Leather: A natural, high-tech material

A summary of a recent study conducted by German chemical specialist Trumpler which compares the renewable organic content of commercially produced leathers and the corresponding synthetic materials. By **Benjamin Autenrieth**, **Matthew P. Walker**, **Ulrich Buckenmayer** and **Jordi Escabrós**.

Introduction and Motivation

We all know and admire leather as the beautiful, versatile, durable, sustainable and unique material that it doubtlessly is. Leather is the material that gives character to countless articles we use in our daily life. Leather is the material on our waterproof hiking boots, our highly stressed wallets, handbags, belts, motorbike outfits and seat covers are made of. Leather provides a stylish and luxurious look, a pleasant touch and a distinctive odour, not to mention the inherent technical properties such as an incomparably high wear resistance, to name just one.

These countless positive aspects and the deeply rooted attraction and admiration of leather have driven the development and marketing of a growing number of artificial materials that are designed to look like leather and to imitate some of its most indisputable properties. Some of these artificial materials are cheaper and easier to produce and to handle; some are, admittedly, great materials in their own right. Others though plainly are cheap imitations, damaging the reputation of genuine leather. This extensive experimental study seeks to highlight one of leather's most prominent attributes: its natural origin.

Using highly sophisticated methodology, namely radiocarbon technology, applied by means of the analytical method ASTM-D6866, the bio-based (renewable) content of various commercial leather auxiliaries is established.[1,2]

Beyond that, a selection of commercial leathers and leather articles is examined. The measurements result in definite values, which are compared to the ones found for diverse synthetic imitations and the respective articles fabricated from such materials.

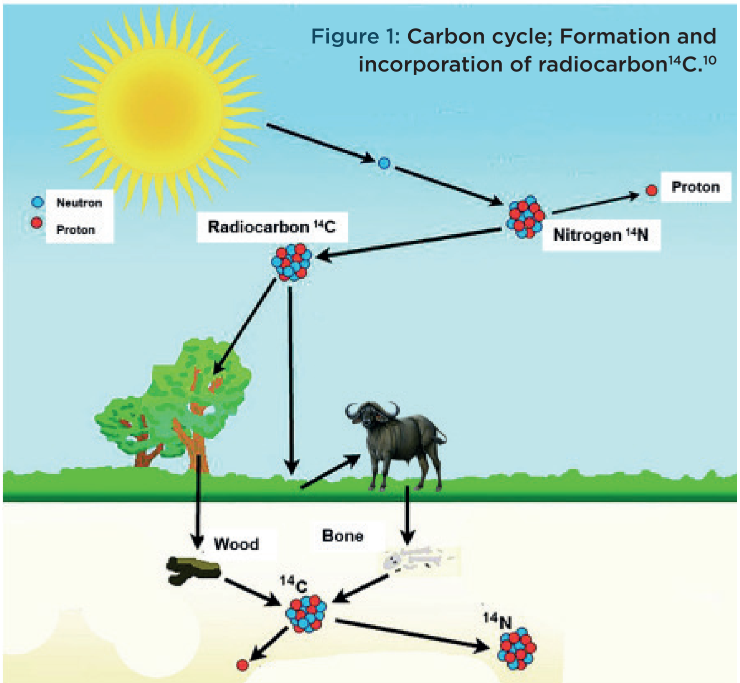


Figure 1: Carbon cycle; Formation and incorporation of radiocarbon ^{14}C.[10]

The Term Sustainability

The term 'sustainability' nowadays is an omnipresent slogan commonly used for promoting more or less new products and technologies. In spite of the existence of official definitions, the term sustainability is often employed solely to give a more or less justified impression of environmental compatibility and a positive social impact. To be fair, sustainability is a complex matter involving many factors which must be taken into account to ensure a full and rounded assessment. For the valuation of some of these factors, there are no generally agreed rules and subjective judgements have to be made.[3,4]

This study focuses on only one, yet a quite essential requirement for sustainability: renewability.

Renewability can only be achieved by using natural products. These are products derived from vegetable or animal sources. It should be noted that a substance cannot be sustainable without being renewable, however the converse is not always true. A material, which is in principle renewable, may actually be being harvested at a rate and in a dimension that causes severe damage to our environment and society. We all need to be aware of this substantial responsibility.

