The Circular Economy of Equine Surfaces: Investigating the Recyclability of Surfaces Produced by Equestrian Surfaces LTD.

By

Steven Nicholson

In collaboration with

Equestrian Surfaces LTD.

Supervisors: Dr Julien Doulcet, Dr Mark Ashton

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Declaration

I declare that this thesis, completed in fulfilment for the degree class of Masters by Research in Chemistry (MRes), has been completed by myself and the results included within it are entirely my own work. This thesis has not been submitted for any other degree or professional qualification.

Steven Nicholson, Department of Chemistry, Lancaster University.

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Abbreviations

ASTM – American Society for Testing and Materials

BS – baseline surface

CE – circular economy

CRUK – Carpet Recycling UK

DCM – dichloromethane

DMC – dimethyl carbonate

EDX – energy dispersive X-ray

ES – Equestrian Surfaces LTD

EOL – end-of-life

FID – flame ionisation detector

FTIR – Fourier Transform infra-red

GC – gas chromatography

GPC – gel permeation chromatography

HPLC – high-performance liquid chromatography

IR – Infra-red

MS – mass spectrometry

NIST – National Institute of Standards and Technology

PAH – polyaromatic hydrocarbons

PET – polyethylene terephthalate

PP – polypropylene

PTFE – polytetrafluoroethylene

SEM – scanning electron microscopy

THF – tetrahydrofuran

Glossary of Terms

End-of-life surface – a used equestrian surface which shows signs of degradation.

Baseline surface – a surface prepared by Equestrian Surface specially for this project. It has not been laid as a surface and has not been subject to use. It has all materials present in the original percentages following manufacturing.

Waxed sample – a sample tested in its original form as acquired by Equestrian Surfaces. This surface has not been subject to extraction and as such is in its waxed form.

Dewaxed sample – a sample isolated following extraction of the surface with an organic solvent. This sample has had the wax coating removed from it.

Abstract

As an ever-growing sector, the equestrian industry is constantly developing, with a range of synthetic surfaces available in the market. Typically, synthetic equine surfaces comprise three major components – sand, wax, and fibre. Currently, most equine surfaces are disposed of in landfill when they reach the end of their life. This is an unsustainable waste solution; hence alternative strategies need to be explored.

This project has been completed in collaboration with Equestrian Surfaces LTD, with the main aim of this research being the development of a more sustainable end-of-life (EOL) solution for equine surfaces that allows the individual components to be recovered and potentially recycled into new surfaces. Equestrian Surfaces LTD are a company specialising in the production and installation of synthetic equine surfaces, offering a range of surfaces suitable for indoor and outdoor use in all weathers and for all disciplines.

The research presented in this thesis focusses on the small-scale extraction and separation of the individual surface components (sand, wax, and fibre) as well as identification of any changes to the quality and physio-chemical properties of the separated materials compared to their composition at time of manufacturing. After presenting the general context for this work (chapter 1), the results section is comprised of 4 chapters focusing on the following aspects: experimental methods (chapter 2), wax extraction (chapter 3), sand and fibre separation (chapter 4), and conclusion and future work (chapter 5) as well as an appendix containing additional experimental detail.

Results discussed in chapter 3 show that wax can be extracted efficiently from used surfaces using a range of organic solvents, with ethyl acetate identified as a suitable non-toxic, high-yielding green solvent. Alternative green extraction routes were also explored, with microemulsion extraction proving promising for removal of wax from surfaces. The major obstacle with this technique was the recovery of organic material from the aqueous solution, with this highlighted as an important area for further research. Analysis of extracted wax using a range of analytical techniques (GC-MS, IR, DSC, and CHNS elemental analysis) showed that wax decomposes rapidly and is lost from surfaces progressively over time. The extracted wax can be purified (silica gel column chromatography) however, since a considerable mass of wax is lost during usage, and the yield of reusable wax recovered following purification was as low as 9.5%, this was deemed an unsustainable solution.

Chapter 4 focussed on utilising size-based separation techniques to isolate the sand and fibre from surfaces. Results discussed in this chapter revealed that surfaces, in both the waxed and dewaxed forms, can be separated in this way, with sand recovery yields of up to 93% recorded for some used surfaces. It was also discovered that the extent of wax remaining on a surface affects the efficiency of separation, with high remaining wax content resulting in poor sand recovery. The quality and purity of the isolated sand was evaluated using analytical techniques including SEM, EDX and IR spectroscopy, showing that the recovered sand has a particle size distribution similar to that of the supplier sand.

Results discussed in chapter 4 also revealed how fibres can also be separated from surfaces by utilizing size-separation techniques; however, the fibres recovered from used surfaces appear heavily

contaminated with sand and other solid materials. The quality of the fibres was briefly evaluated via SEM-EDX analysis and tensile strength tests, both of which highlighted a reduction in quality and purity following surface usage. Further testing is necessary to evaluate the reusability of the fibres, however, since this material is already recycled it may not be economically viable to pursue further recycling. In this way, further research to provide an end-of-life solution for the used surface fibres should be conducted.

We concluded that, equestrian surface recycling is not a trivial process, and that wax removal from surfaces is a complex, costly, and unnecessary step that can be avoided due to loss of the coating during surface usage. The small-scale separation techniques developed in this report provide a tool that can be used by Equestrian Surfaces LTD to determine the EOL state of their surfaces. Surfaces which meet the set requirements detailed in chapter 5 can be deemed as fully EOL and subsequently subject to direct mechanical separation without the need for wax removal. This has been recognised as the most suitable recycling strategy for use in industry due to the simplicity of separation and the high yields of sand recovery attainable. The sand recovered from this process can then be incorporated into newly manufactured surfaces, with further testing needed to establish the quality of the surfaces made from reused non-dewaxed sand. Further research is also required to improve the circularity of the proposed process, with the ability to reuse both the large fibres and microplastics isolated from surfaces being key examples.

The Circular Economy of Equine Surfaces: Investigating the Recyclability of Surfaces Produced by Equestrian Surfaces LTD.

Chapter 1 – Introduction

The equestrian sector is a rapidly growing industry, with the demand for high-quality equine arena surfaces increasing dramatically in recent years. The surface a horse trains, works, and competes on plays a crucial role in both enhancing or limiting the horse's ability to perform and in determining the risk of injury; hence, to achieve high-level performance the physical properties of the surface, as well as how it is used need to be carefully considered.[1]

A range of synthetic equine surfaces exist within the market, with most surfaces being sand based. As well as this, different materials can be added to surfaces to help tune performance properties. This includes the addition of fibrous material, to aid comfort, and the coating of the surface in a wax binder, permitting all year-round surface usage.

The environmental impact of equestrian surfaces has not been fully established in technical and scientific literature, but it is an area that warrants consideration as the number of artificial arenas continues to increase. Disposal of synthetic arena surfaces poses a significant problem for arena owners and operators. These surfaces are highly heterogenous, containing a significant volume of sand-based material which will not re-integrate into the environment without pre-treatment or evaluation of its components prior to disposal.

Presently, the sole credible 'complete-disposal' route for equine surfaces involves sending them to landfill. Disposal through this means is often highly costly, with several countries implementing a fee-based system per tonne of material disposed. In the United Kingdom this is currently £99 per tonne (as of April 2022). This is not a sustainable method of disposal and hence it is critical that alternative end-of-life options be explored.

1.1 Project Aims

Research presented in this thesis aims to participate in developing a circular economy strategy for equine surfaces that can be implemented in industry by Equestrian Surfaces LTD. In order to achieve this, the company envisaged that the principal elements of old surfaces (sand, wax and fibres) could be isolated and subsequently reincorporated into new surfaces. Thus, the aims of this project are first to separate each component and assess the quality of the isolated material by testing the physical properties of each comparing them to that of the pre-surface equivalents. Once this is done, focus can be placed on developing sustainable lab-scale methods to separate (and purify, if necessary) the surface materials; ideally these methods should also be well-suited to scaling up in industry.

In this, the method should permit isolation of the individual surface materials allowing them to be potentially reincorporated into new surfaces.

Initial research will focus on the small scale (~ 1 kg) separation of horse-riding surfaces into the three primary components (sand, wax, and fibre) followed by analysis of the physico-chemical properties of each separated component. This will include separation of both used and unused surfaces to establish a baseline of comparison. A range of analytical and characterisation tools will be employed to assess the quality of the materials before and after usage, allowing any major changes to the materials that may affect their capacity for reuse to be identified. Where necessary, the feasibility and cost of purification methods will be explored since this may be required for certain surface materials to be reused.

More specifically, it is anticipated that mechanical separation techniques will be required to enable separation of the sand and fibre from surfaces; hence this project also aims to assess the viability of size separation techniques (sieve and trommel separation) for isolation of reusable material from surfaces. If successful, further research will be carried out to increase the scale of separation in order to more accurately reflect the large scale that will be used in industry.

As well as this, Equestrian Surfaces LTD currently do not have any scientific methods to estimate the end-of-life state of customers surfaces; thus, the work carried out in this thesis will also be used to develop a simple and low-cost protocol for assessing the state of used surfaces.

1.2 Synthetic Equine Surfaces

As a result of the growing demand for high quality arena surfaces, the number of surface manufacturers and products available has increased dramatically. There are a range of factors which have driven this increased demand, including greater participation in equine sports, more competitions at entry level, weather patterns, and better awareness of injury risk factors.[1] The variation in products on offer worldwide are diverse, and there are currently few guidelines highlighting how the functional properties and characteristics of the surface vary with composition.

There are many distinct types of engineered artificial surfaces on the market for the various equestrian sports, which can be sold as individual components or mixed with additives according to the requirements of the buyer and the intended use of the arena. Unlike natural turf, these artificial surfaces boast enhanced riding performance, reduced variability, reduced maintenance, and increased safety and durability under heavy use conditions.[2] The surfaces used most in training arenas by dressage riders in the UK are woodchip, sand, sand and rubber, and sand and polyvinylchloride (PVC).[3] The components of an engineered surface are in themselves specialized products, and their proportion in the surface mixture greatly affects riding characteristics and performance.[2]

Natural silica sand is a desirable material for riding surfaces because of its mineral hardness, weather resistance, surface roughness and its sub-angular particle shape which increases the shear resistance of the material.[2] Most state-of-the-art surfaces consist of a base of silica sand of varying grain sizes, to which a range of materials are added. The way the sand responds to any of the added materials depends on the particle size distribution of the grains, which affects the bulk density, compaction, and water retention of a surface. In the UK sand based surfaces appear to be most popular for dressage riders, with Murray and co-workers reporting that at least 77% of British dressage riders opted for a sand based arena surface.[4]

As well as these base components, surfaces often contain additives to modify the surface properties. These additives can include synthetic or natural fibres, rubber, cloth or felt strips. The addition of shredded fibres to surfaces stabilises the sand to prevent windblown loss and create a firm but responsive (springy) riding surface that conveys moisture retention and frost resistance benefits. The recent surge in popularity of fibre-based surfaces is due to a combination of customer demand and optimum performance.[5]

Furthermore, surfaces can also be coated with chemical treatments and binding agents which act to control moisture, add cohesive strength, and aid in dust suppression.[1] Wax-coated surfaces often come at a more premium cost because the properties of these surfaces allow for long-term performance under a variety of circumstances. The hydrophobic nature of the wax minimises the effect of moisture on a surface, allowing it to be used all year round regardless of conditions.[1] The wax used in most cases is a slack paraffin wax made primarily of linear n-paraffins containing of 18-60 carbon atoms, hydrocarbon oil, and a small percentage of branched iso-paraffins and cyclic alkenes. It has been reported that wax-coated surfaces are more uniform and less sensitive to weather conditions, and when compared to woodchip and sand surfaces, the incidence of lameness and injuries is also reduced.[4] This is supported by data from Chateau and co-workers who compared the performance of a wax-coated track to a classic sand track; observing a significant reduction in impact shock for the waxed track compared to the sand track.[6]

One of the most important features that impacts surface lifetime is its shear strength. This is a result of the bonding between the components, and it is strongly influenced by the wax binder. Over time, the synthetic surface is subject to both environmental and mechanical induced degradation, which has a direct impact on the durability of the surface as it causes the wax binder to become less effective and the surface performance to decline.[1] Additionally, the wax can also be subject to chemical changes during surface usage. This was evidenced by Bridge and co-workers who found that wax in horse surfaces was subject to oxidation over a 7-year period.[7] The chemical and compositional changes caused by this oxidation were found to hinder the mechanical performance of the surfaces, reducing the safety for the horse and rider.

