This approach must be placed in a liquid nitrogen engine potential revolution with all the challenges and developments in future.

5. Patents

P07501/IT

Author Contributions: Conceptualization, Maurizio Masi; Data curation, Filippo Rossi; Formal analysis, Omar Salmi and Simone Gelosa; Funding acquisition, Filippo Rossi; Investigation, Omar Salmi; Methodology, Omar Salmi, Simone Gelosa, Filippo Rossi and Maurizio Masi; Project administration, Filippo Rossi and Maurizio Masi; Resources, Omar Salmi; Supervision, Maurizio Masi; Validation, Omar Salmi and Simone Gelosa; Visualization, Filippo Rossi; Writing – original draft, Omar Salmi; Writing – review & editing, Filippo Rossi and Maurizio Masi.

Funding: This research received no funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank Dr. Fabio Pizzetti for the analysis support.

Conflicts of Interest: The authors declare no conflict of interest. The sponsors had no role in the design, execution, interpretation, or writing of the study.

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