The Analytical Method ASTM D-6866

For a chemical supplier it is often not difficult to calculate with reasonable accuracy the proportion of renewable and non-renewable ingredients in a given product.[5,6] Rape oil, for example, is very likely to be renewable, and paraffin oil is clearly non-renewable. This strategy is, however, not without its limitations, and there are many cases in which the

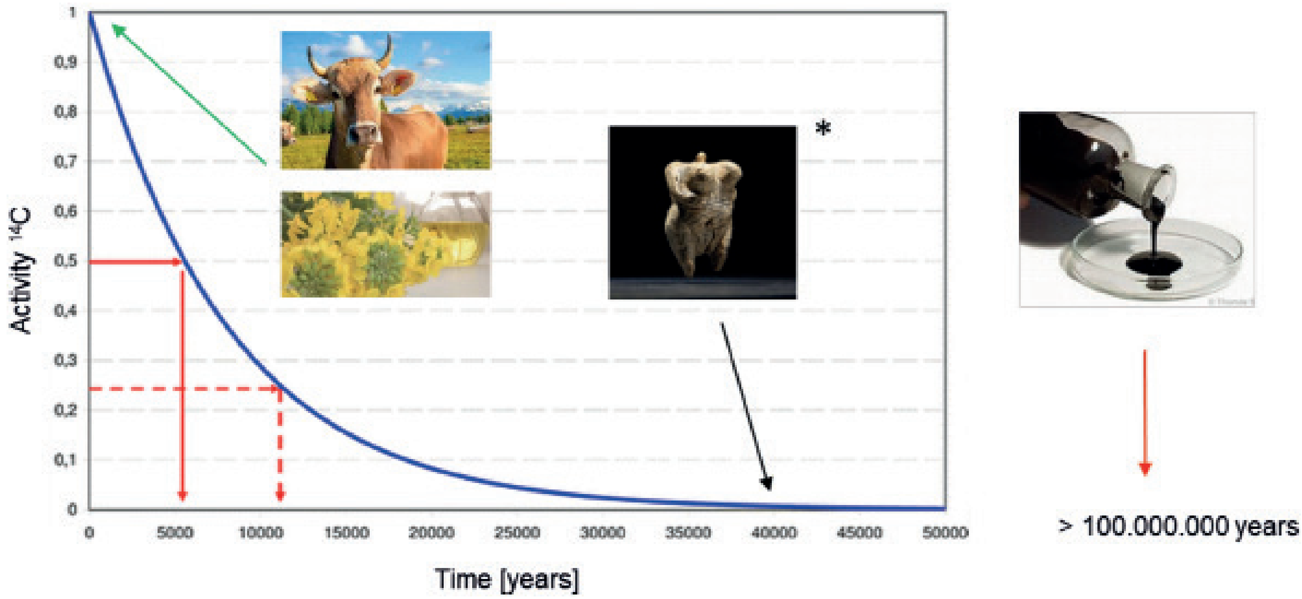


Figure 2: Decay curve of radiocarbon ^{14}C

situation may not be so clear. There surely exist chemical substances that can be derived from either renewable, natural or non-renewable, fossil resources. Stearyl alcohol is only one example of a substance that exists in both varieties in commerce. Identical at the molecular level, it is often merely the price that hints at the origin of the base material.

Understandably, such a sufficiently accurate but somewhat informal approach is less convincing than an established, experimental test method that yields definite and reliable values.

Such a test method indeed does exist and forms the centre of this study.[1]

The principle of the method presented and utilised here, is actually the same as that used for carbon dating of archaeological artefacts. The technique was established by U.S. American scientist Willard F. Libby who was awarded the Nobel prize in Chemistry in 1960 for this fundamental achievement.[7]

The basics of this test method are briefly introduced below.

The basis of all animal and vegetable matter is carbon. This chemical element exists as three natural isotopes present in different abundances: ^{12}C (ca. 99%), ^{13}C (ca. 1%) and ^{14}C (ca. 1.36 Atome pro 1012). In contrast to the isotopes ^{12}C and ^{13}C, which are stable over geological time, ^{14}C (radiocarbon) is radioactive, decaying with a half live of approximately 5730 years to ^{14}N.[8]

^{14}C constantly forms by the reaction of solar radiation with nitrogen in the upper atmosphere, to describe it in a simplified way. The radiocarbon ^{14}C is eventually oxidised to carbon dioxide ($^{14}CO_2$) which is taken in by plants, together with the dioxides of the other carbon isotopes, in the process of photosynthesis. As herbivores eat the plants, and carnivores the herbivores, the three carbon isotopes are incorporated into all living organisms. A constant equilibrium ratio between the three carbon isotopes ^{12}C, ^{13}C and ^{14}C (reflecting the ratio in our atmosphere) is found in all living organisms. The reason for this is the continuous uptake and metabolism of further ^{14}C by living organisms (Figure 1).[9]