As well as the constituent components of a surface, there are several external factors which also effect surface performance, including the drainage system, environment (temperature for wax surfaces, moisture content for sands surfaces), surface age, and surface usage. These factors interact and contribute to the overall safety and performance of a surface.

Uneven surfaces with varying moisture content, compaction and composition result in inconsistent forces acting upon the horse, which in turn is correlated with higher injury risk.[3, 8] With this in mind, arena owners typically employ maintenance strategies to improve surface longevity and consistency. This can include topping up a surface with new material, or re-coating a surface with new wax.

1.3 Surface Testing

Although there are a range of equine surfaces available, surface testing suffers from a lack of standardised procedures available in industry. This has made it difficult to accurately compare the properties and function of different surfaces. The majority of surface testing that has been done to date has employed mechanical equipment to replicate the interaction between horse hoof and surface. Equipment such as the Orono Biomechanical Hoof Tester has been used to analyse surface properties by simulating the action of a horse's hoof using a mechanical system. However, such advanced testing equipment is expensive to develop, operate, and use. As a more accessible alternative, equipment designed to measure human locomotion has also been used to study surface performance. Although these devices allow large, repeatable, and comparable data sets to be obtained, they do not provide collisions equivalent to those of a horse, and hence are fundamentally flawed as a surface testing tool.[9]

Laboratory testing is suitable for small-scale surface testing and has been used to evaluate surface properties including wax and fibre content, durability, permeability, and triaxial shear resistance.[2] Testing is aimed primarily at characterizing the physical composition of a surface and the properties of its individual components. Hence, even though laboratory-based tests can provide information on material properties, they cannot provide complete information on the characteristics and performance of surfaces due to the absence of the underlying materials and loading conditions which are representative of the true surface loading exerted by a horse.

In short, there are two main perspectives from which to measure the response of a surface: one being repeatable measurements using mechanical testing equipment, and the second being measures obtained via small scale lab tests. Both methods are limited by issues surrounding replicating and being able to quantify the combination of factors experienced by a horse. Consequently, a hybrid approach is often used to ensure repeatability and to aid understanding of the individual surface components.

The lack of standards and general information surrounding surface testing and evaluation causes issues for arena owners who do not have simple and inexpensive tools at their disposal that can be used to verify manufacturers performance claims and develop appropriate maintenance plans.[9] This makes it difficult to assess how the properties of a surface change over time and establish at what point the surface can be classified as end-of-life. This is therefore an area of research which requires further investigation.

1.4 The Circular Economy Solution

Traditionally, the dominant practice of business in industry has been based on a linear economy model in which raw materials are used to produce a product as well as waste material which is then discarded. However, for the world to manage dwindling natural resources and deal with ever-growing volumes of waste, we must move away from this traditional take-make-dispose ethos and instead embrace closed loops that place value on all resources used or generated.[10]

The only long-term viable alternative involves transitioning towards a circular economy (CE) model, where the value of products, components, materials, and resources are maintained in the economy for as long as possible. This concept revolves around the reuse of end-of-life materials, focussing on turning such goods into resources for other uses and hence minimising waste. Moreover, a CE aims to create value from waste by revering and reusing resources. For example, recycling can close the loop of a circular economy by re-introducing waste products into the market; reducing the consumption of raw materials and lowering both energy consumption and CO_2 emissions.[11] A summary of the linear and circular economies models is visualised in Figure 1.

Product recovery has become increasingly important in transitioning to a circular economy. This involves the management of all used and discarded components and products to recover as much of the economic and ecological value as possible – thereby reducing the amount discarded as waste.[13] This is key to the success of a circular economy for end-of-life products – those deemed no longer suitable for their purpose.[14]

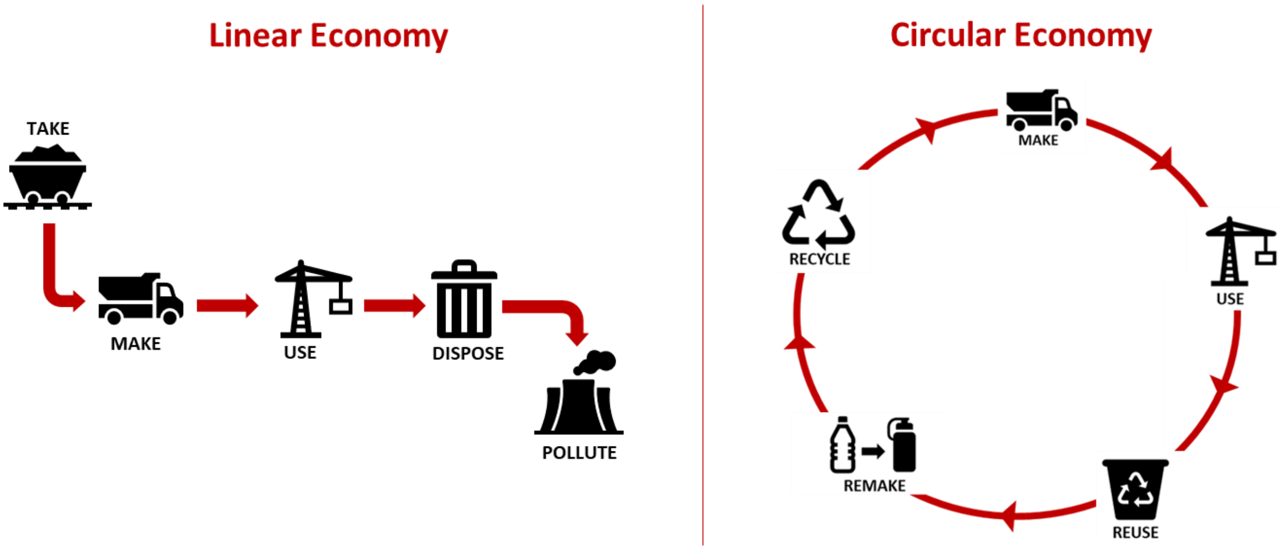


Figure 1. *Comparison of linear and circular economy models.*[12]

Current practices of waste management do not yet support the CE concept as a whole and new solutions in which waste can be reused to minimise resource usage are vital.[15] To initiate CE strategies, the European Commission has set goals within its circular economy package, including targets for the recycling of municipal solid waste (minimum 65% by 2030) and landfilling of solid waste (maximum 10% by 2030). In 2015 they defined a new action plan focusing on sectors with the largest resource usage and where the potential for improving circularity is high, such as the plastic sector.[15]

Whilst the concept of a CE is easy to understand, quantitative indicators to assess the circularity of material cycles and product life cycles need to be developed to facilitate successful implementation.[16] It wasn't until a 2012 report from the Ellen Macarthur Foundation: 'Towards the Circular Economy: Economic and Business Rationale for an Accelerated Transition' that the economic and business opportunities offered by a CE were pragmatically considered.[12] Despite this, there is still a huge amount of work to be done before circular economy strategies are successfully implemented into large manufacturing sectors.

1.5 Circular Economy of Equine Surfaces

As an ever-growing sector, the equine industry is a key area where transition towards more sustainable synthesis and disposal strategies are needed. Indeed, the equine industry is a sector with high environmental impact; involving a multi-step supply chain, which is associated with large energy consumption, use of chemical substances, water and air pollution, waste production, and finally microplastic generation.

Currently, surfaces are made using a range of materials, with many manufacturers promoting wax-coated surfaces as the major all year-round surface option. Wax is regularly used because of its hydrophobicity, cohesive capability, and high melting point (> 60 °C), enabling consistent surface performance, regardless of environmental conditions.[17] However, by changing the chemical composition of a surface it complicates any recycling or reuse applications as the individual components need to separated and isolated in pure form. For synthetic surfaces this involves extraction of the wax binder from surfaces, followed by mechanical separation of the remaining sand and fibrous material. It is therefore essential that suitable EOL strategies be developed enabling the reuse of all surface materials either for use in new equine surfaces or for diversion into other streams.

Equestrian Surfaces LTD are a surface manufacturing company offering a range of products including both waxed and non-waxed surfaces. Each artificial surface offered by ES is a blend of sand, fibre, and wax designed to enable optimum performance whilst ensuring high quality and comfort. Based in the North West of England, they chiefly operate from two bases including a manufacturing plant in Sandbach and a headquarters and factory in Burnley.

As a company, Equestrian Surfaces place large emphasis on sustainability, and are always looking for ways to minimise the waste and emissions associated with surface manufacturing. They are looking to transition towards a circular economy model, in which the value of all surface components is retained for as long as possible. By creating a suitable reuse cycle, tonnes of surface can be diverted from landfill, with the constituent materials being repurposed into new products. Not only will this allow ES to recycle their own surfaces, but it will also enable them to offer removal and recycling of competitors surfaces as an additional source of business.

For a suitable circular economy solution to be developed, it is necessary to consider the individual surface components and explore appropriate methods to both isolate and evaluate the purity of the raw materials before and after usage.

1.5.1 Sand

The sand used by ES in their products is supplied by Bathgate Silica Sand, a company offering a range of different graded sands for use in equestrian, horticultural, and construction industries. Specialising in equestrian sands, they have developed products consisting primarily of sub-angular grain sands, which represent the industry standard in terms of quality, drainage properties and durability. The sand procured by ES is listed as Moist 60 sand; the properties and grading of this, as well as other products in this range, are shown in Table 1.

		Moist 40	**Moist 50**	**Moist 60**
Classification	Sieve Size (mm)	% Retained	% Retained	% Retained
Very Coarse Sand	2.00 – 1.00	0.0	0.2	0.1
Coarse Sand	1.00 – 0.50	25.5	3.5	1.4
Medium Sand	0.50 – 0.25	46.7	50.2	33.0
Fine Sand	0.25 – 0.125	22.0	45.4	59.1
Very Fine Sand	0.125 – 0.063	5.9	0.7	5.8
Clay/Silt	<0.063	Trace	Trace	0.6

Table 1. *Classification and grading of sand supplied by Bathgate Silica.*

1.5.1.1 Sand Extraction

Sourcing of sand as a raw material for equine surfaces is a complicated procedure with various processes involved including extraction, purification, and transport. Sand is typically extracted from mines or quarries or dredged from the sea/riverbeds. Numerous types of sand processing methods are used in industry, ranging from simple screening methods to more sophisticated techniques including magnetic separation, sand attrition, and hot acid leaching.[18]

Whilst the most basic sand processing can be used for building applications, this is not suitable for application to sport surfaces where a sand washing plant is essential. Such plants not only wash the sand but also separate the sand into two or more different grades. This is a continuous process which uses gravity to sort sand whilst dispersed in water.[19] This is critical for application to equine surfaces since the size and angularity of the sand particles influence surface performance. This is critical for application to equine surfaces since the size and angularity of the sand particles influence surface performance.[6] This was confirmed by Murray and co-workers who found that fine sand remained more stable than coarse sand under hot and dry conditions.[3] Typically, dry sand has low shear resistance because the particles move easily against each other, potentially resulting in the surface giving way against the force of hoof contact rather than providing stability.[3] It is therefore important that the grading of the sand particles be considered when creating a surface.

