Killer Threads – what's the opposite to fast fashion materials?

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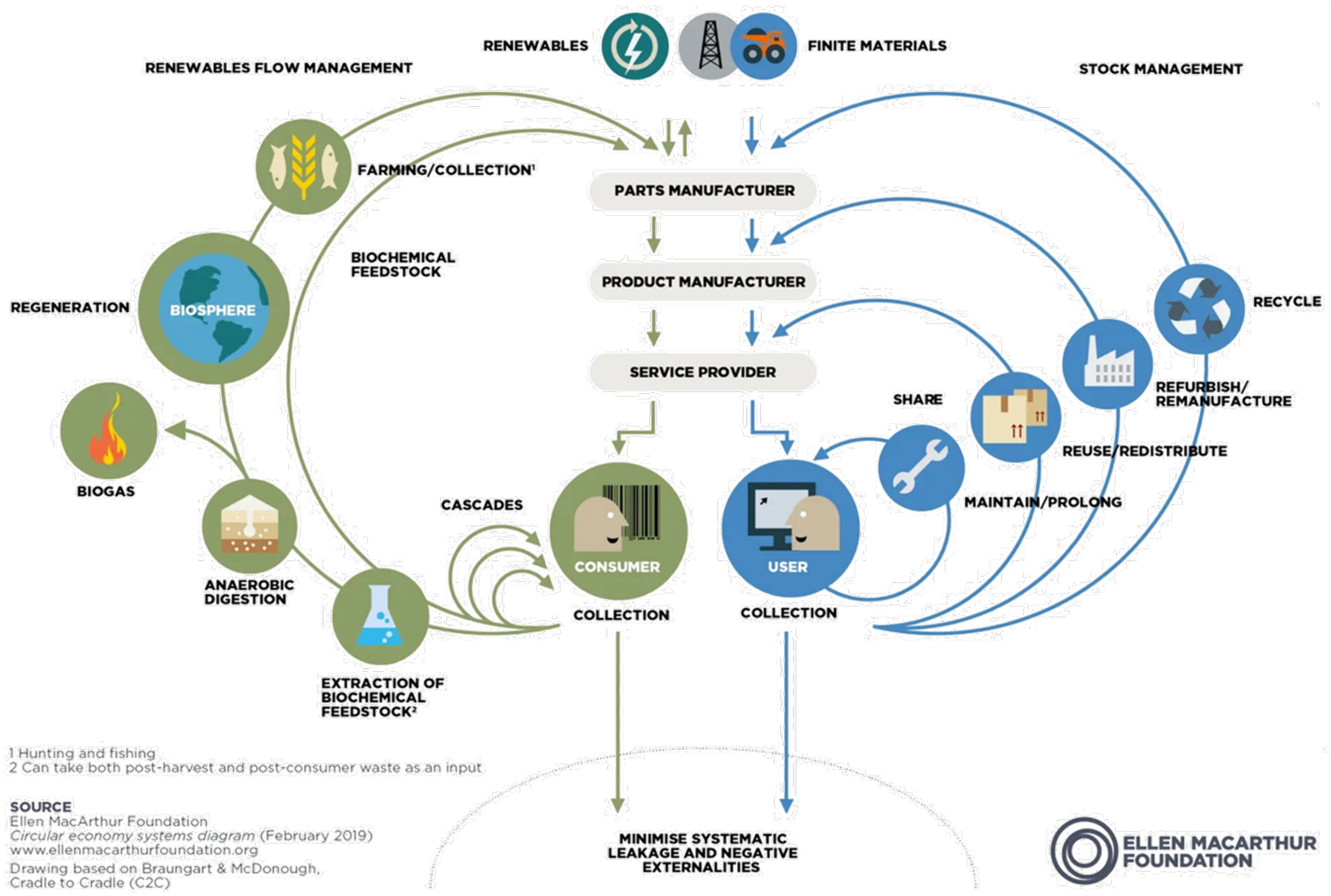
Introduction

- Fast fashion and leather are incompatible
  - High value of leather vs cheaper ‘plastic’
  - Not worth paying more for a short-lived product.
- Leather is often not understood,
  - Oldest biotechnology industry.
  - There is also misinformation/ disinformation that can muddy the waters further.
  - Alongside other natural fibres (e.g. wool) it’s often demonised.
- What is its place in a ‘circular economy’?

