SUSTAINABLE ACRYLIC RESIN FOR LEATHER RETANNING

Olga Ballús[1], Anna Bacardit[2], Meritxell Guix[3], Ricardo Micó[4]

[1]Cromogenia Units S.A, c/ Feixa Llarga 1-3, 08040 Barcelona (Spain), email: oballus@cromogenia.com. Phone. +34.932.643.464

[2]Universitat de Lleida, Av. Pla de La Massa 8, 08700, Igualada (Spain), email: anna.bacardit@udl.cat. Phone. +34.938.035.300

[3]Cromogenia Units S.A, c/ Feixa Llarga 1-3, 08040 Barcelona (Spain), email: mguix@cromogenia.com. Phone. +34 934.479.856

[4]Cromogenia Units S.A, c/ 40, 14 – 16, 08040 Barcelona (Spain), e-mail: rmico@cromogenia.com. Phone. +34. 934 329 418

ABSTRACT

All definitions of a sustainable product have one point in common: a sustainable product must have a minimum environmental impact. Also, Cromogenia considers that a sustainable product must meet certain requirements, such as high biodegradability and high content of renewable raw materials, and must comply with restricted substances lists, such as the Zero Discharge of Hazardous Chemicals (ZDHC) list. For this purpose and based on previous results, Cromogenia has developed a new biopolymer based on a high percentage of alternative raw materials (protein derivatives) in order to obtain more sustainable products.

A life cycle assessment (LCA) of the new biopolymer versus a standard acrylic resin was conducted to determine the environmental impact. The biodegradability of both products was also determined by BOD5/COD ratio measurement. Both products were characterized by IR, gel permeation chromatography (GPC), and Carbon-14 content.

The new biopolymer showed higher biodegradability and higher renewable content than previous products. LCA allowed concluding that the new biopolymer reduces the environmental impact of 17 of the 19 impact categories analyzed; in particular, the carbon footprint was reduced by 57% vs. the standard acrylic resin.

Our results showed that the new biopolymer meets the requirements of a sustainable product (high content in renewable raw materials, higher biodegradability, lower environmental impact (in particular, a much lower carbon footprint), and complies with the ZDHC restricted substances list.

Key words: sustainability, LCA, biodegradability, acrylic resins, carbon footprint

1. Introduction

The word sustainability has been heard more frequently over the past decade, although its origin is older. It is currently one of the greatest challenges for humanity and is related to any discipline or industry, from energy to food or transportation. “The future will be sustainable… or there won’t be one” is a sentence that very well describes the importance of this term.

Any product or process that we consume or use affects the environment, the economy, and society. Accordingly, sustainability consists of three pillars: environmental sustainability, economic sustainability, and social sustainability.

Several definitions of a sustainable product can be found:

1. A sustainable product is one that has a minimum environmental impact throughout its entire life cycle (X. Zhang et al. 2020).
2. A sustainable product is one that is fully compatible with nature's ecosystem throughout its life cycle (Jaafar et al. 2007).

3. A sustainable product is one that is successful in the market, for which less dangerous substances are used, and that has less impact on the environment and society than a comparable product (Reihlen et al. 2011).
4. A sustainable product is one that aims at improving environmental and social quality (Seuring and Müller 2008).

They all have one point in common: they must have a minimum environmental impact. Perhaps, however, the most complete definition is Reihlen's, which takes into account the economic, the environmental and the social aspects. In this sense, Philippe Marion et al (Marion et al. 2017) comments on the complexity of defining the sustainability of a product, and suggests a number of requirements for a product to be considered sustainable:

1. The product must be non-toxic to the environment and human beings. In addition, it must be **biodegradable** or recyclable.
2. The product must be synthesized through a safe and eco-friendly process (sustainable synthesis) to allow saving water and energy or **reducing greenhouse gases**, among others.
3. The selected product must be a true scientific or technological breakthrough that improves safety, the **environmental impact** or the economic impact, among others.
4. The product must generate a profit.
5. The product must be accepted by the consumer, within the social pillar. This implies educating on and explaining the novelties to the population.
6. The product must be of **renewable** and/or recycled origin, and preferably from resources that are not used in the food industry.
7. The price of the product must be in accordance with its application, so that the consumer can make both an affordable and sustainable choice.
8. The product must not be used to make products that harm humans, such as weapons or drugs.
9. If the sustainable product has a higher cost than the standard product, this additional cost must be borne by the consumer, the manufacturer and the public authorities through support policies or regulatory changes that favor sustainable products.
10. The analysis of **the life cycle** of a product or process gives a global vision and therefore helps understand sustainability. One way to calculate the sustainability of a product is through life cycle analysis (Ögmundarson et al. 2020; Hoekstra 2015). Life cycle analysis is a powerful tool to detect hot spots or points that have the greatest environmental impact during the life of a product.

