GSC GROUP PERSPECTIVE TOWARDS IMPLEMENTATION OF BIO-BASED CHEMICALS FOR A GREENER LEATHER TECHNOLOGY

Federico Lombardo,[1] Riccardo Pasquale,[1] Tomaso Pellegrini,[1] and Francesco Serafini[1]

[1]GSC Group S.P.A., Via dell'industria, 5, 36054 Montebello Vic.no, Vicenza Italy, +39 0444 670949, federicolombardo@gscspa.it, riccardopasquale@gscspa.it , tomasopellegrini@gscspa.it and francescoserafini@gscspa.it

ABSTRACT
Recently, global and new EU perspectives are driving the needs for the development of new materials less environmental impacting; besides, the interest in protecting the environment by not only using products made from fossil fuels as raw materials but the utilisation of natural renewable resources has been steadily and rapidly increasing. The leather industry has already embraced such enterprise, and is already committed for the reduction of hazardous chemicals and the utilisation of new and renewable substances for the leather processing. *Bio-based* derivatives are gaining remarkable importance for the leather processing, thus becoming more and more impacting and effective in the supply chain of the raw materials for leather processing. However, despite such efforts, it is still quite debatable whether such chemicals might perform equally to their actual fossil-fuels counterparts: this investigation showed how *bio-based* chemicals can eventually replace the fossil-fuels derivatives. In addition, an overall overview of the tanning, retanning and finishing processes and the chemicals involved with respect to the *bio- based* content have been carried out: The investigators focused on the estimation and the measurement of *bio-based* derivatives contribution to each phase of the leather processing, their application and therefore the assessment of the leather performances. As a result, a correlation between *bio-based*, fossil contents and the leather performances were established, aiming at demonstrating the possibility of highly quality leather production with less impacting chemicals and therefore a more sustainable process.

Keywords: leather, bio-based, circularity, sustainability.

1. Introduction

The unprecedent increase in GHGs atmospheric concentration due to anthropogenic activities and more specifically industrialisation has prompted the need and the scouting for novel and alternative solution to tackle environmental degradation.

Climate change is indeed one of such consequences and it represents a subject of concern for all humankind.

The concept of sustainable development has then intertwined within industry and the entire social compartment, questioning the way mankind uses its resources, the design of the processes and the waste generation.[1] Ultimately, industry must face this challenge *via* the implementation of less environmental impacting technologies; alternatively, industry should address its attention to the utilisation and evaluation of alternative raw materials and the substitution of fossil fuel derivatives to reduce carbon footprint and overall emissions.

Sustainable resources for industrial production are the pillar for a sustainable economic growth, and raw materials based on fossil fuels are then not considered sustainable and therefore they must be replaced by less impacting materials such as *bio-based* derivatives.

The preparation of industrial products from agricultural raw materials is a concept defined in 1920 as *chemurgy* and defined the positive synergy between farmers and automotive industry, which led to the utilisation of natural products such as hemp and soybean to build the car interiors.

Such concept was very close to the more actual and modern term *bio-based*, which essentially defines all the raw materials derived from a renewable source *via* biological processes, that making agriculture strictly intertwined with industry.[2]

Bio-based products include plant, animal or marine materials; these materials include all plant and animal mass derived from carbon dioxide (CO_2) recently fixed via photosynthesis, per definition of a renewable resource.[3]

The *European Community* EC describes *bio-based* products as those who are wholly or partly derived from materials of biological origin, excluding materials involved in geological formations and/or fossilised.[4] Despite such promising results, approximately in 1950 *chemurgy* was abandoned and almost entirely replaced with petrochemical raw material.[5]

The reason for that was due to the cheaper and more competitive availability of raw materials based on petrochemicals. However, was it only a market reason? Were there any practical issues and/or technical drawbacks in using the *bio-based* materials?

The outlook with respect to the leather industry reflects the same trend: within the past few years, the utilisation of *bio-based* raw materials had constantly increased, taking a remarkable share of the overall chemical productions. Besides, the leather industry has always relied on *chemurgy* and agriculture raw materials: natural oils such as soy or rapeseed oils, lecithin, lignin, starch, caseins etc. are some of the most valuable examples of the integration between leather industry and *bio-based* materials.

Thus, their application is already part of consolidated *know-how* and all-day practise, although the scouting and recruitment of novel source of natural-based materials is still very important and crucial for the leather industry.

The investigators will then focus on the assessment of the *bio-based* materials, their qualification and quantification *via* UNI EN 16640 and EN 16785-2:2018, to provide a correct and exact estimation of the *bio-based* content with respect to the auxiliaries employed during the leather processing from the beamhouse to finishing.

Particular attention will be addressed on the tanning and retanning processes and the chemicals involved in such crucial steps.

2. Material and Methods

2.1 Bio-based evaluation

^{14}C determination was carried out according to UNI EN 16640 using radiocarbon analysis by a third- part laboratory.[a]

The method involves the tracking of the radioactive ^{14}C isotope which occurs naturally in all living organisms (plants, animals etc.) in a fixed concentration of 1.2x10-12 %.

This data expresses the radioactive activity of C14 which decays with a half-life of about 5700 years once the organism is no longer alive.

The third-part laboratory carried out the analyses on leather samples and on finishing products to provide qualitative and quantitative assessment of the ^{14}C.