1.5.1.2 Environmental Concern

Sand is an important mineral for society, but the practice of sand mining is becoming a growing environmental issue as the demand for sand increases in industry. Sand mining activities are mostly deemed unsustainable, not only because they exploit resources, but also because they destroy the environment and leave impacts that are irreversible.[20] For example, excessive mining leads to land degradation, reduction in biodiversity, land subsidence, and noise pollution. As well as these, sand quarrying is an energy intensive process and as such has implications in both air and water pollution, something that is only amplified by transportation of material following extraction.[21]

It is the increasing demand for sand, combined with increasing environmental concerns surrounding quarrying that have highlighted sand recycling as a necessary process for a sustainable future. Sand accounts for over 80% of equine surfaces, hence the ability to separate and reuse this is incredibly important for this industry. Research into this is scarce, however sand separation is expected to be trivial due to its smaller particulate size. The main concern surrounds the properties of the used sand and how these may change over time. If the shape and properties of the sand change during usage it is unlikely that this will be suitable for reincorporation into new surfaces, meaning other streams for reuse may need to be explored.

1.5.2 Fibre

As well as silica sand, equine surfaces often contain shredded fibres. These fibres are incorporated into the surface allowing the mechanical strength of the surface to be tuned.[7] Typically, it is both post-industrial and post-consumer carpet waste that are used as the fibre component in surfaces, providing a cheap filler material that enhances comfort and allows equine surface companies to advertise as being eco-friendly.[8]

1.5.2.1 Carpet Recycling

Each year 400,000 tonnes of carpet waste are buried in UK landfill sites. This is a huge concern because these materials are very bulky and there is a physical limitation on the number of landfill sites available in the UK.[22] It costs £99 per ton to landfill waste in the UK, and this is quickly becoming an unacceptable option for carpet waste.[0]

There is also an environmental concern with landfilling carpet waste because the materials do not biodegrade and can be heavily contaminated, leaching chemicals into the environment. A major alternative to landfill includes energy from waste incineration. This involves incinerating the fibres and using them as fuel to replace traditional fuels, such as coal, for use in cement kilns or boilers. The calorific values obtained for burning synthetic carpets are similar to the values obtained for diesel and petrol, confirming carpet fibres as useful sources of fuel. Although this energy recovery may be feasible for all types of carpet waste, the problem with incinerating carpets is the generation of ash waste and toxic gases.[22]

Alternative recycling options for carpets have been explored to find a more sustainable solution. Presently, the major recycling stream for synthetic fibres is the equestrian industry, with research by Carpet Recycling UK highlighting this as the primary source of carpet recycling in the UK, with 34% of carpet waste diverted from landfills used in this industry (Figure 2).[7]

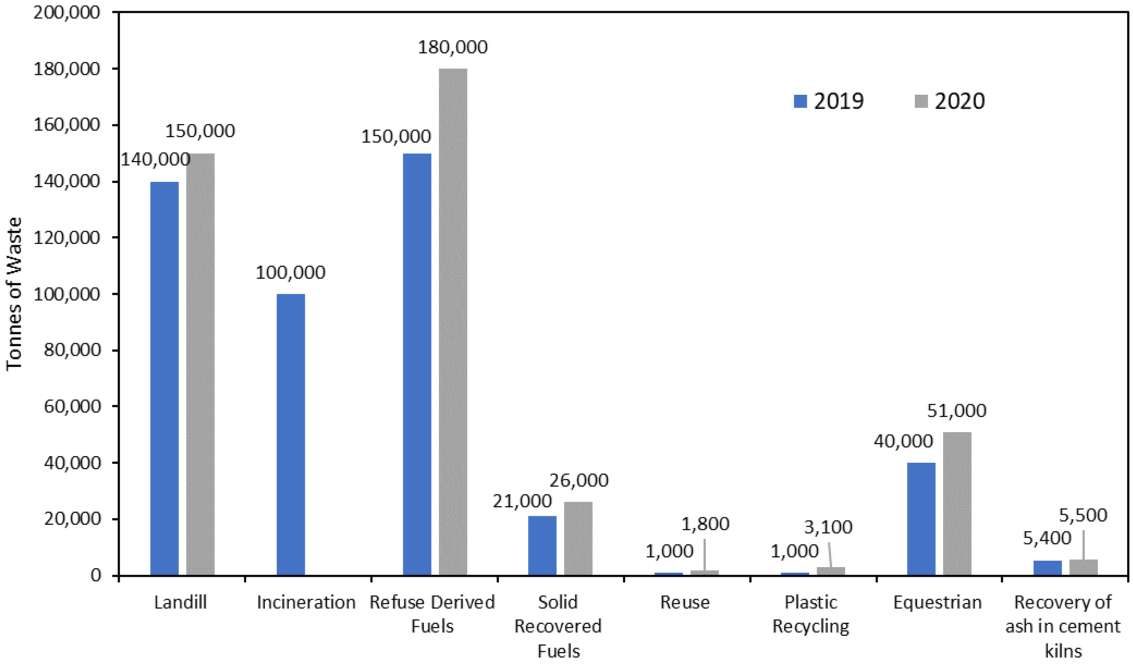


Figure 2. *Carpet waste recycling outcomes 2019-2020.*[1]

1.5.2.2 Fibre Processing at Equestrian Surfaces

Carpets accepted by ES comprise a range of fibres and fibre blends including wool, polyamide, polypropylene, polyethylene terephthalate, polyester, and polyvinyl chloride. Because of the range and complexity of fibres received by ES, it is critical that appropriate procedures are in place to ensure only suitable carpets are incorporated into equestrian surfaces. Previous research by Miller and co-workers in partnership with ES explored the different methods available to determine the composition of post-consumer and post-industrial carpets.

Currently, after delivery to site, carpets are sorted using a handheld near infra-red (IR) gun which facilitates the trivial and efficient identification of carpet types based on face fibres. The range of the IR spectrum that is being investigated is between 1600 and 2400 cm^{-1}. This is used in conjunction with visual identification to sort the fibres into natural and synthetic piles. Following identification of polymer types, 100% polypropylene (PP) and wool carpets are separated and excluded from the manufacturing process. 100% PP carpet is removed as input to higher value alternative plastic markets and wool is taken out as it degrades too rapidly to be used in equestrian surfaces. Using IR, in conjunction with TGA, and DSC allowed the relative composition of the synthetic carpets arriving at the yard to be determined (Figure 3).

Following identification, suitable carpets are subject to shredding using a Doppstadt slow-speed shredder. Carpets are sometimes re-shredded to reduce the maximum particle size to 100 mm. The shredded fibres are then ready for further size reduction using a granulator, before eventually being incorporated into a surface during manufacture. As well as fibres, ES also receive post-consumer and post-industrial underlay which is subject to similar inspection and shredded in the same way as the fibres. Again, only underlay samples which pass inspection are shredded and used in surface manufacturing.

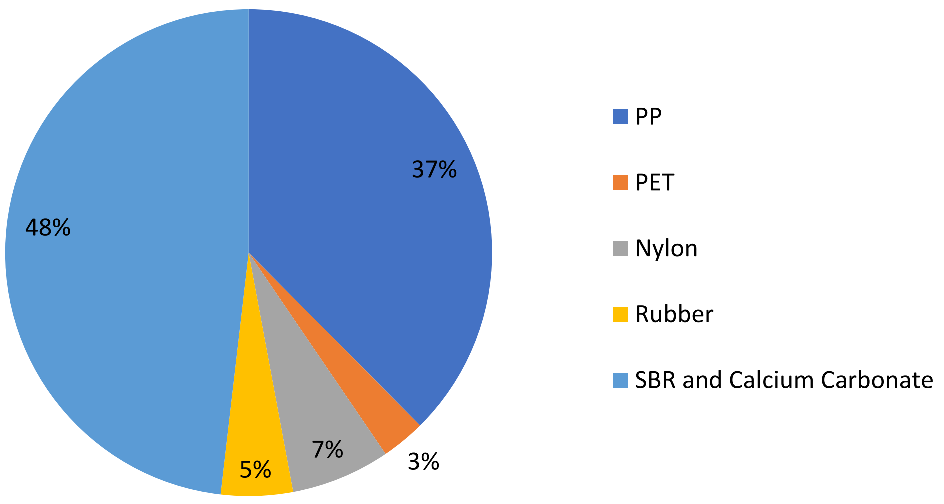


Figure 3. *Chart showing the % distribution of the different post-consumer and post-industrial carpet fibres received by ES.*

1.5.2.3 Persistent Organic Pollutants

Carpet recycling is not a straightforward process as there are significant regulations in place which control the use of post-consumer and post-industrial carpet waste. This is because waste carpets often contain organic contaminants which have potentially toxic properties. A prime example of this surrounds the presence of persistent organic pollutants (POPs) in post-consumer carpet waste.[23] POPs is a broad term encompassing a range of organic polymers which are thought to break down in the environment, releasing potentially toxic chemicals into food chains. Previously, these POPs were incorporated into carpets to reduce flammability and provide stain resistance. However, some of these compounds have now been designated as being persistent in the environment as well as carcinogenic and/or toxic to humans, animals, and aquatic organisms. Halogenated flame retardants such as some polybrominated diphenyl ethers, and polychlorinated biphenyls are common classes of POPs (Figure 4).[24]

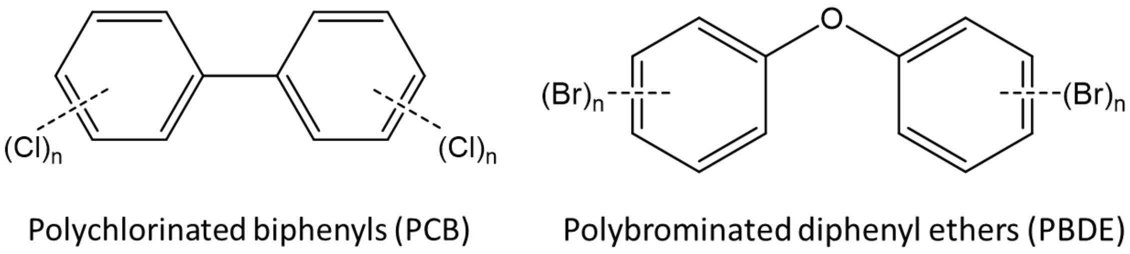


Figure 4. *Chemical structures of polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs).*[23]

To prohibit the release of POPs into the environment, several legislative bodies have developed regulations against reuse of materials which are contaminated with POPs, with the Stockholm Convention on Persistent Organic Pollutants (2001) being a key example.[23] In situations where waste contains POPs above the regulated limits the waste cannot be recycled, reused, or mixed with other waste; instead, the contaminated waste must be sent to an authorised treatment site that can completely destroy the POPs or irreversibly transform them, so that the remaining waste does not exhibit the characteristics of POPs.[23]

Given that the UK has complying with the treaty since 2004 when it was signed, and the expected maximum lifespan of carpet is 15 years, with most being disposed of before this date, the majority of POPs-containing carpets are expected to have already left the waste stream. However, POPs-containing carpets still enter the waste stream meaning it is important to consider the presence of POPs when recycling carpet fibres.