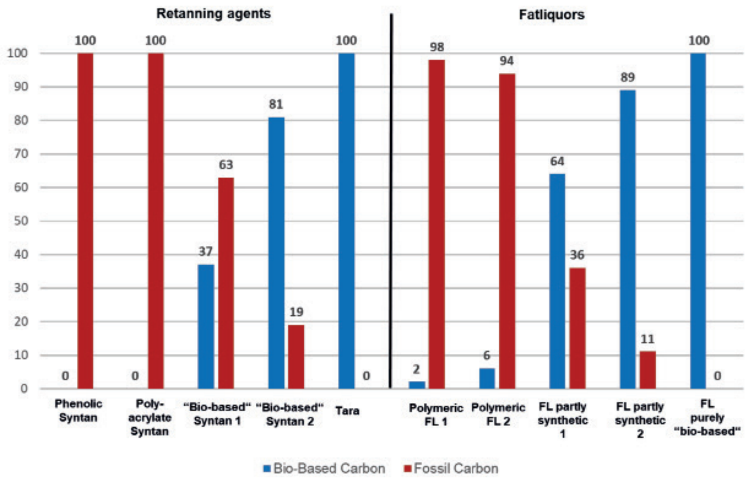
Once an organism dies, its metabolism stops as well. From this moment on, no further radioactive carbon is taken in. The ^{14}C that the organism contains at that moment, however, continues to decay. Consequently, the amount of ^{14}C and the ratio of ^{14}C to ^{12}C steadily decreases at a known rate over time (Figure 2).

The ratio of ^{14}C and ^{12}C in a sample of organic matter can thus be used to tell how long it is since it was alive.[9]

After about fifty thousand years, the quantity of ^{14}C in the once-living organic matter has decreased effectively to zero. This means that samples of higher age as, for example petroleum, with an age of perhaps 60 to 180 Million years, contain essentially no ^{14}C. The logical corollary is that chemicals and materials derived from that petroleum contain no ^{14}C either.

Let us consider the example mentioned above again: A sample of a natural vegetable oil will contain the original and well-known ratio of the three carbon isotopes ^{12}C, ^{13}C and ^{14}C established in the atmosphere and all living organisms. Paraffin oil, in contrast, is produced from mineral oil and therefore will contain no ^{14}C. The carbon content of paraffin oil thus is entirely made up of the 'fossil' isotopes ^{12}C and ^{13}C. Measurement of the ^{14}C : ^{12}C ratio in a mixture of vegetable and paraffin oil would therefore allow us to calculate the relative proportions of the two oils and with that the ratio of renewable and non-renewable (fossil) material.

Figure 3: ASTM D-6866 measurements on different commercial retanning agents (left) and fatliquors (FL, right).



When applied to multi-component products, an obvious limitation to this technique is that only the organic material is considered. A somewhat striking example is that a mixture of 5% sugar with 95% salt will be returned by the analysis as 100% renewable. This limitation obviously needs to be taken into account appropriately. When attempting to calculate the renewable proportion of a product by weight, it is therefore necessary to know how much organic material it contains. For many materials this can conveniently be done measuring moisture and ash contents of the sample and assuming that the remainder is organic:

Z% Organic material = 100% - X% Water – Y% Ash content

For ASTM D-6866 measurements the sample is heated at 900°C in the presence of oxygen. At that temperature the organic material is combusted, converting the carbon isotopes present (^{12}C, ^{13}C and ^{14}C) into a mixture of the corresponding dioxides. These in turn have different molecular weights and can be separated by a special type of spectrometry (accelerator mass spectroscopy, AMS).[11] The proportion of the forms of carbon dioxide directly corresponds to the proportion of the different carbon isotopes. Taking this ratio, the content of renewable and fossil materials in the sample can be calculated.