The investigators focused on the estimation of the *bio-based* carbon content of the auxiliaries using the EN 16785-2:2018 as reference.

[a] Both ASTM D6866-21 and UNI EN 16640 use radiocarbon method for the assessment of the *bio-based* carbon. They differ in the definition of the *bio-based* carbon: ASTM D6866-21 refers to *bio-based* carbon with respect to the organic carbon of the targeted product, whilst the UNI EN 16640 refers to the total carbon.

2.2 Leather application

2.2.1 Wet-end application

Wet-end procedures for tanning, retanning and fatiquoring have been herein reported and have not involved commercial trade names.

Phase	Class of auxiliary	Utilisation (%)	Biobased content (%)
TANNING	Auxiliary	0,50%	0,00%
	Fatliquor	0,40%	23,99%
	Preserving agent	0,20%	0,00%
	Tannin	1,00%	47,00%
	Tannin	10,00%	100,00%
	Tanning agent	10,00%	0,00%
	Water	130,00%	0,00%
CRUST	Fatliquor	2,00%	78,28%
	Fatliquor	7,50%	82,94%
	Formic acid	4,50%	0,00%
	Polymer	2,00%	0,00%
	Surfactant	0,30%	0,00%
	Tannin	8,00%	29,16%
	Tannin	8,00%	100,00%
	Tannin	20,00%	100,00%
	Water	650,00%	0,00%

Table 1: Representative application formula for chemical application (AVO technology, tanning and retanning).

Phase	Class of auxiliary	Utilisation (%)	Biobased content (%)
TANNING	Formic acid	0,15%	0,00%
	Neutralising agent	0,52%	0,00%
	Preserving agent	0,10%	0,00%
	Tanning agent	12,00%	0,00%
	Water	190,00%	0,00%
CRUST	Auxiliary	2,50%	0,00%
	Dyestuff	4,00%	0,00%
	Fatliquor	1,00%	0,00%
	Fatliquor	3,00%	0,00%
	Fatliquor	3,50%	63,20%
	Fatliquor	8,00%	82,94%
	Formic acid	4,00%	0,00%
	Neutralising agent	2,00%	0,00%
	Polymer	1,00%	0,00%
	Polymer	3,00%	0,00%
	Polymer	4,00%	50,00%
	Polymer	4,00%	100,00%
	Preserving agent	0,10%	0,00%
	Surfactant	1,00%	0,00%
	Tannin	1,00%	0,00%
	Tannin	4,00%	0,00%
	Tannin	5,00%	0,00%
	Tannin	6,00%	0,00%
	Tanning agent	2,00%	0,00%
	Tanning agent	3,00%	0,00%
	Water	1689,00%	0,00%

Table 2: Representative application formula for chemical application (chromium technology, tanning and retanning).

Phase	Class of auxiliary	Utilisation (%)	Biobased content (%)
TANNING	Fatliquor	1,00%	23,99%
	Neutralising agent	0,40%	0,00%
	Preserving agent	0,20%	0,00%
	Surfactant	1,00%	0,00%
	Tannin	2,00%	0,00%
	Tanning agent	2,50%	0,00%
	Water	100,00%	0,00%
CRUST	Fatliquor	0,50%	78,28%
	Fatliquor	1,50%	78,28%
	Fatliquor	1,50%	89,24%
	Fatliquor	2,00%	89,24%
	Fatliquor	4,00%	89,24%
	Formic acid	1,00%	0,00%
	Formic acid	1,50%	0,00%
	Formic acid	2,00%	0,00%
	Polymer	2,00%	57,00%
	Polymer	5,00%	0,00%
	Surfactant	0,30%	0,00%
	Tannin	3,00%	0,00%
	Tannin	18,00%	29,00%
	Tannin	18,00%	29,14%
	Water	50,00%	0,00%
	Water	150,00%	0,00%
	Water	200,00%	0,00%
	Water	250,00%	0,00%

Table 3: Representative application formula for chemical application (glutaraldehyde technology, tanning and retanning).

Phase	Class of auxiliary	Utilisation (%)	Biobased content (%)
TANNING	Fatliquor	1,00%	64,42%
	Neutralising agent	0,10%	0,00%
	Neutralising agent	0,15%	0,00%
	Silicone auxiliary	0,10%	0,00%
	Slipping agent	0,10%	35,00%
	Tanning agent	4,00%	0,00%
	Tanning agent	5,00%	23,00%
	Tanning agent	7,00%	35,00%
	Water	100,00%	0,00%
	Water	200,00%	0,00%
CRUST	Auxiliary	0,20%	0,00%
	Auxiliary	2,00%	0,00%
	Auxiliary	3,00%	0,00%
	Dyestuff	2,00%	0,00%
	Fatliquor	1,00%	78,28%
	Fatliquor	1,00%	89,24%
	Fatliquor	1,00%	91,25%
	Fatliquor	3,00%	78,28%
	Fatliquor	3,00%	89,24%
	Fatliquor	5,00%	89,24%
	Fatliquor	6,00%	0,00%
	Formic acid	2,00%	0,00%
	Polymer	2,00%	57,00%
	Polymer	4,00%	0,00%
	Surfactant	0,50%	0,00%
	Tannin	2,00%	0,00%
	Tannin	2,00%	100,00%
	Tannin	2,40%	0,00%
	Tannin	3,00%	58,00%
	Tannin	4,00%	0,00%
	Tannin	4,00%	100,00%
	Tannin	4,80%	100,00%
	Water	50,00%	0,00%
	Water	100,00%	0,00%
	Water	150,00%	0,00%
	Water	200,00%	0,00%

Table 4: Representative application formula for chemical application (GOAST technology, tanning and retanning).