A recent study by the Department for Environment, Food and Rural Affairs (DEFRA) found high levels of brominated flame retardants in discarded sofas.[25] In light of this, the environment agency issued guidance that ‘if an item of domestic fabric waste is upholstered you should assume that it contains POPs, and manage it as a POPs waste, unless you can demonstrate that it does not contain POPs’. The introduction of this regulation shifted the burden of proof from the manufacturer to the disposer, meaning in order to recycle carpet waste it is necessary to test samples regularly in order to ensure POPs contents remain below the threshold.[26]

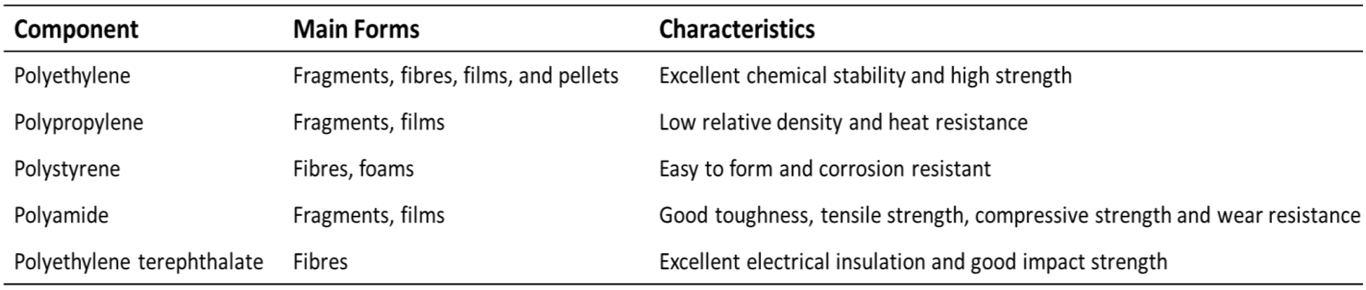
The presence of such contaminants in equine surfaces prompted the environmental agency in 2021 to introduce new regulations surrounding the use of carpet fibres in equine surfaces. The new regulations cover the usage of both recycled carpets and waste offcuts from new carpets. Both types of carpet must be treated post-consumer, with all physical contaminants removed. Only after this can the fibres be shredded and incorporated into the surface.[27] This has had a detrimental impact on the carpet recycling industry since the additional cost associated with POPs testing deters people from using post-consumer carpet fibres.

Because of this, Equestrian Surfaces regularly test the post-consumer and post-industrial carpet fibres coming into their site to ensure POPs contents, if any, remain below threshold levels.

1.5.2.4 Microplastics

In addition to POPs, the use of shredded fibres in sport surfaces is further complicated by the production of microplastics (MPs). During usage, the fibres can degrade and be kicked up off the surface. This process produces tiny plastic particles which can be inhaled by the horse or rider or washed into waterways where aquatic life and later humans consume them.

Microplastics are classified as micro-sized particles composed of synthetic polymers smaller than 5 mm in diameter.[28] They are complex in nature and have a range of characteristics that differ between samples; including size, shape, polymer type, and the presence of any additives. The main characteristics and structures of common microplastics are shown in Table 2 and Figure 5, respectively.[29]



Component	Main Forms	Characteristics
Polyethylene	Fragments, fibres, films, and pellets	Excellent chemical stability and high strength
Polypropylene	Fragments, films	Low relative density and heat resistance
Polystyrene	Fibres, foams	Easy to form and corrosion resistant
Polyamide	Fragments, films	Good toughness, tensile strength, compressive strength and wear resistance
Polyethylene terephthalate	Fibres	Excellent electrical insulation and good impact strength

Table 2. *Characteristics and main forms of common microplastic components.*[29]

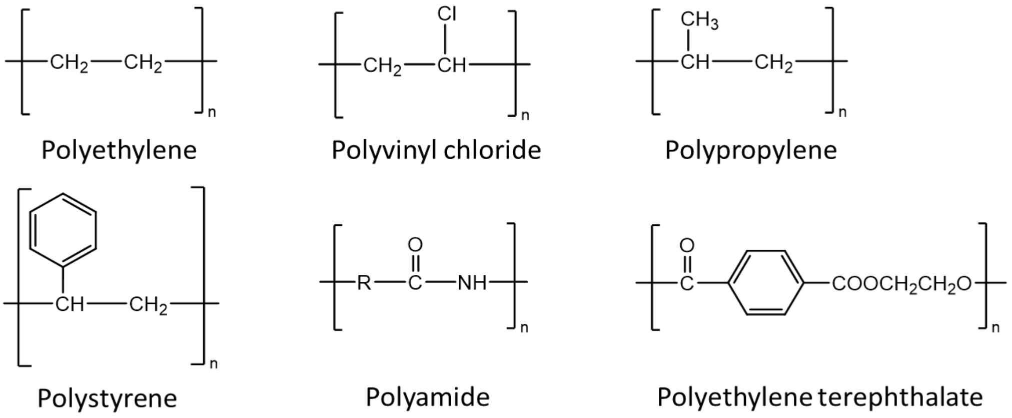


Figure 5. *Molecular formula of common microplastic components found in marine environments.*[28]

Microplastics can be sub-divided into primary and secondary MPs. Primary MPs are those which are intentionally made and added to products to enhance certain properties (for example, microbeads added to skin care products).[30]

In contrast, secondary MPs arise unintentionally from the degradation and weathering of larger plastic items.[31] A major example of this includes the washing of textiles in which microplastic fibres are released from clothing items and then disposed of into the environment via wastewater. Research by Napper and co-workers reported that a wash load of 6 kg of acrylic clothing could release over 700,000 MP fibres.[32] In addition, to investigate the release of MPs from carpets, Alipour and co-workers characterised MP fibres in the wastewater of two carpet washing workshops. They found that the wastewater from both workshops contained a significant number of MPs, with over 3000 MP fibres per square metre being identified in one workshop.[33] This research confirmed the carpet industry as a major contributor towards the production and release of MPs, hence the use of such fibres in the equestrian industry is also likely implicated in MP release.

The concern around MPs arises from their high surface-to-volume ratio which gives them a high ability to absorb organic pollutants and heavy metals in the environment, allowing them to act as vectors for potentially toxic species.[34]

The ability of MPs to act as vectors for organic and inorganic micropollutants was demonstrated by Arvaniti and co-workers who studied the sorption properties of two drugs onto polystyrene microplastics.[35] They found that both drugs successfully adsorbed to the MPs, and that this sorption was pH dependent and significantly enhanced under acidic conditions. Examples of toxic chemicals which have also been reported to bind to MPs include heavy metal ions (Fe, Mn, Pb, Zn) and persistent organic pollutants including organochlorine pesticides and polychlorinated biphenyls.[36] Additionally, MPs may also leach plastic additives, some of which have been found to be toxic, endocrine disrupting, or carcinogenic.[34]

Because plastics degrade so slowly, MPs have a high probability of ingestion, incorporation into and accumulation in the bodies and tissues of many organisms. Extensive research into the impact of microplastic consumption on human function has been carried out, with MPs being detected in both human blood and lung tissue.[37] Research has suggested that, under conditions of high concentration, microplastics may cause inflammatory lesions, originating from the potential of their surface to interact with tissues in the body. The increasing incidence of neurodegenerative diseases, immune disorders and cancers has also been linked to the increased exposure to environmental contaminants, including microplastics. However, knowledge of the effects of exposure to microplastics on human health is limited, leading to high uncertainties surrounding the findings of many MP studies.

The concern around MP production is amplified in cases of uncontained uses, such as the equine industry. For example, in 2021 the Plastic Health Channel found that children are being exposed to MPs in sporting facilities and equestrian arenas, hence the use of fibres, and subsequent production of MPs is something that must be taken into careful consideration for the future of equine surfaces.[38]

Although the impact of MPs on public health and aquatic ecosystems is not yet fully understood, the ubiquity of MPs and their negative effects for marine and freshwater biota have been widely reported, highlighting this as a critical area for further examination. With the predicted increase of these synthetic materials in our environment, more studies are needed to fully understand the risk of microplastics to human health, requiring knowledge on human exposure, pathogenesis, and effects.[38]

1.5.2.5 Microplastic Regulations

Currently, few regulations have been introduced surrounding the production and usage of MPs. The only example of MP legislation in place in the UK surrounds the creation and usage of primary microplastics for use in rise-off consumer products including body scrubs and face washes. Technical bans on primary MPs does not reduce the impact or creation of secondary MPs. This can only be prevented by considering (macro)plastic waste collection, ideally as part of the transition towards a circular economy.[30] This is an area that warrants further investigation before more MP legislations can be put in place.

1.5.2.6 Microplastic Waste Strategies

Although the area of MP research is vast, strategies for microplastic isolation and recycling are limited. A new and exciting MP extraction technique was developed by Sturm and co-workers in 2022. This used a harmless hybrid silica gel compound to extract MPs from contaminated water solutions. When placed in a tank with the polluted water, the microplastics clump to the silica gel, forming large lumps which rise to the surface and can be skimmed off. Once the agglomerates have been removed from solution, they can be reused in different streams, with use as paving material highlighted as a major reuse stream.[39]

In terms of microplastic recycling, one method which has been highlighted as a potential reuse pathway includes the cracking of microplastics into carbon nanotubes (CNTs). Carbon nanotubes have wide applicability due to their excellent mechanical, electrical and chemical properties, hence the ability to convert MPs into CNTs provides an exciting waste management tool.[40] A further example of MP recycling includes the work of Caniato and co-workers who utilised MP waste in the development of an open-cell foam. Because of its excellent thermal and acoustic properties, the MP foam was found to easily compete with traditional insulators, such as rock wool and polyurethane foam. Moreover, they found that the sound absorption properties of the material could be tuned by modifying the MP content, reinforcing this as a sustainable, clean, and environmentally friendly method for the recycling of MPs.[41]

Although research into MP recycling and reuse has gained traction in recent years, many of these concepts are only in the initial stages of development. Currently, the only viable disposal route for MPs is incineration. This prevents MP waste from re-entering the environment, however, it is a highly unsustainable method due to the large emissions and energy costs associated with it.

1.5.3 Wax

Incorporation of a hydrophobic wax binder into sport surfaces reduces the effect of moisture on the surface, allowing them to be used all year round. Generally, the wax used in equine surfaces is a slack paraffin wax obtained as a by-product of oil manufacturing. Typically, paraffin waxes consist of a mixture of linear chain aliphatic alkanes of high molecular weight, ranging from C_{16}-C_{60}. Varying proportions of slightly branched-chain paraffins (C_{18}–C_{36}) and naphthenes may also be present. They are highly sought in industry due to their applications which include for household chemicals, pharmaceuticals, and cosmetics.[42]

The uses of paraffins are dictated by a combination of their physical (melting or freezing point, hardness, and viscosity), functional (flexibility, adhesiveness) and chemical properties (colour, odour, heat stability). Most of these properties are typically assessed by following routine procedures established by ASTM (American Society for Testing and Materials) international.[43]

The reuse capacity of any wax extracted from surfaces is highly dependent on any changes to the chemical and physical properties resulting from surface usage. Previous research by Bridge and co-workers highlighted how, over a 7-year period, the wax coating of a synthetic surface was subject to both chemical change and breakdown.[44] The wax binder was extracted using solvent extraction, with iso-octane as the solvent. By repeating this procedure with samples of the same surface at different stages of life, they were able to identify any key changes in characteristics over time. For example, DSC data confirmed a decrease in melting enthalpy for the wax samples with increased surface age. The successive decrease in melting enthalpy suggests a decrease in wax crystallinity over time, which in turn suggests breakdown of the wax molecules.