Currently, most of the products for the leather industry come from petroleum chemistry, e.g., formaldehyde and phenol for phenolic synthetic retanning agents, acrylic acid for acrylic resins, or mineral oil for fatliquoring products. These products, therefore, depend on the price and availability of petroleum, which is not always constant (B. Zhang 2014). The dependence on oil in the countries of the European Union was 88.3% in 2013 (European Commission 2017). Besides, petroleum is a non- renewable and finite resource, and greatly contributes to climate change (Okkerse and Van Bekkum 1999; Sun 2005). Likewise, its transformation requires or results in products or residues that are toxic to both humans and the environment, and a high amount of energy is needed for its transformation ─currently 20% of the total energy used in the industry (Ögmundarson et al. 2020). This is why petroleum is considered a non-sustainable resource (Zimmerman et al. 2020). On the other hand, biomass (bio-based products) can be used as a substitute for fossil resources (B. Zhang 2014), and biomass is currently considered the sustainable source of organic carbon for the industry (Serrano-Ruiz, Luque, and Sepúlveda-Escribano 2011; University of Bologna and Fraunhofer ISI 2018).

Acrylic resins are widely used in the wet blue leather retanning process; indeed, their high affinity for chrome provides very good properties. The acrylic resins used in the tanning process are generally high molecular weight polymers, and the properties they provide to the leather basically depend on the type of monomers used during synthesis and on the molecular weight of the resins (Ballús 2018). Acrylic resins come from petroleum and therefore are considered non-sustainable products.

On the other hand, acrylic polymers can be added to biomass derivatives to obtain graft copolymers, thus improving biodegradability and reducing the environmental impact caused by the synthesis of acrylic resins.

The biodegradability of a product can be determined by analyzing the BOD_5/COD ratio (Gawande et al. 2016; Kalyanaraman et al. 2013; Qiang et al. 2011; Kalyanaraman et al. 2012; Inescop 2013). This ratio does not provide absolute biodegradability results, but rather an idea of the low, medium or high biodegradability of the product. The biodegradability ratio is shown in Table 1 (Luo et al. 2010).

Biodegradability	Low biodegradability	Medium biodegradability	High biodegradability
Ratio BOD_5/COD	<0.2	0.2 - 0.45	>0.45

Table 1. Biodegradability

Finally, the life cycle analysis (LCA) is a tool that allows determining the environmental impact of a product. LCA is an ISO standard method that identifies, quantifies and evaluates the environmental impacts of a product, and allows environmental impacts to be compared between products of similar use.

1.1 Previous studies

In previous studies, a new protein-derived biopolymer was developed in which 23% of a biomass derivative was incorporated (product AP). LCA was carried out versus a standard acrylic resin (0% derived from biomass). An improvement in 17 of the 19 selected categories and an improvement of 47% in the carbon footprint versus the standard product, were obtained. In all categories, acrylic acid was the largest contributor to the different impacts. On the other hand, a sensitivity analysis was carried out by replacing the protein derivative with a polysaccharide derivative in order to select the biomass derivative with the lowest environmental impact. An improvement in 4 of the 19 categories was obtained. On account of these results, the decision was made to continue working with the protein derivative.

1.2 Current study

This study aims to develop a product with a higher percentage of protein derivatives to reduce the environmental impact and obtain a more sustainable product. To this end, the LCA of the new product will be carried out versus product AP from previous studies and the standard acrylic resin. A biodegradability study of the products and residual baths will also be carried out.

2. Materials and methods

Like most retanning acrylic resins, the product was synthesized by radical polymerization. In order to obtain a satisfactory product, different syntheses were performed by adding different percentages of protein derivative at different stages of the synthesis.