Phase	Class of auxiliary	Utilisation (%)	Biobased content (%)
TANNING	Fatliquor	1,00%	64,42%
	Formic acid	0,20%	0,00%
	Neutralising agent	1,80%	0,00%
	Preserving agent	0,30%	0,00%
	Slipping agent	0,20%	35,00%
	Tannin	3,00%	0,00%
	Tannin	16,00%	100,00%
	Tanning agent	1,00%	0,00%
	Tanning agent	2,20%	0,00%
	Water	200,00%	0,00%
CRUST	Fatliquor	2,00%	0,00%
	Fatliquor	3,00%	0,00%
	Fatliquor	4,00%	63,20%
	Fatliquor	7,00%	82,94%
	Formic acid	1,00%	0,00%
	Formic acid	2,00%	0,00%
	Polymer	4,00%	0,00%
	Polymer	5,00%	100,00%
	Polymer	6,00%	0,00%
	Preserving agent	0,15%	0,00%
	Slipping agent	0,50%	35,00%
	Tannin	0,50%	0,00%
	Tannin	3,00%	0,00%
	Tannin	6,00%	0,00%
	Tannin	6,00%	100,00%
	Tannin	12,00%	0,00%
	Water	1360,00%	0,00%

Table 5: Representative application formula for chemical application (vegetable extracts tanning technology, tanning and retanning).

2.2.2 Finishing application

General procedure for the finishing systems (standard and enriched in bio-based content) are depicted in Table 6, Table 7 and Table 8. All the layers were dried for 90 seconds at 80°C.

Standard-Products	Bio Content %	T.S. %	Preground	Ground	Intermediate for Embossing	Hybrid	Topcoat
Pigment Black	-	38	50	120		80	10
Preground PU based	-	25	950				
Crosslinker NCO (21,5 NCO)	-	100	10				
Water				150	500		
Silica Duller	-	17		150			
Naural Waxes emulsion	75	20		30			
Polyether Pu	-	30		400			
Polyether Pu	-	35		150			
Rheology Modifier	-	12		10			
Crosslinker NCO (21,5 NCO)	-			10			
Inherent Matt Polyurethane	-	15			500		
Water						75	185
High wear resistance silicone	-	60				30	60
Soft touch silicone	-	50					30
Inherent Matt Polyurethane	-	28				250	250
Silica Matt Polyurethane	-	27				250	250
Polyether soft pu	-	35				100	100
Polyether soft pu	-	30				200	
Polyether hard pu	-	35					100
Levelling agent	-	33				15	15
Rheology Modifier	-	12				10	10
Crosslinker NCO (21,5 NCO)	-	100				55	55
Wet grams per square foot applied			**4**	**9**	**1,5**	**4**	**2 x 2,5**

Table 6: standard finishing formula.

Bio-Products 1	Bio Content %	T.S. %	Preground	Ground	Intermediate for Embossing	Hybrid	Topcoat
Pigment Black	97	38	50	120		80	10
Preground PU based	67	27	950				
Crosslinker Bio-NCO(16 NCO)	16	100	10				
Water				150	500		
Silica Duller	-	17		150			
Naural Waxes emulsion	75	20		30			
Polyether Pu	70	30		400			
Polyether Pu	53	38		150			
Rheology Modifier	-	12		10			
Crosslinker Bio-NCO(16 NCO)	16			10			
Inherent Matt Polyurethane	65	15			500		
Water						75	185
High wear resistance silicone	-	60				30	60
Soft touch silicone	-	50					30
Inherent Matt Polyurethane	64	31				250	250
Silica Matt Polyurethane	66	35				250	250
Polyether soft pu	53	38				100	100
Polyether soft pu	70	30				200	
Polyether hard pu	51	32					100
Levelling agent	-	33				15	15
Rheology Modifier	-	12				10	10
Crosslinker Bio-NCO (16 NCO)	16	100				55	55
Wet grams per square foot applied			**3**	**8**	**1,5**	**4**	**2 x 2,5**

Table 7: bio-based version 1 finishing formula.

Bio-Product 2	Bio Content %	T.S. %	Preground	Ground	Intermediate for Embossing	Hybrid	Topcoat
Pigment Black	97	38	50	120		80	10
Preground PU based	67	27	950				
Crosslinker Bio-NCO (16 NCO)	16	100	15				
Water				150	500		
Silica Duller	-	17		150			
Naural Waxes emulsion	75	20		30			
Polyether Pu	70	30		400			
Polyether Pu	53	38		150			
Rheology Modifier	-	12		10			
Crosslinker Bio-NCO (16 NCO)	16			15			
Inherent Matt Polyurethane	65	15			500		
Water						75	185
High wear resistance silicone	-	60				30	60
Soft touch silicone	-	50					30
Inherent Matt Polyurethane	64	31				250	250
Silica Matt Polyurethane	66	35				250	250
Polyether soft pu	53	38				100	100
Polyether soft pu	70	30				200	
Polyether hard pu	51	32					100
Levelling agent	-	33				15	15
Rheology Modifier	-	12				10	10
Crosslinker NCO (16 NCO)	16	100				90	90
Wet grams per square foot applied			**3**	**8**	**1,5**	**4**	**2 x 2,5**

Table 8: bio-based version 2 finishing formula.