In addition, chemical changes in wax composition were monitored using FTIR, with Bridge observing increased absorbance around 1700 cm^{-1} and 1000 cm^{-1} with increased surface age.[44] This was taken as strong indication of chemical change since the 1700 cm^{-1} region corresponds to the carbonyl (C=O) functional group present in oxidized hydrocarbon compounds including aldehydes, ketones, and carboxylic acids. This oxidation activity is common to aged oils and was found to occur predominantly within the oil of the wax binder. The presence of such polar carbonyl groups permits formation of intermolecular forces between molecules, causing them to exhibit properties different to the original unoxidized wax. This can increase the cohesiveness of the binder and potentially reduce the hydrophobic nature of a surface by allowing increased water absorption, thereby reducing the drainage ability.

Using DSC, and FTIR, combined with GC, Bridge and co-workers concluded that the wax was subject to both molecular and oxidative changes during usage. They attributed this to the direct exposure of the surface to air as well as to natural weathering processes including UV radiation exposure, suggesting this is likely to also be the case for many outdoor synthetic surfaces. Photooxidation mechanisms are well understood in polymers and are more easily facilitated in light molecular weight hydrocarbons such as those in the high-oil wax binders studied by Bridge.[44]

The study carried out by Bridge and co-workers provides a good basis for the research in this project, highlighting the importance of analytical techniques for establishing changes to surface materials over time. The techniques used by Bridge, as well as the others, will be used to study different wax samples extracted from used surfaces, allowing any changes in structure and purity to be determined.

1.5.3.1 Wax Extraction

To isolate the individual surface components, it is necessary to extract the wax from surfaces. Extraction is often the first step to separate the desired products from raw materials. Extraction methods used in industry include solvent extraction, distillation, pressing and sublimation.[43]

Solvent extraction (SE) is the most widely used method for extraction of soluble organic material. In the SE process, samples are washed with an organic hydrocarbon solvent, which is then separated from the desired extract by evaporation. The purpose of the solvent is to solubilise solutes selectively and effectively as well as allow for easy separation and recovery of solute after extraction. The properties of the extraction solvent, the particle size of the raw materials, the solvent-to-solid ratio, the extraction temperature, and the extraction duration will all affect the extraction efficiency.[18]

Waxes can be isolated using various extraction techniques. This includes both Soxhlet and solvent extraction techniques. Solvent extraction is a simple technique which typically involves stirring the material in an organic solvent for a prolonged duration. During this period, the organic material will dissolve into the solvent after which it can subsequently be isolated following filtration and solvent removal. Although trivial, this method requires large volumes of solvent and suffers from scalability issues with solvent removal.

In contrast, Soxhlet is a continuous extraction process that utilises heat for extraction of lipid material. A schematic illustration of the Soxhlet workflow is shown in Figure 6. In the first step, the sample is placed in a disposable thimble. During extraction, the solvent is heated to boiling point, producing vapour which is returned to liquid by the condenser. This causes the Soxhlet extractor to slowly fill up with condensed solvent. Which is then returned to the reservoir below once full via the siphon mechanism. During this process, the extracted solvent carries the materials extract with it. The cycle then repeats continuously until heating is stopped. Typically, this extraction method uses a large amount of solvent and needs to be run for several hours, making this an energy and time intensive process.[45]

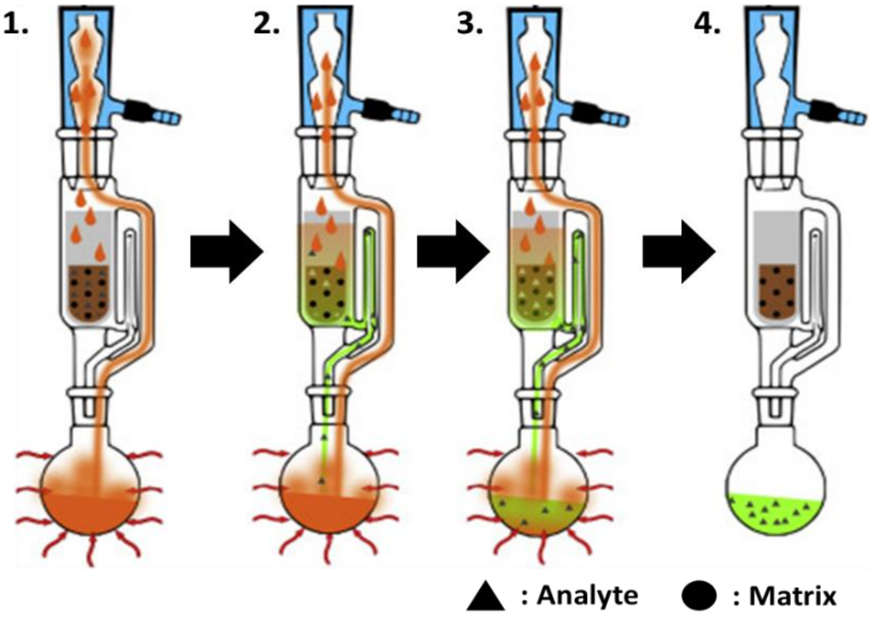


Figure 6. *Schematic illustration of Soxhlet Extraction. 1) Solid matrix is placed in thimble. Solvent is heated under reflux. 2) Condensation and extraction with solvent. Solutes are transferred from the extraction chamber into the reservoir. 3) Repetition of extraction. 4) Complete extraction.*[46]

Both solvent and Soxhlet extraction techniques have proved effective for extraction of organic material from solid samples, however these techniques are hampered by the large volumes of toxic and flammable solvents required for successful extraction. This has initiated a surge in research into developing greener extraction strategies, focussing on both green solvents and green extraction techniques.

1.5.3.2 Solvent Considerations

The selection of the solvent is crucial for solvent extraction. Selectivity, solubility, cost, safety, and environmental impact should be considered in selection of solvents. Typically, solubility is based on 'like-dissolves-like' i.e., molecules with similar structures and properties have greater solvent-solute properties.[47] Because waxes consist largely of long alkyl chain hydrocarbons, they are highly lipophilic in nature, meaning low polarity organic solvents – such as hexane, heptane or iso-octane – are required for their extraction.[45] This is due to the propensity of hydrophobic interactions that exist between solvent and solute.[42]

Although hydrocarbon solvents provide the ability to dissolve organic species in extractions, they are highly flammable and their low water solubility is linked to bioaccumulation and aquatic toxicity.[48] Government regulations have limited the use of select organic compounds in certain manufacturing processes because of adverse health effects and environmental concerns. To the extent possible, the manufacturing sector has tried to eliminate the more toxic and hazardous organic solvents from industrial processes in favour of the safer and more environmentally friendly 'green' solvents.[49]

To eliminate undesirable solvents, replacement strategies typically seek structurally similar compounds with analogous properties. A major example of this includes the replacement of benzene, following its recognition as a carcinogen, with toluene. However, this is still not an ideal replacement as toluene is still highly flammable, toxic, and suspected of damaging the unborn child. Solvents that are structurally similar can be easily sourced as drop-in replacements but are likely to present many of the same environmental, health, and safety (EHS) problems as the previous solvent.[50]

To highlight the EHS profile of different common organic solvents, scientists from Sanofi, GSK, Pfizer, the University of York, and Charnwood Consultants created a solvent selection guide with emphasis on regulatory controls, collectively known as CHEM21.[51] The findings of the CHEM21 consortium were used to produce a summary of solvent safety (Table 3). A consensus in the categorisation of solvents was not always found, hence the introduction of intermediate categories of ‘recommended or problematic’ and ‘problematic or hazardous’. The inconclusive positioning of some solvents in this hierarchy is due to different interpretations of what it means to be green. The diversity of the greenest solvents is clearly limited, emphasising that new solvents must be designed to replace the hazardous amide, chlorinated, and hydrocarbon solvents especially.[52]

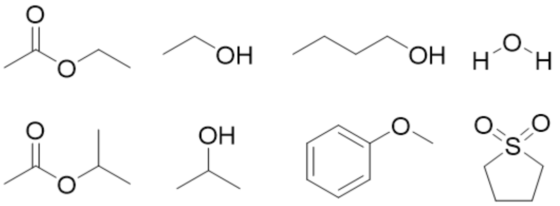
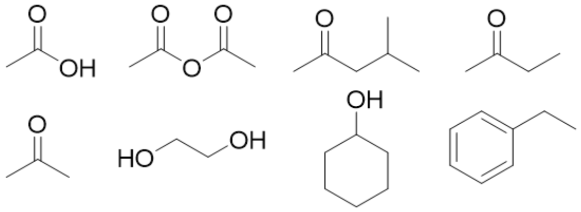
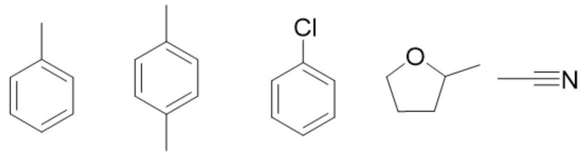
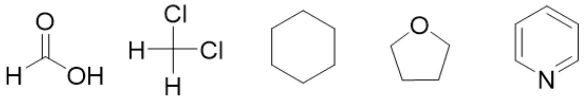
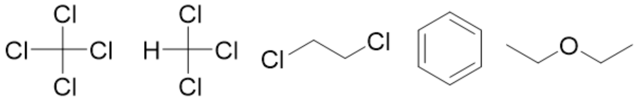
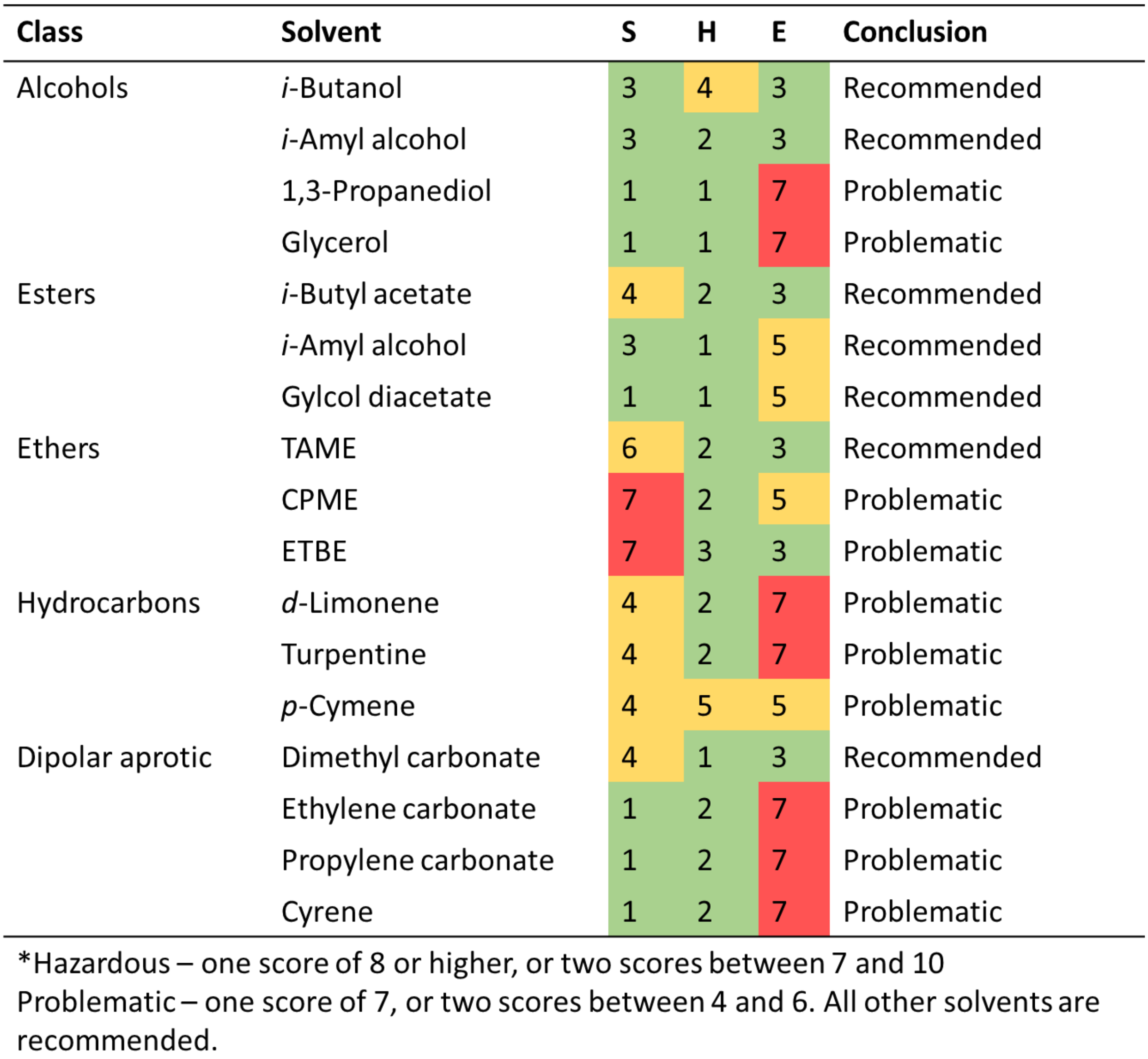
Category	**Solvents**
Recommended	
Inbetween recommended and problematic	
Problematic	
Inbetween problematic and hazardous	
Hazardous	