Introduction

- Fast fashion typically follows a linear economy
  - Inroads are being made in facilitating moving it to the blue circular approach.
  - Challenges lie in use of mixed material and construction.
- Cannot indefinitely recycle ‘polymers’ leading to greater emphasis on renewables.
- Leather very much the ‘green’ side
  - Overview of leather production to follow



Introduction – leather production

- Preservation
  - Range of ways of preserving,
  - Most commonly ‘salting’ – application of about 25% NaCl (by mass) – roughly 7500 tonnes of salt each month in the UK alone.[1]
  - Other methods are used e.g. cooling
  - Fresh hides can be used – but only if you are ‘next door’ to the abattoir.
- Soaking
  - Must take into account the method of preservation – lack of salt can cause issues.
  - Rehydration of hide – surfactants and enzymes.
  - Removal of unwanted components – moved into the effluent system.
  - Extensive use of biotechnology.

1. Monthly UK statistics on cattle, sheep and pig slaughter and meat production– February 2022 (published 10 March 2022) https://www.gov.uk/government/statistics/historical-statistics-notices-on-the-number-of-cattle-sheep-and-pigs-slaughtered-in-the-uk-2022/monthly-uk-statistics-on-cattle-sheep-and-pig-slaughter-and-meat-production-february-2022-published-10-march-2022 (accessed March 2024)

Introduction – leather production

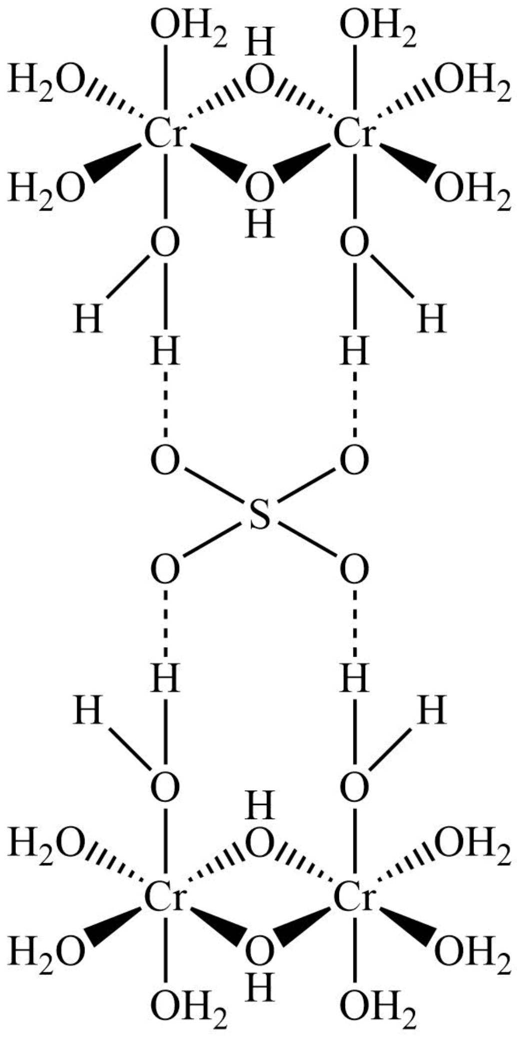
- Liming
  - Increase pH (≈12.5) to remove fats – saponification.
  - Swelling occurs through lyotropic effects.
  - Normally involves hair removal step – 'hair burn' involves sulphide.
    - Although sodium sulphide used – unlikely to be 'sulphide' that actually unhairs.
  - Strides made in now saving the keratin for other uses.
- Deliming
  - Historically involves urine – two old sayings come from this.
  - Most commonly involves the use of quaternary ammonium salts.
  - Increasingly uses CO_2 as deliming agent
  - Removes the calcium – or does it?
  - Primarily about reducing the pH

Introduction – leather production

- Bating
  - Famous for its use of dog excrement
  - Application of proteolytic enzymes to modify the mechanical performance
  - Different enzymes sources for different pH's
    - Consider what pH needed – CO_2 deliming gives a different pH to that of ammonium salts.
- Pickling
  - Just like the food – low pH and salt.
  - Salt stops osmatic swelling of pelt – salt does not stop swelling in the earlier liming phase.
  - Choice of acid can impact on tanning steps – particularly colour due to coordination chemistries.