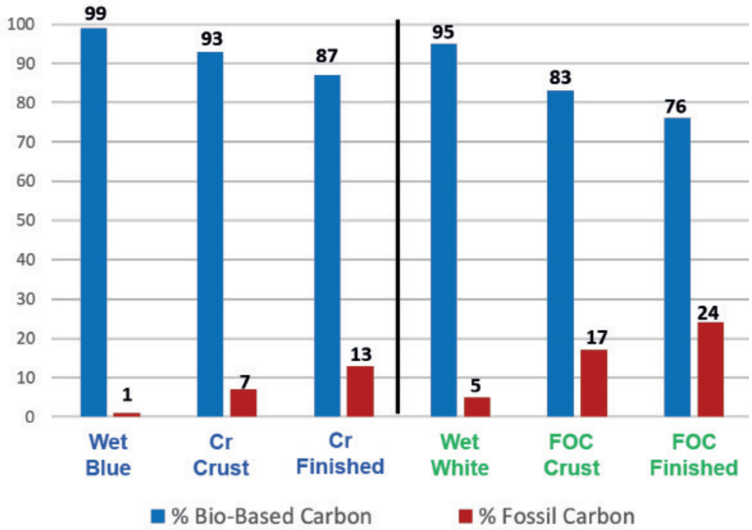


Figure 4: ASTM D-6866 measurements on Cr-tanned and FOC automotive leathers.

Results – leather chemicals

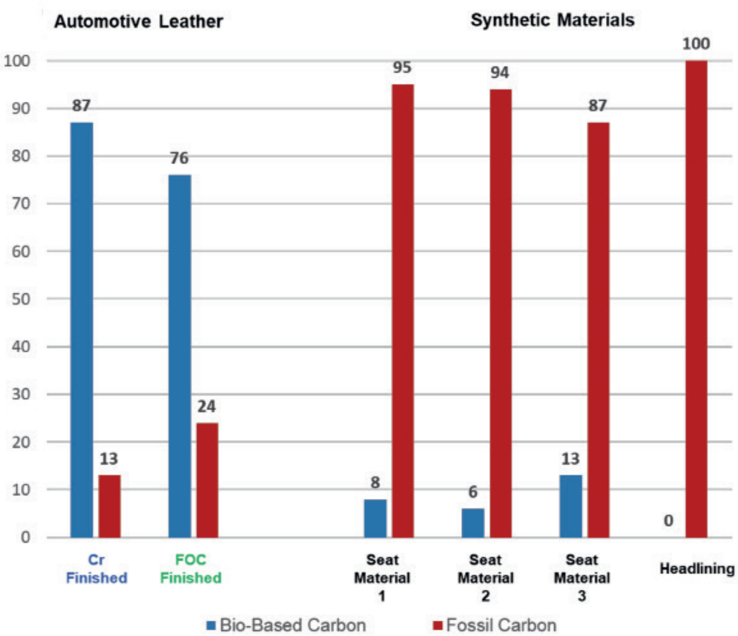
A range of commercial leather auxiliaries has been tested using ASTM D-6866. Within the scope of this study we decided to consider chemical products which are applied during the retannage process and which, in accordance with their intended effect, remain within the structure of the final leather. All samples were taken from commercial production.

Results of these examinations are depicted in Figure 3 for selected retanning agents (left) and fatliquors (right).

Neither the traditional phenolic syntan nor the acrylate syntan tested contain any renewable carbon. These products clearly are of fossil origin. Tara powder was analysed as a reference whose organic content is entirely renewable. This sample contains no petrochemically derived, organic ingredients. Results for effective retanning agents containing variable proportions of renewable organic raw materials besides fossil syntans are located between the two extremes ("bio-based" syntans 1 and 2). Examples for such products are mixtures of traditional syntans with protein hydrolysates. The ratio between renewable and non-renewable organic content is clearly reflected in the test results.

For lubricating agents, the situation is very similar. We purposely examined commercial products with very different amounts of renewable and fossil organic ingredients. The samples of established commercial lubricating polymers contain essentially no renewable carbon and thus essentially no renewable, organic substances. These products are clearly based on petrochemically derived raw materials. Depending on their formulations, commercial fatliquors based on natural raw materials may have a very high renewable content as is shown in Figure 3 (right). Using the analytical method ASTM D-6866 it is possible to establish the content of renewable, organic matter in chemical products. In case of known chemical compositions, we experienced that there is a good agreement between the results from theoretical calculations and those yielded via ASTM D-6866.

Figure 5: ASTM D-6866 measurements on synthetic automotive materials compared to finished automotive leather.



Results – leather and synthetic materials

The examination of different commercial leathers and synthetic materials is essentially the heart of our study. The appearance of the synthetic materials is designed to imitate the look of genuine leather, partially with astonishing accuracy. An overwhelming majority of end consumers might find it quite difficult to differentiate between these substantially different materials. Using ASTM D-6866 measurements, we like to highlight a fundamental distinguishing feature in a clear and factual manner.

First, we like to consider the examinations of different leather samples that all came from commercial automotive leather production.

Figure 4 shows results from testing a) dried chrome tanned leather (wet-blue), b) chrome crust and c) finished chrome tanned leather. The results are compared to the corresponding leathers from a chrome free system.