Table 3. *Simplified version of the CHEM21 solvent selection guide.*[51]

1.5.3.3 Bio-based Solvents

Current regulations are encouraging industries to transition towards using bio-based solvents in place of standard organic solvents because they have low toxicity and are environmentally benign. When a bio-based solvent is used, the cycle of bio-based carbon is closed at the end of life, if not recycled, these bio-based compounds are usually incinerated or lost to the atmosphere as carbon dioxide, which in turn is fixed during photosynthesis, allowing for the carbon to be reincorporated back into bio-based solvents.[53]

The *Green Chemistry* journal recently published a solvent guide incorporating a range of unconventional bio-based solvents (Table 4). Such solvents are favoured over classical solvents since they have reduced health impacts and minimal toxicity issues.[54] However, bio-based solvents with high boiling points (>200 °C) receive high environmental scores due to issues surrounding solvent removal and product drying. This is often the downfall of many hydrocarbon-based bio-sourced solvents, such as cyrene, as the energy intensive process required to remove the solvent drastically hinders the overall green score.



Class	Solvent	S	H	E	Conclusion
Alcohols	*i*-Butanol	3	4	3	Recommended
	i-Amyl alcohol	3	2	3	Recommended
	1,3-Propanediol	1	1	7	Problematic
	Glycerol	1	1	7	Problematic
Esters	*i*-Butyl acetate	4	2	3	Recommended
	i-Amyl alcohol	3	1	5	Recommended
	Gylcol diacetate	1	1	5	Recommended
Ethers	TAME	6	2	3	Recommended
	CPME	7	2	5	Problematic
	ETBE	7	3	3	Problematic
Hydrocarbons	*d*-Limonene	4	2	7	Problematic
	Turpentine	4	2	7	Problematic
	p-Cymene	4	5	5	Problematic
Dipolar aprotic	Dimethyl carbonate	4	1	3	Recommended
	Ethylene carbonate	1	2	7	Problematic
	Propylene carbonate	1	2	7	Problematic
	Cyrene	1	2	7	Problematic

*Hazardous – one score of 8 or higher, or two scores between 7 and 10
Problematic – one score of 7, or two scores between 4 and 6. All other solvents are recommended.

Table 4. *GSK solvent guide for common bio-based solvents.*[55]

For this reason, focus has shifted towards development of renewable ether solvents as low-boiling point replacements for nonpolar aprotic hydrocarbon solvents like toluene. An example of this includes the use of 2,2,5,5-tetramethyloxolane (TMO) which possess a comparable boiling point (112 °C) to toluene (111 °C).[53] The viability of TMO as a safer, potentially renewable alternative to classic volatile non-polar solvents was investigated by Byrne and co-workers.[56] The authors probed its solvent properties by testing its performance in Fischer esterification, amidation and Grignard reactions, with the solvent mirroring the behaviour of toluene in all cases.[56]

Despite the growth in research into green bio-based solvents, their applicability is fundamentally restricted by issues surrounding the expense of mass production and removal. Large scale investment is necessary for production of such solvents to be affordable. Even with this investment many green solvents are intrinsically limited due to their high boiling points, meaning the transition towards green solvents is not a trivial process.

1.5.3.4 Green Extraction Techniques

With growing concern surrounding use of organic solvents, chemists are looking towards new extraction methods that minimise the employment of hazardous and non-renewable materials. These typically offer advantages over conventional methods such as lower organic solvent consumption, shorter extraction times and higher selectivity.[18]

One approach which has received significant attention includes the use of supercritical CO_2 ($scCO_2$) as a replacement for conventional organic solvents. Despite the negative connotations around CO_2, it can be a valuable renewable resource for use in industrial processes. Carbon dioxide is a highly non-polar molecule so as expected $scCO_2$ is a very non-polar hydrophobic solvent with high selectivity for non-polar molecules including oils, waxes, and lipids.

According to the principles of green chemistry, the use of CO_2 as an extraction solvent for wax has double benefits as not only can the extraction help regenerate valuable material from feedstock, but it also utilises an industrial by-product, avoiding unnecessary production of organic solvents.[40] Furthermore, it is regarded as a much safer alternative to organic solvents, especially in industry as CO_2 is non-carcinogenic, non-toxic, non-flammable, inexpensive and completely recoverable. Under $scCO_2$ conditions, the temperature of extraction tends to be lower than for organic solvent extraction, hence thermal destruction of the raw materials is reduced as are heating costs.[45]

The most crucial properties of a supercritical fluid are its density, viscosity, diffusivity, and heat capacity. The physical properties of supercritical CO_2 and liquid CO_2 are highlighted in Table 5 where they are compared with common organic solvents.[40] As the extraction is carried out under pressure, the system can be depressurised after completion, leaving both the raw materials and extracts completely solvent-free, removing the need for any further extraction techniques.

Solvent	Density (gL^{-1})	Viscosity (Pa.s)	Heat Capacity ($kJkg^{-1}K^{-1}$)
DCM	1326	4.06×10^{-4}	1.19
Hexane	655	2.95×10^{-4}	2.27
Ethanol	789	1.07×10^{-3}	2.44
Ethyl Acetate	894	4.31×10^{-4}	1.90
$scCO_2$	956 (at 313K and 40 MPa)	1.06×10^{-4} (at 313K)	0.846 (at 313K)
Liquid CO_2	1000 (at 298K and 40 MPa)	1.20×10^{-4} (at 298 K)	3.14 (at 283K)

Table 5. *Comparison of the properties of different solvents used for wax extraction.*[40]

An example of $scCO_2$ extraction includes the work of Yao and co-workers who explored the use of supercritical fluid extraction for purification of waxes derived from polyethylene and polypropylene plastics. This not only included improving the colour and odour of the waxes, but also included removal of organic and inorganic contaminants that were created during the depolymerisation process.[40] The authors observed a significant reduction in impurity content following supercritical fluid extraction, highlighting this as an effective, environmentally friendly process to purify and extract waxes.

Up to now, the use of CO_2 as an alternative extraction technology has struggled to replace existing processes. This is primarily due to the high capital and operating costs associated with this, as well as the specialist equipment required. With $scCO_2$ systems running at high pressure, large energy consumption is inevitable, and this is reflected in high operating costs. This is one of the biggest obstacles inhibiting $scCO_2$ extraction from being used in industry.

Another method which has shown potential as a green extraction technique includes aqueous extraction where surfactants are employed to aid extraction of organic materials. Although water is the ideal solvent for chemical processes, due to its safe and inert properties, its capacity for extraction of organic material is limited by the incompatibility between the polar water molecules and the non-polar organic material. This can be overcome by the addition of molecules called surfactants to the solution. Surfactants are amphiphilic compounds containing both an organic compatible (hydrophobic) and water compatible (hydrophilic) group.[57] The dual action of the surfactant reduces the interfacial tension between the organic material and the water, allowing the hydrophobic material to breakup into small droplets surrounded by the surfactant – forming an emulsion.[58]

Emulsions are heterogeneous systems consisting of at least one immiscible liquid dispersed in another in the form of droplet with the help of a surfactant. They are used in many industries, such as food, pharmaceutical, petroleum, paint, and coating. Emulsion formation typically requires elevated temperatures due to the inherent instability of the solution. This hinders the green nature of this extraction technique due to the additional costs and emissions associated with the heating process.[59]

In response to this, microemulsion techniques have been developed, where a co-surfactant is used in conjunction with a surfactant to enhance emulsification under ambient conditions.[60] Microemulsions are thermodynamically stable isotropic dispersions consisting of surfactant, co-surfactant, oil, and water. They have potentially infinite lifetimes depending on storage conditions, making them suitable for the extraction of organic material.[60] The co-surfactant is often critical to successful microemulsion formation. Typically, the co-surfactants used are short/medium chain alcohols such as 1-pentanol or 1-hexanol, with n-alkanes are often used as the oil phase.[59]

Unlike conventional emulsions, microemulsions form upon simple mixing of the components, and do not require the high shear conditions used in the formation of standard emulsions. Hence, as well as avoiding the use of hazardous organic solvents, the use of microemulsions also allows extraction of material at ambient temperatures and low surfactant concentrations. Because of their structure, microemulsions exhibit good wetting ability, moderate viscosity, low interfacial tensions and high solubilization for both hydrophilic and hydrophobic compounds. Following extraction, separation of organic material is typically achieved using centrifugation – a lower cost and greener alternative to standard evaporation techniques.[60]

A range of studies have demonstrated the ability of microemulsion extraction methods to compete with conventional solvent extraction procedures. An example of this includes the work of Baglioni and co-workers who explored the ability of microemulsions to remove wax spots from artwork. They prepared a novel microemulsion which included Triton X-100 (TX-100) as the surfactant and p-xylene and n-nonane as co-surfactant and solvent, respectively. TX-100 has been widely used in microemulsions as an effective surfactant for removal of hydrophobic material. As a non-ionic surfactant, TX-100 offers low toxicity, high biodegradability, and high power in removing hydrophobic contaminants.[61] This is due to its amphiphilic structure, consisting of a non-polar octyl-phenyl head group and polar oxyethylene tail groups (Figure 7).[62] The microemulsion was able to successfully remove organic material from artworks, establishing microemulsion extraction as a low cost, practical method of extraction.