Introduction – leather production

- Tanning
  - Most well-known step – most public refer to the whole process of making leather as simply tanning it.
  - Many different chemistries can be used, very loosely broken into the following categories:
    - Mineral tanning – any inorganic compound but most famously the use of chromium (III) sulphate (80% of the worlds leather)
    - Important to understand the relationship between the counterion, pH and speciation
      - Some don't tan as well as others e.g. chromium (III) chloride
      - Some don't tan at all e.g. chromium (VI) compounds and polymeric chromium species
    - Progress from the two-bath process



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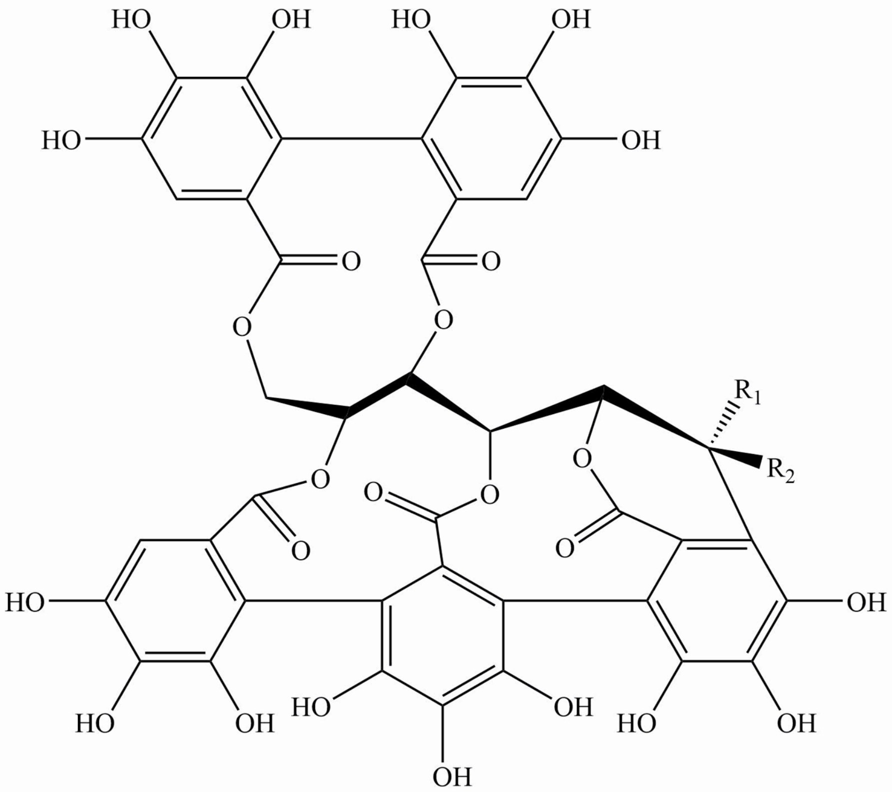