2.1 Product characterization

2.1.1 IR analysis

IR spectra in the range of 600 - 4000 cm-1 were measured on a Perkin Elmer Spectrum One. The samples were polymer films onto ZnSe base.

2.1.2 Molecular weight analysis

Agilent model 1260 Infinity coupled with 1260 MDS refractive index detector was used to determine the molecular weight by gel permeation chromatography (GPC). The products were analyzed using a column set comprising three Ultrahydrogel columns 7.8 x 300 mm (Waters) with 120, 250 and 500 pore sizes, providing the following molecular weight range: 1000-80000g/mol, 10000-400000g/mol, and 10000-1000000g/mol. The columns were packed with hydroxylated polymethacrylate gel, and the particle sizes for Ultrahydrogel 120 and 250 and for Ultrahydrogel 500 were 6µm and 10µm, respectively. A 0.1M sodium nitrate aqueous solution at a flow rate of 0.7 ml/min was used as mobile phase. The calibration curve was made with polyacrylic acid standards.

2.1.3 Biobased carbon content

The biobased carbon content of the products studied was analyzed according to standard ASTM D6866- 18 Method B (AMS).

2.1.4 Chemical oxygen demand (COD)

The COD was determined using the micro digestion method, where the appropriate amount of sample was transferred into the vial and the vials were placed into a COD reactor and heated for 2h at 150ºC. Lastly, the vials were removed and cooled to room temperature, and COD values were determined colorimetrically.

2.1.5 Biological oxygen demand (BOD_5)

BOD_5 was determined by neutralizing the sample with 2% sodium hydroxide up to pH 6-7. A series of dilutions was performed and samples were incubated in darkness at 20ºC for 5 days. The dissolved oxygen concentration was determined before and after incubation. The concentrations of oxygen consumed per liter of water were calculated.

2.2 Residual bath and leather assessments

Chrome-tanned cattle hide of Spanish origin shaved at 1.4-1.5mm was used. The hide was cut along the backbone. Standard acrylic resin and product A2P were applied on the left and right halves, respectively. Product AP was also applied for the analysis of the residual baths. The application formula is shown in Table 2.

The residual bath (for nitrogen, COD and BOD_5 determinations) and pieces of leather (for degree of whiteness and lightfastness tests) were collected after retanning. COD and BOD_5 were measured as mentioned previously. Total nitrogen of residual bath was determined with the Kjeldahl method (TKN). Lightfastness and heat resistance tests were performed according to IUF 402 (UNE EN ISO 105-B02) and IUF 412 (UNE EN ISO 17228), respectively, at 102ºC for 100h. The degree of whiteness was determined with a Datacolor Spectraflash SF-300 colorimeter. Finally, after the dyeing/fatliquoring processes, the rest of determinations were performed: softness according to UNE EN ISO 17235, thickness according to IUP 4 (UNE EN ISO 2589), tensile strength according to IUP 6 (UNE EN ISO 3376), and tear load according to IUP 8 (UNE EN ISO 3377-2) with Zwick TMZ2.5/TN1S.

Process	Remarks
100% Water at 35ºC, 2% Sodium formate. Run 15’	
0.5% Sodium bicarbonate. Run 60’	pH=5.5 Drain - Wash
100% Water at 40ºC, 5% of product (related to active matter). Run 60’	Drain - Wash
Assessments: Fastness tests, residual bath analysis	
100% Water at 45ºC, Dyestuff (Acid brown 83). Run 45’	
5% Sulfochlorinated oil, 5% Sulfated oil. Run 60’	
2% Formic acid. Run 60’	pH=3.8 Drain - Wash
Assessments: Physical determinations	

Table 2. Application formula

2.3 Life cycle assessment (LCA)

LCA was performed to evaluate all impacts associated with the production of A2P versus a standard product. Calculations were performed with the EF2.0 midpoint categories for Life Cycle Impact Assessment (LCIA). OpenLCA 1.8.0 software and the Ecoinvent 3.7.1 database were used. 1 Kg of manufactured product was used for calculations. The limits of the system included raw material extraction, raw material transformation, and product manufacture. Distribution, use and end-of-life were omitted.

Nineteen impact categories divided into four large groups (resources, health, climate change, and ecosystem) were considered.