As can be seen, the chrome tanned leather has a very high renewable, organic content which decreases somewhat as it progresses through the production process. This is clearly due to the application and incorporation of retanning, dyeing, fatliquoring and ultimately finishing materials. The employed chemicals clearly contain petrochemical derived (fossil) carbon, and this can be detected.

As expected, the same pattern is shown in the chrome free leather production. Most interestingly, the higher quantities of both tanning and retanning materials necessary to achieve satisfactory leather from a chrome-free system can clearly be seen in the values. Again, there is a practical explanation for the observation made.

The tested finished leathers of both types intrinsically possess a very high amount of renewable organic material. Due to the processes and chemicals employed, the renewable content in chrome tanned automotive leather (87%) is noticeably higher than the one in the chrome free version (76%).

We then compared the tested automotive leathers with synthetic competitor materials. As with the leather samples, these come from actual commercial production and represent materials being used in the car interior in contexts where leather could be used instead. The results of these measurements are summarised in Figure 5.

Although individual values are not reported here, all leathers and synthetic materials had very similar ash contents, indicating that in no case was a substantial proportion of inorganic material present. The comparison therefore is between materials of similar organic content.

Due to the natural collagen, leather exhibits an intrinsically high content of renewable material.

As can be seen clearly, none of the automotive plastic materials has a significant renewable content. All samples are based on petrochemically derived raw materials.

Leather competes with synthetic imitations in many more areas of our daily life. Consistently, examinations of various other leather and plastic based articles have been conducted. We have carried out comparisons of shoes and handbags purchased on the high street for the purpose of this study. To represent the garment sector, a commercially purchased nappa sheepskin was compared with a correspondingly embossed PVC based material. Again, striking is the purposely similar design of both types of articles, the ones fabricated from genuine leather and the ones made from synthetic imitations.

The results of this comparison are highlighted in Figure 6.

In every single case, as can clearly be seen, the leathers contain a very substantial amount of renewable substance whereas for the competitor materials the reverse is true.

The leathers tested in this study represent a large part of the spectrum of commercial leather types, and they all have very high renewable contents. The high content of renewable material is by no means generated artificially but is a very fundamental and intrinsic property of genuine leather and stems from its most basic raw material: the hide or skin of an animal. In contrast to leathers, all the competitor plastic materials tested in this study have low or negligible renewable contents. Not seldom promoted to be 'greener' or explicitly 'free of leather', most of the commercial competitor materials are based on fossil, non-renewable raw materials.

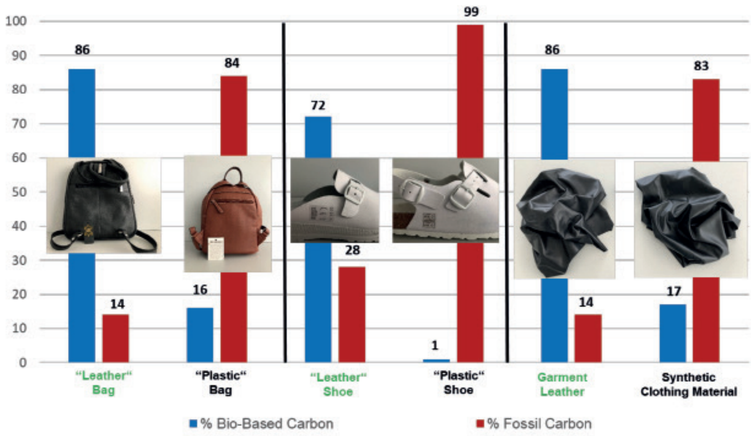


Figure 6: ASTM D-6866 measurements on different leather types compared to corresponding synthetic materials.

Summary

Measurement of carbon isotope ratios by ASTM D-6866 can be used to give an objective and sensitive measure of the renewable organic content of a material sample. The technique can be applied to auxiliaries as well as to complex, finished articles.

This study compares the renewable organic content of commercially produced leathers and the corresponding synthetic materials. All materials are actually applied in different areas of our daily life.

Due to the natural collagen from which it is produced, leather exhibits an intrinsically high content of renewable material, whereas all competitor materials tested in this study feature very low renewable contents. For the manufacture of leather, the effect of various sophisticated chemicals is crucial. The contribution from process chemicals on the renewable content of finished leather is not negligible, and the impact of a selection of chemical products on the bio-based content of leather is quantified and discussed.

Leather is a unique, natural, and beautiful material and we can acknowledge and promote it as such. The aim of the present contribution is to support this claim with clear and provable facts. ●

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