R_1 = H, R_2 = OH, castalagin

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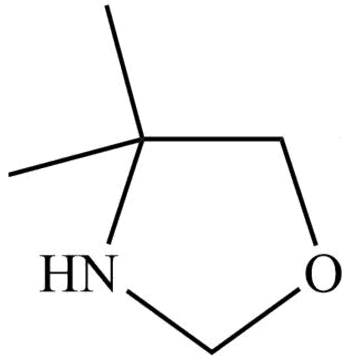
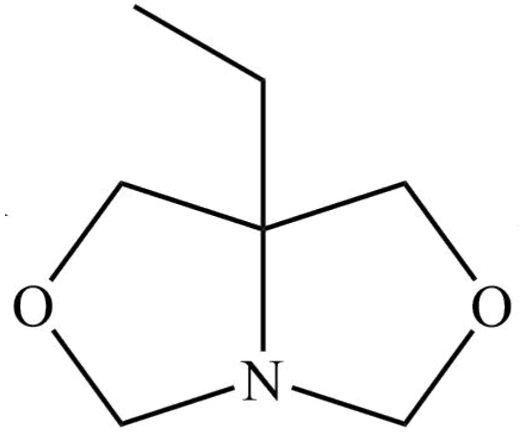
    - Vegetable tanning – rapidly expanding area of investigation in strive for perceived sustainability of tanning agents
    - Synthetic tannages – include 'simple' aldehydes, oxazolidines as well as much more complex systems.





Introduction – leather production

- Tanning
  - Most well-known step – most public refer to the whole process of making leather as simply tanning it.
  - Many different chemistries can be used.
  - Imparts biological stability and hydrothermal stability
    - Both impact on use and 'sustainability'
  - Some of the latest advances in tanning are not fitting in a category well.
    - E.g. use of light weight sugars

Introduction – leather production

- Post-tanning
  - Penultimate step, but arguably has the most choice of chemistries
  - Most important step in imparting physical properties
  - Broken into three steps
    - Retanning – physical property related
    - Colouring – whole range of dying chemistries used
    - Fatliquoring – additional of fats to prevent fibre sticking and aid softness
- Finishing
  - Halfway between a science and an artform
  - Application of a polymer coating to aid consistency and improve resistance to in use damage
  - Greatest impact on the aesthetics and on recyclability

Introduction – challenges

There are a range of challenges that impact leather

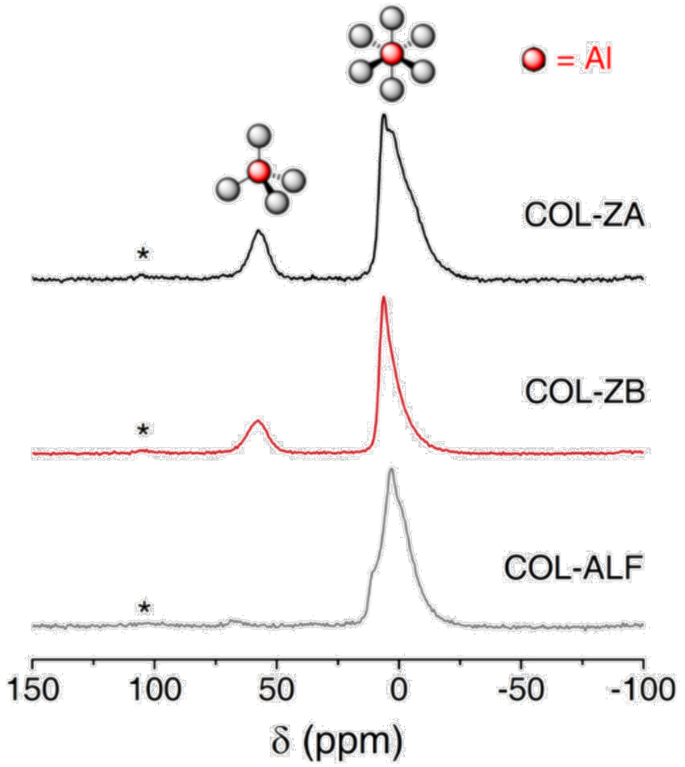
- Time and cost of production
- Public perception
  - The leather industry do not kill animals for their skins
  - 'Vegan leather' – what does it mean?
  - Complexity over measuring 'sustainability'
- Environmental challenges
  - Many can be circumvented or reduced… but at a cost… Are we willing to pay?
    - Minimising water use, reducing contamination of effluent, how to process the effluent, reducing impact for workers, reducing impact for end users e.g. aldehydes
  - How do we get some of the other 'loops' into the green side of the cycle?
  - End of life? Protein very easily biologically decomposed – issues with finish