3. Results and discussion

As mentioned, the purpose of this study was to develop a new retanning biopolymer based on a high percentage of alternative raw materials. For this purpose and based on previous results, a protein-based biopolymer was designed by replacing part of the acrylic acid to obtain a new product, A2P.

IR spectroscopy, a non-invasive, rapid and easy method, was used to identify the functional groups that characterize polymers. IR spectra of A2P and acrylic acid are shown in Figure 1.

The IR of product A2P shows an intense and broad band at 3500 cm^{-1}, corresponding to the N-H and OH group. This broad band is due to the protein and does not appear in the IR of acrylic acid. The band of $-CH_2$ appears at 2940 cm^{-1}, the band of the C=O group appears at 1668 cm^{-1}, and the band of the - NH_3 groups of the protein appears at 1450 cm^{-1}.

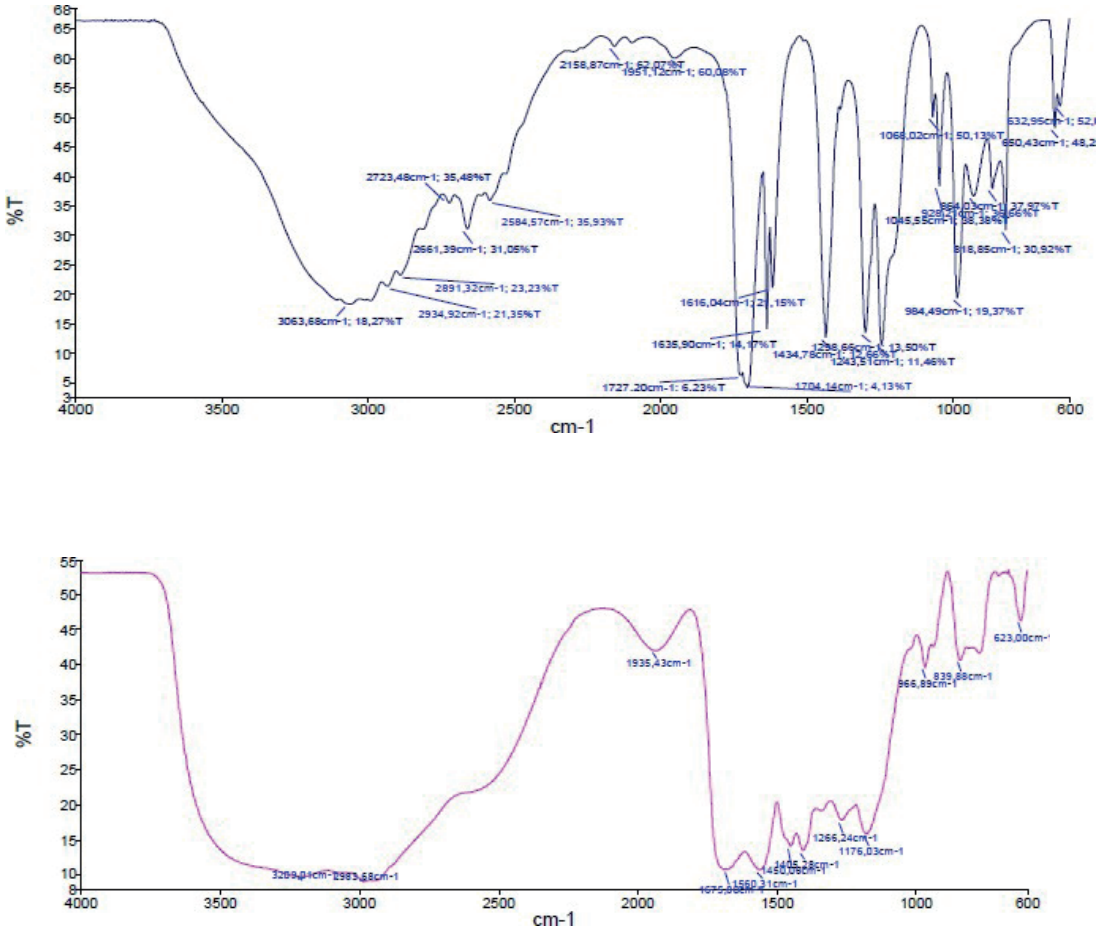


Figure 1. IR spectra of acrylic acid (above) and product A2P (below)

Both products were also characterized by measuring their molecular weight (Mw), biobased carbon content, BOD_5, COD, and relative biodegradability.