Microemulsion extraction has also been successfully applied to soil washing, demonstrating high efficiency for removing hydrophobic organic pollutants.[63] Since soil washing shares similarities with equine surface extraction, it is logical to explore the ability of microemulsions to aid the removal of organic material from surfaces.

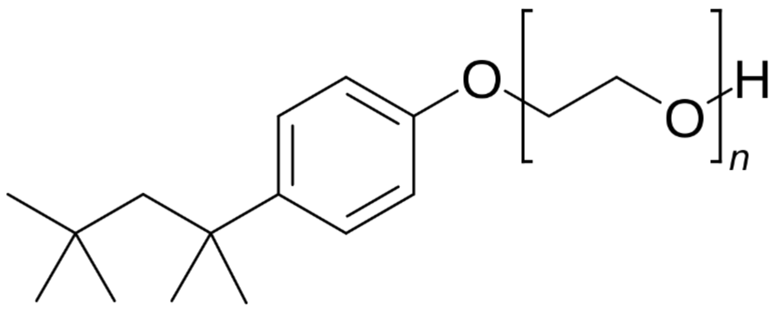


Figure 7. *Chemical structure of Triton X-100 surfactant (n = number of repeating units).*[64]

Although the capacity of both surfactant and $scCO_2$ extraction for wax extraction have been well reported, the wide-spread implementation of these methods in industry is largely hindered by scalability issues.

1.5.4 Mechanical Separation

For successful isolation of the individual surface components, it is critical that the surfaces are subject to mechanical separation. In general, separation systems for processing of solid waste in industry are divided into three categories: density separation, electric and magnetic field separation, and size separation.

Size separation, or screening, involves the separation of a mixture of materials into two or more portions by means of one or more screening surfaces. Trommelling is one of the major size separation techniques used in industry for waste screening.[65] A trommel is a cylindrical screening device that utilises a rotating perforated drum for the separation of material (Figure 8). It is used in a variety of areas including solid waste processing, compost processing, and for classifying construction and demolition debris.[66]

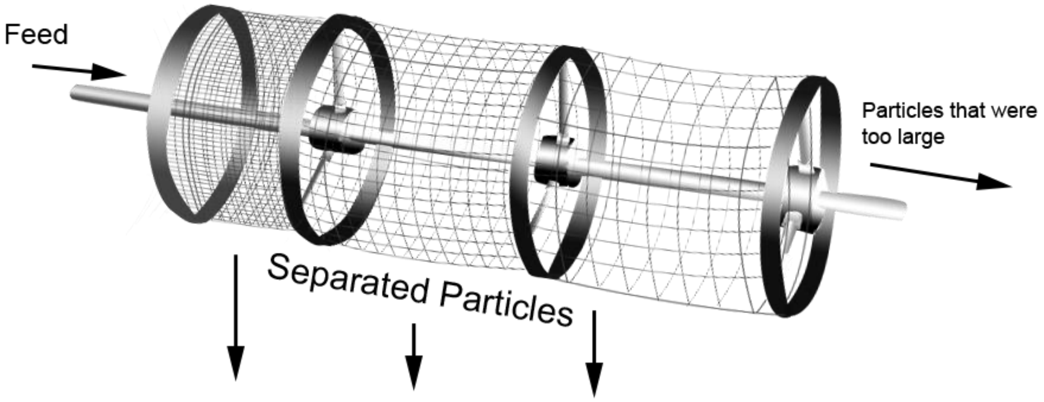


Figure 8. Simplified trommel diagram.[66]

Holes in the trommel cylinder allow smaller materials to drop through the mesh, while larger sized materials remain in the drum. The dragging and dropping motion that is created by material being pulled up the side of the drum helps break up large lumps and allows smaller material to pass through the mesh (Figure 9b). The rotational motion of the barrel as well as its inclination relative to the horizontal dictate how material fed into the trommel impinges on the screen surface.[67] If the trommel drum is spinning too slow, the material will sit on the bottom and form large clumps (a). But if the trommel is spinning too fast, the material begins to centrifuge the screen (c), causing material to adhere to the wall of the cylinder, preventing it from passing through the mesh and subsequently decreasing screening efficiency.[66]

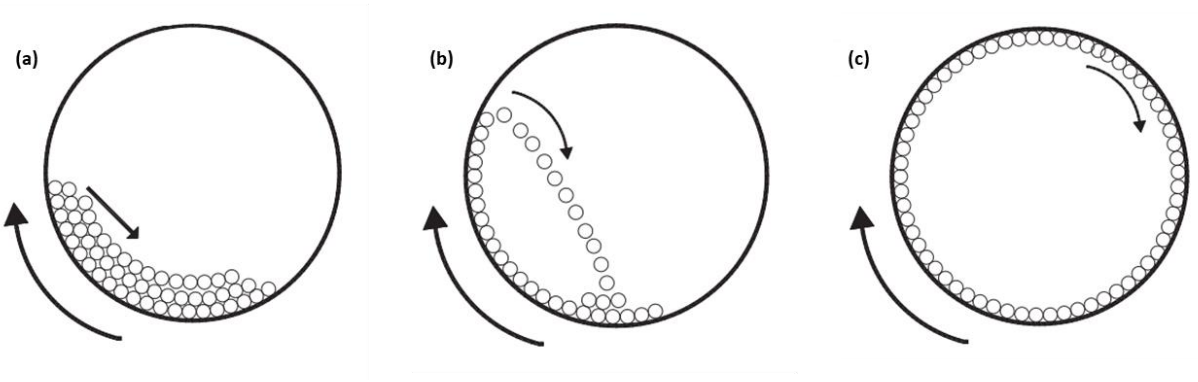


Figure 9. *Forms of particulate motion in rotating cylinders: (a) slumping; (b) cataracting; (c) centrifuging.*[67]

A major advantage of trommel screening over other separation techniques includes the simplicity of separation, as well as the fact that it can be easily tuned to adapt for the driving speed, inclination angle of the drum and pore size of the drum. Furthermore, trommels are relatively inexpensive and require little in the way of operating and maintenance costs compared to other separation systems.[66] It is for these reasons that trommel separation has been identified as the major separation technique for equine surfaces.

The capacity of the trommel to aid separation was previously explored by Rousseaux and co-workers who used trommel separation to assist the isolation of recyclable materials from solid waste. By varying the trommel pore size they were able to determine the optimum pore size necessary for high yielding separation. They found that a trommel with meshes of 25 and 60 mm permitted separation of organic matter and recyclable materials from solid waste by dividing the waste into 3 fractions: fraction <25 mm with high organic matter content, but with significant heavy metal contamination, fraction 25-60 mm with organic matter content 55%, and fraction >60 mm with a high content of recyclable materials.[68] Hence, by trommelling at two different pore sizes, they were able to isolate both organic matter, and recyclable material from solid waste with high purity.

As well as being an effective screening technique, trommel separation can be optimised to allow for enhanced separation. This was demonstrated by Lau and co-workers who exploited trommel screening for the separation of batteries from solid waste.[65] They found that the angle of inclination had a strong impact on battery recovery yield, with larger inclination angles leading to reduced battery recovery due to an increase in material advancement, meaning there was less opportunity for the material to be sieved out of the trommel. Additionally, they found that this decrease in yield was amplified when the rotational speed was increased. This makes sense since higher rotational speed means lower retention time and thus less opportunity for the material to pass through the mesh. By taking all these factors into consideration, Lau and co-workers were able to optimise the recovery of batteries from solid waste, with a feed rate of 1.5 ton/h, rotational speed of 21.4 rotations per minute, and 5° inclination angle giving the highest battery recovery.[65]

As a widely explored screening technique, trommelling has been subject to various customisations that can also help enhance efficiency. This includes the addition of brushes to the trommel exterior to clean the mesh as it rotates, ensuring no material becomes clogged inside the mesh. Furthermore, spiral drums have additional benefits in that the spiral enables control of material through the drum, often resulting in improved screening and product recovery.[67] However, these features come at an additional cost and so it is necessary to consider whether these customisations are necessary for the material in question.

1.5.5 Analytical Techniques for Analysis

To assess the purity of any isolated materials, a range of analytical and physical tests can be employed. By collating the observations from a range of techniques, it will allow conclusions to be made about the purity and composition of the surface materials. Due to the different intrinsic properties of the surface components, different analytical techniques will be used to examine their characteristics.

1.5.5.1 Wax Analysis

Once isolated, the properties of any recovered wax need to be compared to those of the unused wax to establish any changes and ascertain the presence of any impurities. The American Society for Testing and Materials (ASTM) have developed a series of standardised test methods which are widely used in industry. However, traditional wax analyses using ASTM methods, including drop melting point (ASTM D127)[69], congealing point (ASTM D93)[70], needle penetration (ASTM D1321)[71], viscosity (ASTM D1986)[72], and density (ASTM D1298)[73], often do not provide adequate information.[74]

They are usually used in conjunction with instrumental analysis techniques including differential scanning calorimetry (DSC), gas chromatography with mass spectrometry (GC-MS), elemental analysis, nuclear magnetic resonance (NMR) spectroscopy and infra-red (IR) spectroscopy to analyse the waxes in greater detail. Each of these techniques characterises material in a different way. Amalgamating the data obtained from the combination of analyses allows an analysis profile of each wax to be formed.

Over the years, the most popular and useful analytical instrument for wax analysis has been GC-MS. In GC-MS compounds are separated based on their boiling points and polarities. The sample is vaporized to achieve the gas phase. It is then separated into its components in a capillary column. The column itself is coated with a solid stationary phase, and the sample is pushed through the column by an inert gas acting as the mobile phase. Compounds are then separated based on their polarity and affinity for the stationary phase. The compounds are then eluted from the column at different times based on their boiling point and polarity. The retention time (RT) of a single compound, that is the time it takes for the compound to travel through the column, is affected by the length and temperature of the column and the flow rate of the carrier gas.

Following elution from the column, compounds are injected into a mass spectrometer which permits identification of molecular structure by creating a mass spectrum which is unique for each compound. A requirement for GC-MS analysis is that the compounds in the sample are volatile or semi-volatile so that they can be separated from each other with a gas chromatograph and identified by a mass spectrometer. Many gaseous, liquid, and solid samples are suitable for GC-MS analysis without significant pre-treatment. However, the analysis of complex samples or very small sample amounts may require more preparation.

A further method used to analyse wax is differential scanning calorimetry (DSC). This technique uncovers the melting point behaviour of extracted waxes by measuring differences in heat flow rates. In DSC, a sample and a reference material are heated at a controlled rate under an inert atmosphere. A sensor monitors the difference in heat flow to the two samples. From this, temperature ranges relating to onset, partial and complete melting can be determined and compared.[75] It is regarded as a simple and convenient analysis method as it requires no sample treatment and only milligrams of material are needed.[75]

Moreover, Fourier Transform Infra-Red spectroscopy (FTIR) is a key instrument employed to analyse waxes. Atoms, molecules, or other chemical species undergo characteristic changes in their energy states on absorption of electromagnetic radiation. Portions of the incident radiation are absorbed at specific wavelengths, resulting in twisting, bending, rotating and vibrational motions of atoms in the molecule. IR spectroscopy is the measurement of these interactions, producing spectra which reveal the functional groups that make up a molecule.[76] This makes it is a quick and effective tool used to identify functionality, oxidative behaviour, and impurity presence in the wax. It can be used to determine the chemical functionality of waxes based on the assignments provided by Williams and Fleming shown in Table 6.[77]

Functionality	Peak Wavenumber / cm^{-1}	Peak Assignment
Methyl, methylene	2960 – 2850 (s)	C-H symmetric and asymmetric stretching
Methine	2890 – 2880 (w)	C-H symmetric and asymmetric stretch
Alkene	1680 – 1620 (v)	C=C stretch
Methyl, methylene	1470 – 1430 (m)	C-H symmetric and asymmetric deformations
Allyl	995 – 960 (s)	C-H Deformation
Long chain alkenes	720 (w)	Long chain $-CH_2-$ rocking

Table 6. *FT-IR band assignment table (s = strong, w = wide, v =, m = medium).*[77]

Solution state NMR has a wide range of useful experiments that can used for the analysis of various sample types. ^1H NMR is the most widely used technique for the rapid determination of chemical functionality. Peak integrals are proportional to the number of protons in the sample and can be used to measure the concentration of analytes using internal standards. Waxes have a wide distribution of hydrocarbons with similar functionality meaning ^1H NMR spectra often contain peaks with similar chemical shifts that overlap; hence the individual concentrations cannot be easily determined using ^1H NMR. Despite this, NMR remains a useful tool for the trivial identification of any impurities or chemical changes within a sample. The assignment of peaks can be carried out based on known literature values (Table 7).[77] The spectrum for paraffins typically shows the presence of two types of protons, corresponding to CH_2 groups ($\delta = \sim1.25$ ppm) and CH_3 groups ($\delta = \sim0.9$ ppm).