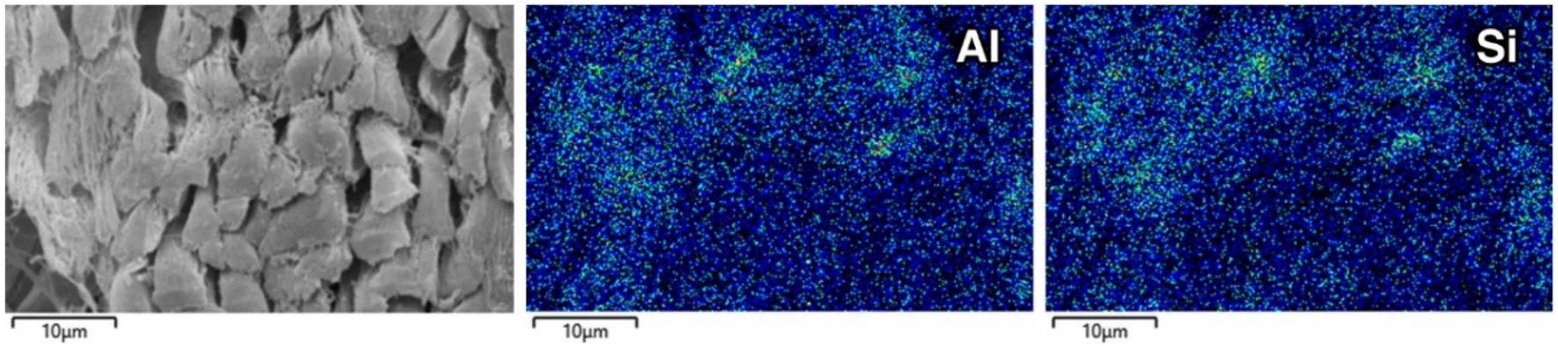
Alternative tannages

- One such approach to sustainability is addressing the primary tannage
  - Reducing the reliance on synthetic, polyolefin-based components.
  - Considering geographically where it has come from…
  - … and what is involved in the production
  - Need to make it easier to process at end of life
- Aluminosilicate tannages (aka zeolites) are an example

Alternative tannages – aluminosilicate[2]

- Benign tannage that produces a biodegradable leather (ISO 20136 or ISO 20200)
- Is this just an aluminium tannage?
  - Is it metal free?
  - It's there, but still in the aliminosilicate structure
  - The presence of 4-coordinate Al relates to aluminate anions, which are inherent to the zeolite structure.
  - Further highlighted in SEM/ EDX images highlighting great similarity in Al and Si distribution





2. W. R. Wise, S. J. Davis, W. E. Hendriksen, D. J. A. von Behr, S. Prabakar and Y. Zhang; Green Chem., 2023, **25**, 4260–4270

Reducing water

- Another challenge with leather production is water use
  - Amount varies hugely depending on the technology being used – but assume it's between 10–35 tonnes of water per tonne of leather
- There are "zero discharge tannery's"
  - Complexities over effluent treatment – not a cheap option
- … but why use water at all?