As shown in Table 3, the molecular weight of the standard acrylic determined by GPC was 734,579 g/mol, which was larger than that of A2P (71,633 g/mol). Mw is an important factor influencing the interaction of the resin with the leather to provide better or worse fullness.

The biobased carbon content measures the amount of biomass-derived carbon (C-14) in a product as compared to its total organic carbon content, and is expressed in percentage. Petroleum-derived products do not contain carbon-14. Therefore, according to the standard AMS method, the standard acrylic has 0% biobased carbon content, while A2P has 50% biobased carbon content.

On the other hand, the COD values for A2P and standard acrylic resin were similar, whereas AP obtained a higher value. BOD_5 was higher than the standard acrylic for A2P, followed by AP. Biodegradability was calculated with the BOD_5/COD ratio. The biodegradability of both the standard acrylic and product AP was low (0.008 and 0.053, respectively), and medium biodegradability was obtained for product A2P (0.212).

Sample	Mw (g/mol)	Biobased content (%)	BOD_5 (mg O_2/L)	COD (mg O_2/L)	Ratio BOD_5/COD
Standard acrylic	734,579	0	2,867	304,000	0.008
Product A2P	71,633	50	64,830	305,802	0.212
Product AP	66,965	23	23,850	452,000	0.053

Table 3. Average molecular weight, biobased carbon content, COD, BOD_5 and biodegradability of the products

Standard acrylic resin and A2P were applied at the retanning stage according to Table 2. As mentioned, product AP was applied only for residual bath determinations. BOD_5 and COD values in residual baths were analyzed. The results are shown in Table 4.

The residual bath of product A2P showed a lower COD and a higher BOD_5 than standard acrylic and AP.

On the other hand, the BOD_5/COD ratio was higher for A2P (as in Table 2) and showed high biodegradability in the residual bath. Since the biodegradability of the standard acrylic and AP did not improve, they are non-biodegradable.

Sample	COD (mg O_2/L)	BOD_5 (mg O_2/L)	Ratio BOD_5/COD
Standard acrylic	4,330	325	0.075
Product A2P	2,690	1,654	0.615
Product AP	4,510	337	0.075

Table 4. COD, BOD_5 and biodegradability in residual baths

TKN in residual baths of product AP versus product A2P. Results are shown in Table 5. Despite the higher content in protein derivatives, product AP residual bath has less nitrogen content than product AP. This might be due to better fixation (lower COD) of product A2P, as shown in Table 3.

Sample	TKN (mg N/L)
Product A2P	128
Product AP	209

Table 5. TKN in residual baths.

The degree of whiteness and accelerated aging (by exposure to light and heat) were determined to prevent yellowing issues. The parameters indicated for degree of whiteness are: L* (luminosity, where the greater the value, the greater the luminosity), a* (red/green, where +a* tends to red and -a* tends to green), and b* (yellow/blue, where +b* is yellower and -b* is bluer). The values of the lightfastness test are expressed in blue scale. An 8-point rating scale was used, where 0 is extremely poor lightfastness and 8 is excellent lightfastness. Heat resistance values were expressed in a 5-point grey scale, where 1 is the minimum value and 5 the maximum value. The degree of whiteness and lightfastness tests are shown in Table 6.

The values of L* are very similar, but the value of a* and b* are slightly different. Product A2P has more positive a* and b* values (more reddish and less blue), thus providing less whiteness to the leather. On the other hand,

regarding the incorporation of protein derivatives into the product, fastness values are good for both products and are within specifications (≥ 3).

Sample	Degree of whiteness			Lightfastness*	Heat resistance
	L*	a*	b*		
Standard acrylic	82.91	-3.71	-2.14	4Y	3/4
Product A2P	82.04	-3.47	-1.32	4Y	3/4

*Y:Yellowing

Table 5. Degree of whiteness and fastness tests

The degrees of softness, thickness and physical resistance in crust hides are shown in Table 7. The percentage of variation between samples for softness, thickness and resistances was also calculated.