2.3 Coating application on release-paper

The investigation used also specially designed release-paper as substrate to normalized any potential difference of matrixes. The application of the auxiliaries was carried out using a *BYKO-DRIVE AUTO APPLICATOR 2122* from BYK and the appropriate spiral-bar coater, followed by drying via forced air oven at 105°C (UF 55 from *Memmert*). The leather auxiliaries involved in the project implementation were provided and produced by GSC Group spa, and included PREGOUND, GROUND, INTERMEDIATE FOR EMBOSSING, BASECOAT, TOPCOAT and SILICONE auxiliaries.

Products	T.S. %	Application	Thik. µ	Forced Air Drying 2' at 105 °C
Preground	27	1 Application Film 100 µm	27	
Ground + 1% (100%,16% NCO)	30	1 Application Film 100 µm	30	Forced Air Drying 2' at 105 °C
Intermediate for Embossing	15	1 Application Film 50 µm	7.5	Forced Air Drying 2' at 105 °C
Hybrid	23,5	1 Application Film 50 µm	11.7	Forced Air Drying 2' at 105 °C
Topcoat	27	1 Application Film 50 µm	13.5	Forced Air Drying 2' at 105 °C
Topcoat	27	1 Application Film 50 µm	13.5	Forced Air Drying 2' at 105 °C

Table 9:standard chemicals formulation for coating

Products	T.S. %	Bio%	Application	Thik. µ	Dry Condition
Preground 11912/5	27	67	1 Application Film 100 µm	27	Forced Air Drying 2' at 105 °C
Ground 11922/B3	30	35	1 Application Film 100 µm	30	Forced Air Drying 2' at 105 °C
Intermediate for Embossing 11923/1	15	65	1 Application Film 50 µm	7.5	Forced Air Drying 2' at 105 °C
Hybrid 11921/1	23,5	60	1 Application Film 50 µm	11.7	Forced Air Drying 2' at 105 °C
Topcoat 11921/2	27	55	1 Application Film 50 µm	13.5	Forced Air Drying 2' at 105 °C
Topcoat 11921/2	27	55	1 Application Film 50 µm	13.5	Forced Air Drying 2' at 105 °C

Table 10: bio-based chemicals formulation for coating

2.4 Physical and Mechanical Testings

The quality of the leather was also assessed and characterised through standard automotive tests such as stick-slip, abrasion trials with Taber tester and Martindale machine, ball plate method, fogging test; rub fastness provided with Veslic tester (wet, dry, alcohol, gasoline), dry-rubbing trial with *Gakushin* tester. For this study, the physical and mechanical tests for stick-slip, abrasion and rub-fastness are reported. Fogging tests, cold flexometry and abrasion tests were also carried out.

2.5 Chemical analyses

VOC determination was carried out according to PV3341 on a GC-MS (*Clarus 580* instrument from *Perkin Elmer* with a *SQ8 S* detector EI equipped with an *ELITE-624 MS* capillary column 30 mt x 0.25 mm i.d. and hydrogen as carrier gas), static headspace combined with a *Turbomatrix HS 40 TRAP* from *Perkin Elmer*, using hydrogen as carrier gas. Aldehydes detection was performed according to ISO 17226-1:2019 using HPLC from *Perkin Elmer ALTUS A-10* equipped with a C18 COLUMN 5 (150 x 4.6 mm) from *Perkin Elmer* and using diode-

array detector (DAD). Chrome VI according to ISO 17075- 1:2017 with spectrophotometer (colorimetric method).

3. Results and Discussion

It is important to underline the boundaries of this investigation in order to set the correct estimation of the *bio-based* content on leather, the auxiliaries involved in the leather processing and the relationship with respect to the leather performance. Thus, the investigators focused on the production of *automotive* leather and the evaluation of *bio-based* content of the chemicals used for the manufacture of such leather. The focus on *automotive* leather production is justified in view of the importance and the sensitivity of such market with respect to circular economy and sustainability.

3.1 The different tanning technologies used for this investigation: an outlook

The investigators focused on different tanning technologies (i.e., chromium, glutaraldehyde, GOAST technology, AVO technology and vegetable extract tannage) and the assessment of their *bio-based* content on tanned leather according to UNI EN 16640. In addition, they also compared the *crust* leather obtained from the abovementioned processes and assessed their *bio-based* content on leather according to UNI EN 16640. Furthermore, the investigators also focused on the auxiliaries involved in such process, particularly on their *bio-based* estimation according to EN 16785. An overall perspective of the tanning technologies considered within this investigation was provided in Table 11.

Tanning technology	Description	Features
AVO technology	Combination of natural and synthetic tanning auxiliaries based on the process of concentration and subsequent condensation of the OMWW (Oil Mill Wastewater).	Sustainable process in terms of circularity and utilisation of natural products.
Vegetable extracts tanning	Combination of natural and synthetic tanning auxiliaries from vegetable extracts.	Sustainable process in terms of circularity and utilisation of natural products. Utilisation of high quantities of water and chemicals
Chromium tanning	Mineral tanning based on chromium salts.	Consolidated technique.
Glutaraldehyde tanning	Aqueous solution of glutaraldehyde is employed for the tannage.	Utilisation of harmful substances.
GOAST technology	Natural and synthetic tanning auxiliaries combined with specially modified acrylic resins.	No harmful substances are involved within the tanning and retanning.