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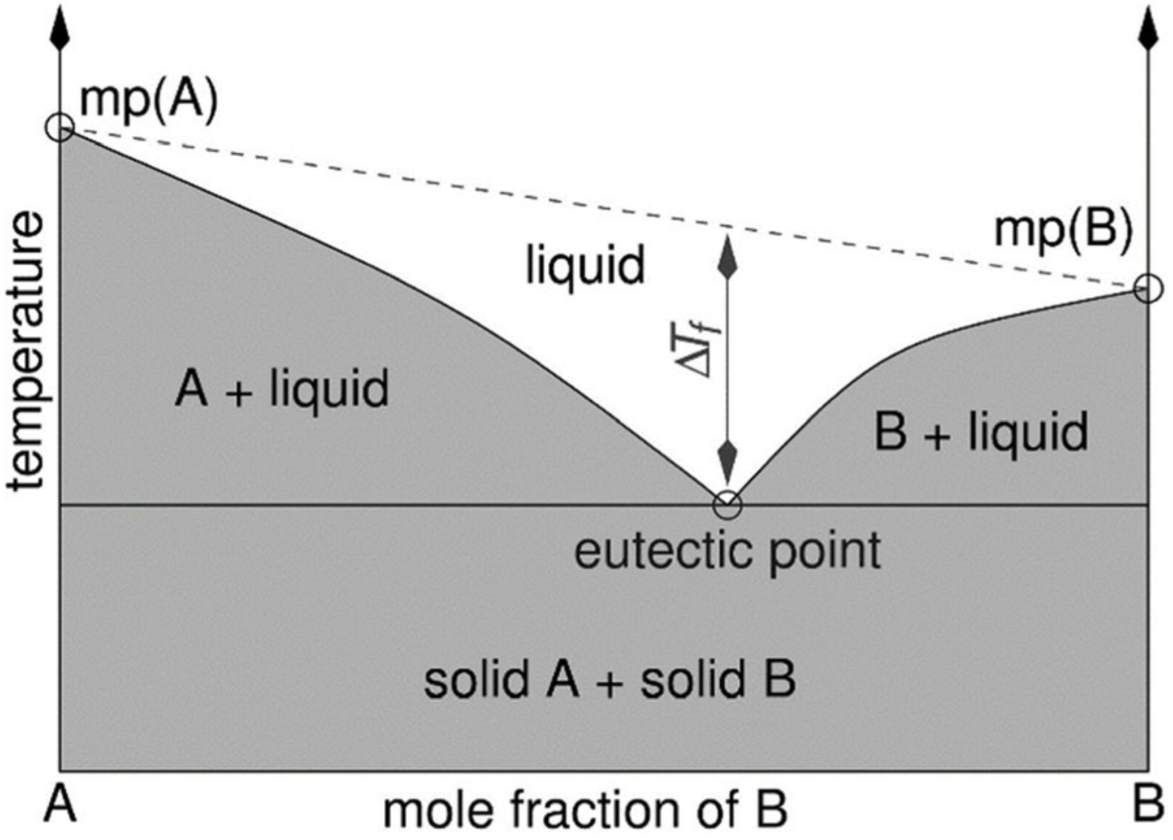
3. A. P. Abbott, O. Alaysuy, A. P. M. Antunes, A. C. Douglas, J. Guthrie-Strachan, W. R. Wise, *ACS Sustainable Chem. Eng.,* 2015, **3**, 1241−1247,
4. A. D. Covington, W. R. Wise, *J. Leather Sci. Eng.*, 2020, **2**, 28

Reducing water – alternative solvents

- Deep Eutectic Solvents (DESs) offer an alternative[3]
  - Has been used to 'probe' the role of water in the collagen structure
  - The idea of making the transport medium also an active component – does away with solution phase chemistry and the environmental issues it can present
  - Can present new technologies that don't work in aqueous mediums.



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Reducing water – polymer beads

- Replacement of water with polymer beads[4]
  - Technology transfer from the laundry issue
  - Challenges conventions around mass transport of chemicals – there is enough water in the system already
  - Challenging implementation at industrial scale.
    - Not drop in technology

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4. A. D. Covington, W. R. Wise, *J. Leather Sci. Eng.*, 2020, **2**, 28

Alternative materials

- Range of alternative materials
  - Carbohydrate based
  - Protein based
  - Polyolefin based
- Importantly, the content of fossil derived carbon can vary[5]
  - Will likely denote which side of the Ellen MacArthur diagram
  - … and how easy it is to exploit ‘loops’
- Many look to emulate the properties of leather
  - With the exception of aesthetics, they’re not quite there.[6]
  - Many use or are investigating the same processing steps used in leather processing – including tanning, fatliquoring and machine operations.

5. F. Carcione, G. A. Defeo, I. Galli, S. Bartalini, D. Mazzotti, *Coatings,* 2023, **13**, 892.
6. M. Meyer, S. Dietrich, H. Schulz, A. Mondschein, *Coatings,* 2021, **11**, 226.