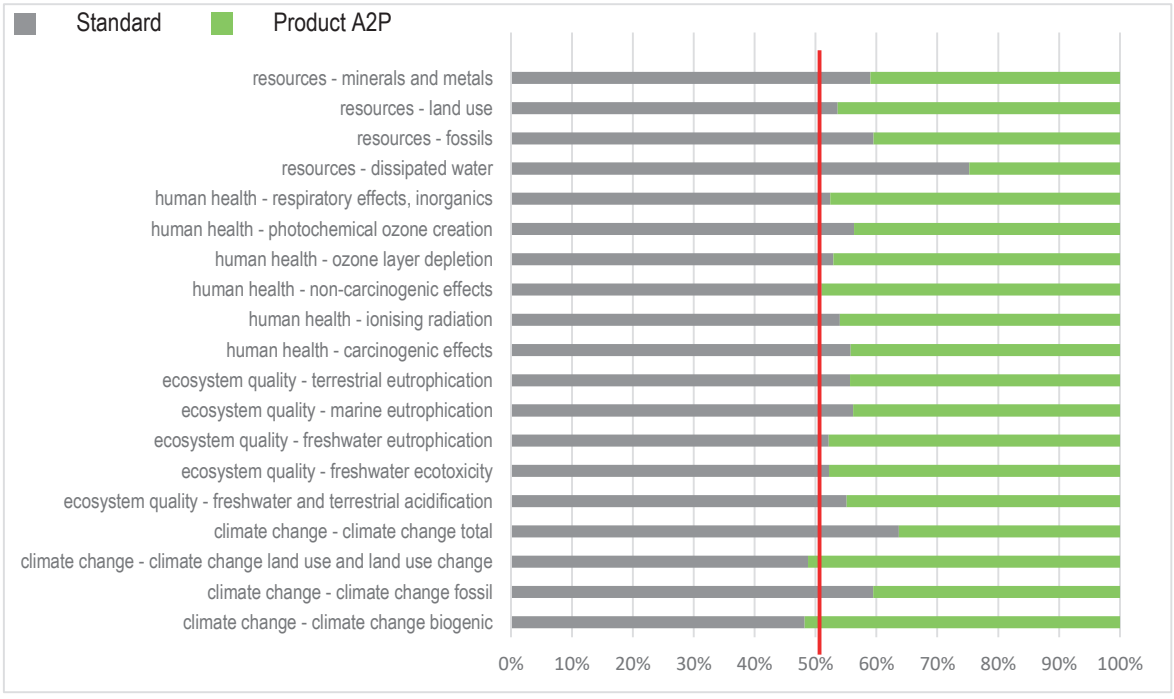
As seen, product A2P was harder, with similar fullness and improved tensile strength as compared to the standard acrylic.

Sample	Softness (1-10)	Thickness (mm)	Tensile (MPa)	Elong. (%)	Tear (N)
Standard acrylic	3.6	1.4	16.97	15.38	103.6
Product A2P	3.3	1.4	22.56	14.42	98.81
Variation	-8	0	+15	-6	-5

Table 7. Degree of softness, thickness and physical resistance.

LCA was conducted to compare the environmental impacts related to the manufacture of product A2P and the standard acrylic. Results are shown in Graph 1 as a stacked bar chart with 50% contribution as red line.

There is an improvement of A2P versus the standard acrylic in 17 of 19 categories studied. Product A2P decreased the carbon footprint (climate change categories) by 57% as compared to the standard acrylic.



Graph 1. Contribution of standard product and A2P to impact categories

On the one hand, the comparison of previous studies (product AP) shows no improvement regarding the number of environmental impact categories. On the other hand, there has been an improvement in climate change, from 47% to 57% due to less acrylic acid used.

4. Conclusions

A new biopolymer has been designed that, according to Cromogenia standards, meets the requirements of a sustainable product: high biodegradability, high biomass content (50%), reduced environmental impact versus a standard product in 17 of the 19 categories, and 57% improvement in carbon footprint. In addition, it is a product that complies with the ZDHC restricted substances list.

The new biopolymer product A2P allows obtaining properties that are similar to those of a standard resin in terms of fullness, softness, firmness, solidity or physical resistance.

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Note