Table 11: tanning technologies considered for this investigation

The leathers produced with such different techniques were also tested for the chemical and physical performances. In addition, the application of the highly-improved *bio-based* finishing system and the standard benchmark were also tested on leather for the most important *automotive* specifications to assess whether enriched chemicals could lead to highly performance leather which might be eventually suitable for this application.

3.2 Bio-based assessment

3.2.1 Bio-based estimation on auxiliaries

The investigation begun by providing the assessment of the *bio-based* content on the leather auxiliaries involved within the tanning process; using the approach depicted in EN 16785, each auxiliary was considered in view of

its chemical composition to give its *bio-based* content with respect to the application formulae (see 2.2.1). Then, the investigators looked at the application of such chemicals within the specific process (i.e., quantity, time etc) and defined the amount of modern carbon per tanning and retanning phase. Such assessment provided relative estimation with respect to the application/technical procedure of the chemicals (it was not an absolute comparison). At a glance, the highest *bio-based* carbon contents (as aggregate for tanning and retanning) were found for AVO technology and vegetable extracts tanning (see Figure 1), whilst both chromium and glutaraldehyde techs showed the lowest; GOAST technology showed intermediate values. These results were expected since the chemistry for both AVO and vegetable extracts tanning systems rely on the utilisation of natural and renewable materials, that meaning they are expected to contribute to the modern carbon content.

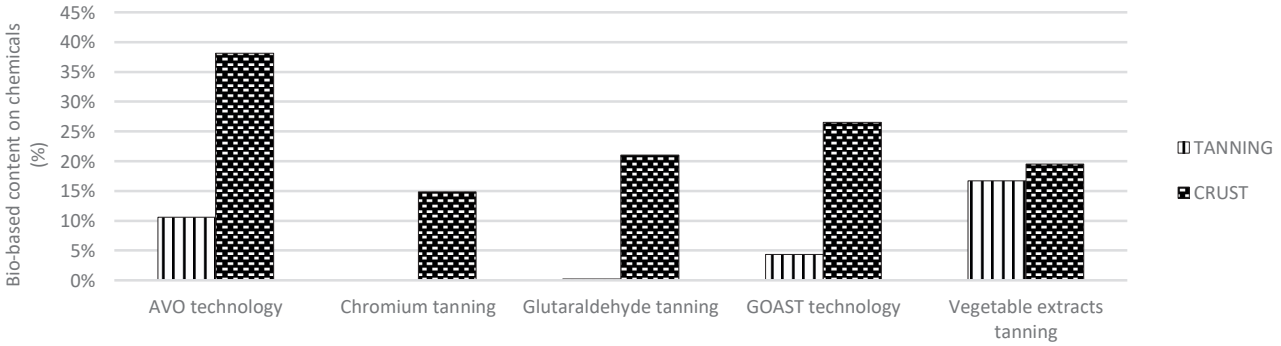


Figure 1: bio-based content from the chemicals with respect to different tanning technologies

3.2.2 Bio-based content estimation on leather

Leather *bio-based* content estimation and the final calculation were carried out according to UNI EN 16640 and UNI EN 13137. The estimation of *bio-based* carbon was initially expressed as the ratio between modern and fossil carbon as a percentage; besides, the estimation was carried also out considering the total carbon of the sample to finally provide its exact amount of modern and fossil carbon. Since the leather comes from breeding and belongs to the food industry, it has to be considered as a source of natural, renewable and modern carbon: its *bio-based* content is then accounted as 100% and has the highest score. A first set of analyses focused on the tannage technology; Figure 2 provides an overall perspective of the *bio-based* assessment for 5 tanned leathers obtained using different technologies. It summarises the ratio of fossil and modern carbon content and quantifies the fossil and *bio-based* carbon with respect to each specific total carbon content. Remarkably, the chromium sample showed the highest *bio-based* content with a 92% of modern carbon ratio, although it was not expected to be: this was due to the fact within such estimation the chromium salts used within the tannage are not accounted; besides, no synthetic organic agents have been used within the process, and therefore the fossil contribution was negligible. The chemistry which is behind the other tanning systems is different with respect to chromium tanning and relies on the utilisation of organic tanning agents: a difference on the ratio between fossil and modern carbon was then expected for the 4 samples. Thus, the results showed a *bio-based* ratio between 80 and 93%; the fossil contribution was higher on GOAST technology, whilst was lower in the vegetable tanning systems and AVO. Surprisingly, the glutaraldehyde tanned leather showed a 92% of *bio-based* content, which could be justified in view of the low amount of chemicals provided within the tannage, which is also showed in the *bio-based* contribution with respect to the total carbon content: the less chemicals are provided, the fewer the influence on the balance of the overall estimation.

Deeper considerations in terms of the carbon content and its qualification with respect to the fossil and modern ratio were also carried out. While looking at the leather substrates and in particular their elemental composition (carbon and nitrogen), the investigators were able to specifically assess the amount of fossil and modern carbon with respect to the total carbon content of each specific sample. In such way, it was possible to focus on the real amount and contribution of the fossil carbon throughout the leather processing.