Concluding remarks

- Leather is already a highly sustainable material
  - Measuring the sustainability is unbelievably complex
  - The industry is not complacent and is pushing to improve
  - It may never become part of "Fast Fashion"
- Have to balance physical performance against sustainability
- Legally there is no such thing as "vegan leather"
- "Alternatives to leather" are not
  - But they are alternative materials and are good in their own right
  - And the bio-derived versions of these materials to offer an exciting opportunity to a range of industries
  - Should not be seen as competition to leather

Thank you for listening

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Supplementary information – if required for discussion

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Biocontent

- pMC = % modern carbon (i.e. not fossil fuel)
- Error = 4 pMC
- Carcione, F.; Defeo, G.A.; Galli, I.; Bartalini, S.; Mazzotti, D. Material Circularity: A Novel Method for Biobased Carbon Quantification of Leather, Artificial Leather, and Trendy Alternatives. Coatings 2023, 13, 892. https://doi.org/10.3390/coatings13050892

Sample	% N	% C	pMC % Biobased
EVA "vegan" sole	4.6	61.6	0.2
Teak Leaf®	1.1	71.3	17.7
Desserto®	3.1	52.5	24.1
Appleskin®	2.0	59.6	25.4
Volar Bio Ultraleather®	0.9	56.9	27.8
Ultraleather® fusion	1.4	53.1	44.8
Coated patent leather	8.4	53.5	47.1
Noani®	0.2	47.1	58.2
Mix synthetic–natural fabric	7.8	50.2	61.0
Fully syntan tanned leather	10.7	58.8	65.6
Vegea®	2.6	64.6	67.9
SnapPap®	1.1	46.7	75.9
Salmon skin	13.5	49.0	82.4
Goatskin suede	12.4	41.8	83.7
Ecotan® shoe upper leather	10.9	51.7	85.7
Sueded split leather	11.4	47.4	87.2
"Parma" baby calf leather	9.2	48.8	89.9
Soft milled leather "Rave®"	11.8	58.2	92.6
Vachetta leather "Toiano"	8.9	50.9	94.8
Minerva box veg tan	8.5	55.3	95.9
Nebraska article veg tan	11.5	47.3	100.3
Kombucha	0.03	41.6	102.2
Chestnut traditional tanning	8.9	49.1	103.3

Performance

Meyer, M.; Dietrich, S.; Schulz, H.; Mondschein, A. *Comparison of the Technical Performance of Leather, Artificial Leather, and Trendy Alternatives.* Coatings 2021, 11, 226. https://doi.org/10.3390/coatings11020226

Physical Properties		Thickness	Tensile Strength	Tear Res.	WVP	WVA	Flex Res.
		ISO 17186-A	ISO 3376	ISO 3377-1	ISO 14268	ISO 17229	ISO 32100
		(mm)	(N/mm^2)	(N/mm)	($mg/(cm^2 \times h)$)	mg/cm^2	Flex Cycles to Grade ≥ 2
Naturally grown material	Leather	1.93	39.5	82.9	4.6	8.4	>200,000
	Muskin®	6.22	0.2	0.5	10.4	6.0	10,000
	Kombucha	0.29	9.7	5.1	0.1	9.2	10,000
Coated textile	PUR coat text.	1.37	10.2	17	1.1	1.4	200,000
	Desserto®	0.88	20.8	37.2	0.5	2.5	30,000
	Appleskin®	1.14	14	18.4	0.4	1.7	50,000
	Vegea®	0.95	9.4	16.6	0.6	3.0	50,000
	Teak Leaf®	0.57	12.2	30.7	0.1	0.1	100
Non-wovens of plant fibers	Pinatex®	1.43	4.5	31	2.5	3.8	150,000
	SnapPap®	0.57	24.9	7.5	10.3	3.7	5,000

(WVP: water vapor permeability; WVA: water vapor absorption; Tear Res: tear resistance).