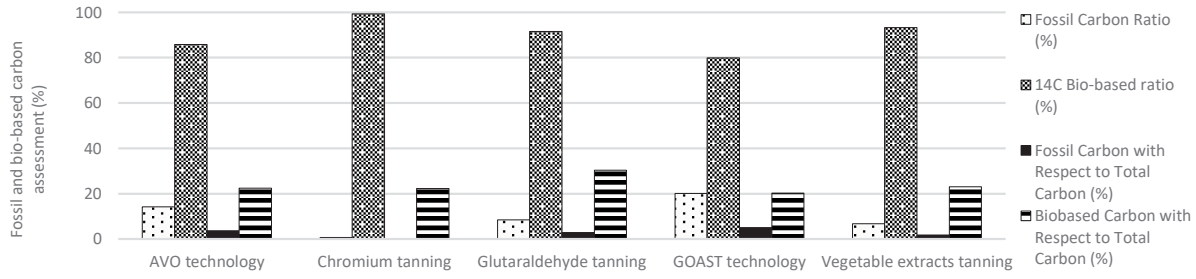


Figure 2: fossil and modern carbon ratio and content on tanned leathers.

The results were different with respect to the previous evaluation: Figure 2 showed then the real fossil and modern carbon content within the tanning stage and demonstrated how the fossil carbon content increased from the first to the latter step in view of the contribution of the chemicals (black and dashed columns). Following the same approach, Figure 3 depicted the ratio between fossil and modern carbon was assessed for the corresponding retanned leather (crust leathers).[b] Overall, the fossil contribution was found to be higher than in the tanning phase, showing a ratio between 17 to 32% of fossil carbon; this could be explained due to the contribution of the wider range of chemicals involved during the retanning step. Remarkably, the vegetable tanning technology showed consistent and high results in terms of the *bio-based* ratio and the carbon content; both AVO and glutaraldehyde technologies showed similar trend for the ratio, whilst the content with respect to the carbon was found to be lower. GOAST technology showed similar results compared to the others, although slightly lower.

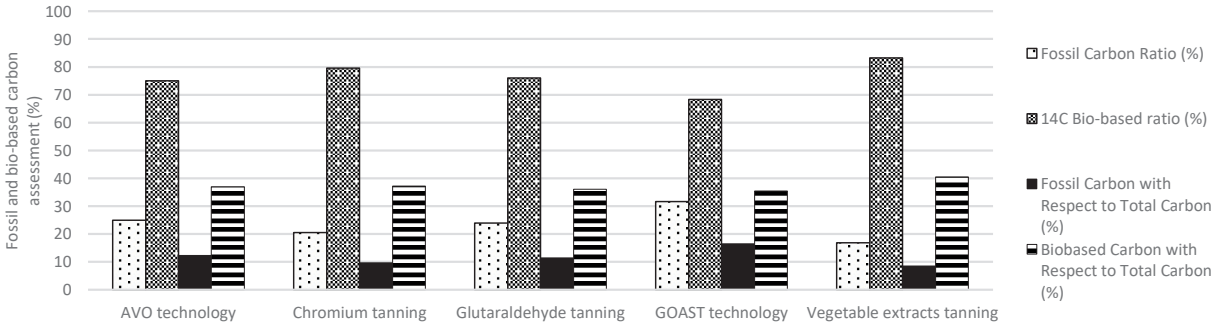


Figure 3: fossil and modern carbon ratio and content on retanned leathers.

3.2.3 Correlation between bio-based content from UNI EN 16640 (leather) and bio-based carbon estimation from chemicals (EN 16785)

The investigators were then able to make a correlation between the results from UNI EN 16640 and the theoretical *bio-based* content to better understand the *bio-based* overall contribution from the chemicals with respect to each tanning technology (Figure 4). Noteworthy, AVO technology brought the highest modern carbon contribution from the chemicals, although this was not translated completely to the leather, leading its *bio-based* content close to 60%. When compared to the vegetable extraction technology, such result is still in favour for the chemicals used in AVO tanning system, whilst the leather exhibited a lesser modern carbon content (60 vs 63% for the vegetable tanning system). Surprisingly, the glutaraldehyde leather showed the highest modern carbon content on the leather: this result was not expected and could be explained by less use of chemicals during its production, that meaning the contribution of ^{14}C was mainly due to the leather on its own. However, this is one critical point

[b]: The retanning operations are those after the tanning step (included the mechanical operations such as samming and shaving), which include the addition of chemicals (resins, retanning agents, dyestuff, fatliquors, preserving agents, flame-retardant agents and other additives for idro-repellency etc.).

of the assessment and the measurement of the modern carbon: in the presence of non-carbon species within the specific matrix to be analysed, the ratio and the amount of ^{14}C increased since they are not accounted.

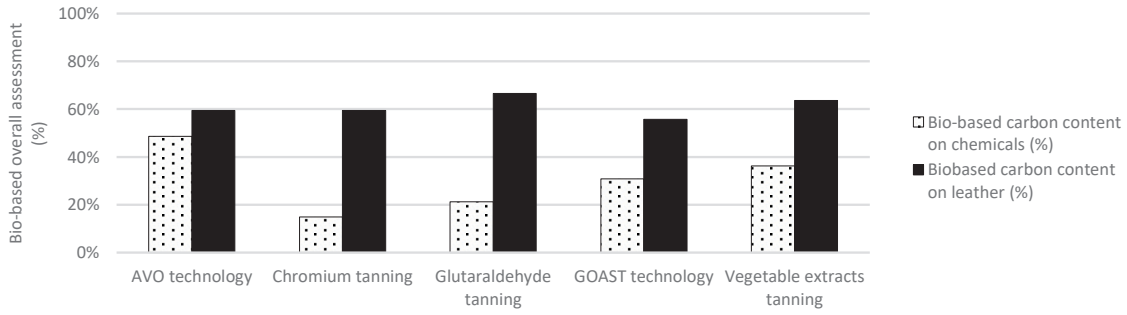


Figure 4: bio-based overall assessment

Conversely, GOAST technology showed moderate to high quantity of *bio-based* carbon on the chemicals, whilst the leather did not exhibit a high modern carbon content: this could be explained by the fact that, despite GOAST technology contains a source of natural and renewable carbon, overall, it required a higher amount of organic chemicals, which contributed more to the fossil carbon. Chromium tanning technology showed the lowest modern carbon contribution for the chemicals (no organic chemicals are used in the tannage), although its contribution to the leather was found to be in line with other results.

3.2.4 Focus on the finishing system and its contribution to the overall *bio-based* content

A specific study on the finishing application was also carried out: the investigators formulated a specific finishing system with high *bio-based* derivatives and compared it against a benchmark; the *bio-based* content of such finishing system was assessed on inert substrate according to UNI EN 16640 and EN 16785 and is depicted in Figure 5. Remarkably, the contribution in *bio-based* carbon content for the specially prepared finishing system was found to be more than 5 times higher than the benchmark. The *bio-based* carbon estimation according to EN 16785 was provided in 2.2.2.

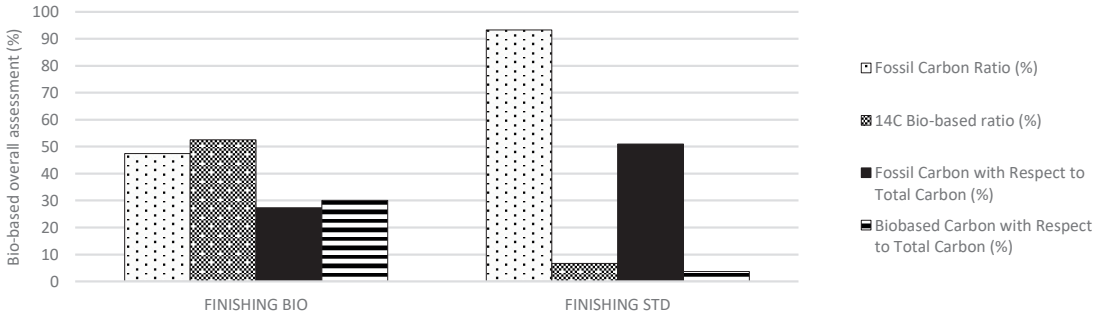


Figure 5: fossil and modern carbon ratio and content on finishing chemicals.

3.3 Evaluation of the leather performances

3.3.1 Chemical and physical tests on leather

A series of chemical and physical tests were performed for the evaluated tanning technologies on either tanned or crust leather; the results are summarised in Table 12. The specifications/limits reported in Table 12 are related to *automotive* leather production and represent a restricted range of the most important parameters that the leather technicians must account for the production of such article.

Tanning technology	ST (tanned leather, °C)	Fogging test (crust, mg)	Aldehydes content (extraction, ppm)	Cr VI after ageing (ppm)	Heat fastness	PV3341 (crust, ppm)
AVO technology	72-77	< 3ppm	N.D.	N.D.	good	< 100ppm
Chromium tanning	>95	< 3ppm	N.D.	traces can arise	best	< 100ppm
Glutaraldehyde tanning	75-78	< 3ppm	traces of glutaraldehyde	N.D.	average	< 100ppm
GOAST technology	70-74	< 3ppm	N.D.	N.D.	good	< 100ppm
Vegetable extracts tanning	70-72	< 3ppm	N.D.	N.D.	average	< 100ppm

[d] ST stands for shrinkage temperature, that meaning the temperature which provides irreversible hydrothermal damage to the tanned hide.

Table 12: main chemical properties for the different tanning technologies

Overall, the most important differences arose on the shrinkage temperature of the tanned leathers, where the chromium tannage showed the highest value, whilst all the other technologies showed temperature values between 70 and 85°C. This is a well reported scenario and is related to the chemistry underneath the tanning technology (and therefore the type of interactions generated between collagen and chemicals).

3.3.2 Physical tests on finished leather treated with enriched *bio-based* finishing system

Industrial free of chrome leather was used as the base for the application the enriched *bio-based* finishind and benchmark.

Almost all of the specifications for *automotive* have been tested for both *bio-based* products and standard applied formula; the results are depicted in Table 13.

In particular, the Bally test showed that the layers on the surface gave the same softness and flexing endurance.

However, light fastness studies (resistance to the Xeno-test/Uv) might have required more trials to give the same results as the benchmark: the *bio-based* polyurethane did not perform as the standard fossil derivate. Taber CS 10 explained the need to use the right ratio of NCO groups in the formula, not the same grams (BIO 1 vs BIO 2). If the percentage of NCO groups were equal in the recipe, the correct abrasion resistance was obtained.

Finish adhesion returned an interesting consideration about the similitudes of the *bio-based* product with the nature of our substrate, not only because of the higher amount of crosslinker. All of the Veslic tests confirmed the importance of the right ratio of NCO in the formula.

3.4 Correlation between *bio-based* content and leather performances

The investigators were not able to find a simple and direct correlation between modern and fossil carbon content and leather performances.

The difference in *bio-based* contribution due to the tanning technologies did not influence the tanned leather, nor the crust substrate, thus indicating the possibility of producing equivalent leather for the *automotive* industry *via* different tanning technologies (see Table 12).

It is still debatable whether the finishing system in terms modern/fossil carbon contribution (which imparts the final properties of rubbing fastness, touch etc.) influences the leather performances.

Test		STD	BIO 1	BIO 2
Flex 100 K		OK/OK	OK/OK	OK/OK
Flex -10°C/30K		OK/OK	OK/OK	OK/OK
Flex after fade 10 K		OK/LR	KO+/KO+	KO+/KO+
Taber test CS 10	cycles	5000	3000	5000
	aspect*	OK-	KO	OK
Taber test CS 10 con cucitura doppia	cycles	400	400	400
	aspect*	OK-	KO	OK-
Finish Adhesion (N/cm)	Dry	14,77	15,88	21,9
	Wet	3,88	3,99	7,17
Veslic alcohol 10 cycles	aspect**	OK-	OK-	OK-
	Grayscale of the felt	4	4	4
Veslic Gasoline 10 cycles	aspect **	OK-	OK	OK
	Grayscale of leather	4/5	4/5-5	4/5-5
Veslic Alkaline Sweat 1000 cycles	aspect**	OK-	KO+	OK-
	Grayscale of the felt	4	2	3/4-4
Veslic Dry 2000 cycles	aspect	REPOLISHED	REPOLISHED	OK
	Grayscale of leather	4	4	4/5-5
Veslic Wet	cycles	2000	2000	2000
	aspect**	OK-	KO+	OK-
	Grayscale of the felt	4-4/5	2	4-4/5
Fogging Test (mg)		3,2	2,6	2,7
Stick-Slip Test VDA 230-206 Part 1	10N-1mm/s	1	1	1
	10N-4mm/s	1	1	1
	40N-1mm/s	1	1	1
	40N-4mm/s	1	1	1
Stick-Slip Test VDA 230-206 Part 1 II	10N-1mm/s	1	1	1
	10N-4mm/s	1	1	1
	40N-1mm/s	1	1	1
	40N-4mm/s	1	1	1

*** Olein test: exposure to 3,5 g of olein with cotton gauze, all closed in aluminum foil, aged at 80°C for 3 hours. Dab the excess of olein with paper and make 1000 cycles of dry Veslic; ** Veslic evaluation scale from worst to best: KO/LIM KO/LIM OK/OK-/OK; *Taber evaluation test from worst to best: KO+/KO/LIM KO/PR/OK.

Table 13: physical and mechanical tests on finished automotive leather

4. Conclusion

Leather performance was not found to be strongly influenced with respect to the modern ^{14}C content. The simple principle of the amount/value of the chemicals used during the tanning, retanning or finishing showed that the most impacting phase was the leather retannage. The carbon content on leather was found to be around 25% (TOC analysis); all the tanning technologies showed similar trend apart for the glutaraldehyde sample which showed higher modern carbon content, particularly at the tanning stage (see Figure 2). The finishing step contribution was found to negligible; its performance was consistent with the benchmark, thus meaning the possibility of producing equivalent leather using highly *bio-based* content chemicals. Overall, the chemicals contribution was overall less impacting than expected;, it was found that modern-carbon enriched substrate and the utilisation of any *bio-based* chemical were less effective than the raw material on its own. Thus, regardless the application of the chemicals (such as in the AVO technology), the investigators found very difficult and less probable to overcome the 60% ratio of modern carbon on leather. The leather industry has been using *bio-based* chemicals form decades: natural fatliquors, natural vegetable extracts etc. have been intensively used and still constitute the basis of the products for many chemical suppliers. A final discussion on the economic impacts due to the utilisation of *bio-based* chemicals has to be done, although it is not the aim of this investigation. Overall, it was proved that from the performance point of view the leather industry could face the transition to enriched/fully *bio-based* chemicals with negligible problems, although it is still debatable whether its economic consequences could limit its widespread use.

5. Acknowledgements

The investigators would like to thank GSC Group spa for supporting this research In addition, GSC Group would like to thank *Conceria Pasubio* for supplying part of the raw materials and *LIFE Programme* (*LIFE16 ENV/IT/000416*). Finally, the investigators would like to thank *Ars Tinctoria* laboratory for performing the UNI EN 16640 analyses on leathers and finishing auxiliaries.

Refernces

1. United Nations Conference on Environment and Development: Proposal of the Chairman of the Preparatory Committee for UNCED on the Declaration on Environment and Development, Rio de Janeiro 1992.
2. P. C.K. Lau, Green Chemistry and Sustainable Technology 2016.
3. M. Niaounakis, Biopolymers: processing and products 2015.
4. https://ec.europa.eu/growth/sectors/biotechnology/bio-based-products_en
5. W. J. Hale: The Farm Chemurgic, The Stratford Co., Boston 1934.

Note