Proton Type	Chemical Shift Range (ppm)
Aromatic Ar-**H**	6.70 – 8.00
Vinyl $\mathbf{H_2}$C=C**H**-, $\mathbf{H_2}$C=CR-, -**H**C=C**H**-	4.50 – 6.00
Allyl H_2C=CH-C$\mathbf{H_2}$-, -HC=CH-C$\mathbf{H_2}$-, Ar-C$\mathbf{H_3}$, Ar-C$\mathbf{H_2}$-R	1.60 – 3.00
Methine R_3C**H**	1.49 – 1.90
Methylene -C$\mathbf{H_2}$-	1.03 – 1.49
Methyl -C$\mathbf{H_3}$	0.60 – 1.03

Table 7. *^{1}H NMR peak assignment table (ppm = parts per million).*[77]

As well as ^{1}H NMR, ^{13}C NMR can also be used to help characterise waxes. Carbon NMR is often used for determining functional groups using characteristic chemical shift values (Table 8). Compared with ^{1}H NMR, ^{13}C NMR can yield more information about functional groups of compounds, owing to less spectral overlap and the broader chemical shift range of ^{13}C NMR. The peaks are greatly affected by electronegative effects, with the presence of electronegative groups shifting environments downfield.[77]

By comparing the NMR spectra acquired for different wax samples, any chemical changes to the structure can be identified based on the presence or absence of certain peaks.

Proton Type	Functionality	Chemical Shift Range (ppm)
-**C**H_2-**C**H_2-	Alkyl	5 – 40
R**C**H_2X	Haloalkanes	10 – 70
RCO**C**H_2-	Carbonyls	20 – 50
R**C**H_2NH_2	Amines	25 – 60
-**C**H_2-O-	Alchols/ethers/esters	50 – 90
-**C**H=**C**H-	Alkenyl	90 – 150
R-**C**≡N	Nitriles	110 – 125
Ar	Aromatics	110 – 160
R-**C**OO-	Ester/acid	160 – 185
R-**C**O-	Aldehyde/ketone	190 – 220

Table 8. *^{13}C NMR peak assignment table (ppm = parts per million).*[77]

Finally, elemental analysis has also proved effective as a tool for analysis of organic extracts. This technique is used to study the relative percentages of common elements, including carbon, nitrogen, sulphur and hydrogen (CHNS).[78] Typically, the analysis process requires high temperature combustion in an oxygen rich environment. During combustion, carbon is converted to carbon dioxide; hydrogen to water; nitrogen to nitrogen gas/oxides of nitrogen and sulphur to sulphur dioxide. Following this, the combustion gases flow through different columns, where they undergo selective separation followed by thermal conductivity detection. By enabling quantification of different elements in a sample, elemental analysis allows comparisons to be made between different samples and hence can generate information about how samples change over time. Due to their simplicity, CHNS elemental analysers have been used for a wide range of applications, including pharmaceuticals, chemicals, catalysts, and food.[79]

The techniques discussed above, will be used to study different wax samples extracted from used and unused surfaces, allowing any changes in structure and purity to be determined.

1.5.5.2 Sand Analysis

As the key footing component of most horse-riding arenas, the quality and grading of sand used has a significant impact on surface performance. Before any isolated sand can be incorporated into a new surface, it is important that any changes in purity and grading are established as these are likely to impact surface performance. Previous research by Bridge and co-workers revealed the importance of sand grading on surface performance, highlighting a relationship between sand shape and injury incidence.[80] With this in mind, the properties of any isolated sands need to be examined to ascertain any major changes to the composition of the sand initiated during surface usage.

Similar to wax analysis, a key method utilised for sand testing includes FTIR spectroscopy. This is used to establish the presence of impurities in the sand by identifying certain functional groups in the spectra. The ability of this technique to establish sand purity was demonstrated by Li and co-workers who examined sand samples which had been treated with surfactant solution following an oil spill. All spectra were found to contain the designated silicon dioxide peaks highlighted in Table 9. However, they also found that the contaminated sand showed distinctive peaks between 2900 and 2800 cm^{-1} – which were assigned to the symmetric and asymmetric CH_2 stretching of the hydrocarbon oil.[81]

Band / cm^{-1}	**Assignment**
1080	Si-O-Si stretching
1175	Si-O-Si stretching
800 – 770	Si-O stretching (2 peaks)
690	Si-O symmetric bending
470	Si-O asymmetric bending

Table 9. *Important IR bands of silica sand along with their assignments.*[82]

In addition, the purity of sand can also be assessed using scanning electron microscopy (SEM) techniques. SEM is considered a rapid, inexpensive, and non-destructive approach to surface analysis. It uses a focused electron beam to scan the surface of a sample and generate a variety of signals which are then used to produce magnified images for analysis.[83]

As well as SEM, energy dispersive spectroscopy (EDX) is another useful tool employed to verify purity. This technique uses X-rays to identify the elemental composition of materials. Interestingly, EDX can be used for both qualitative and quantitative analysis, enabling users to identify both the type of elements present in a sample as well as their relative percentage concentration. Again this technique requires little to no sample preparation and is non-destructive, meaning that it doesn't damage the sample.[84] It is often used in combination with SEM to assess surface properties of samples.

The capacity of SEM-EDX analysis for characterisation of sand samples was verified by Li and co-workers, who studied sand samples isolated following an oil spill. The samples were examined before and after treatment with a surfactant solution. The authors found that the surface of contaminated sands appeared coated in crude oil, causing binding of individual sand grains into clumps (Figure 10a). In contrast, sands treated with surfactant solution appeared much cleaner with the individual sand particles now appearing more defined (Figure 10b).[85] The different sand samples were then analysed using EDX, where it was found that the contaminated sands showed higher C:Si ratios compared to the surfactant-treated sands.[85] The carbon element is the main indicator of hydrocarbon coating, hence higher carbon Wt.% was taken as indication of more substantial oil coating. This research reinforces SEM-EDX techniques as useful tools for analysing the surface properties of solid materials such as sand.

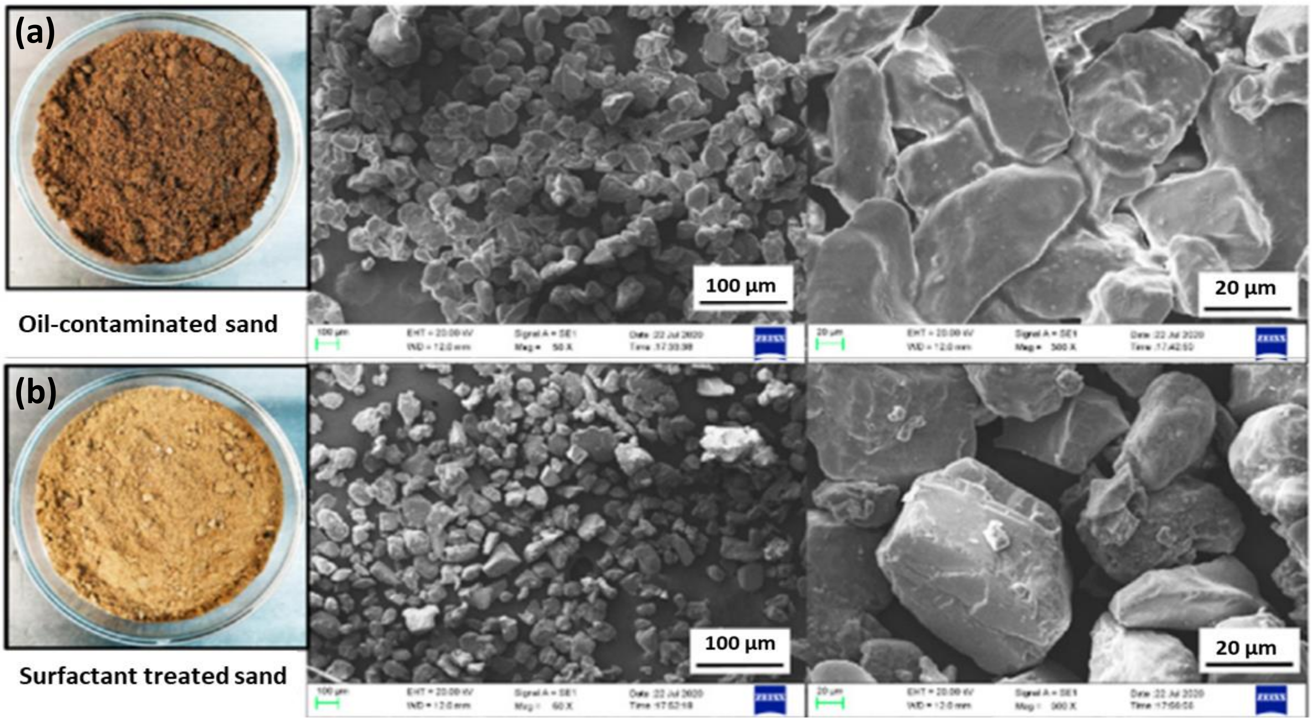


Figure 10. *SEM images of oil sands studied by Li and co-workers.*[64]

1.6 Summary

Synthetic equine surfaces are becoming increasingly popular in today’s market, hence, for the equine industry to become sustainable, alternative disposal strategies for surfaces are required. Wax coated synthetic surfaces have the benefit of being suitable for all-year round usage, making them very popular for usage in arena surfaces. Research by Bridge and co-workers revealed that wax-coated equestrian surfaces were subject to chemical changes over a 7-year period resulting from oxidation of the oil in the wax, as well as changes in wax molecular structure.[44] Such chemical changes may impact the recyclability of equine surfaces, as changes to any of the surface components could alter the performance properties of a recycled surface. As well as this, the presence of POPs in carpet fibres, and the creation of microplastics during surface usage are two important factors that also complicate surface recycling.

Many methods exist which can be explored for separating the individual surface components, with most literature examples highlighting solvent extraction and mechanical separation as the most appropriate strategies for equine surface separation.[1] These techniques will be explored here for the separation and analysis of surface components of both baseline and EOL surfaces, enabling any changes to the chemical and physical properties of the materials to be identified. Depending on the success of each method, the scale of tests will be increased, with the aim to develop a suitable separation process which can be easily and effectively employed by ES in industry.

Chapter 2 - Methodology

2.1 Materials

Lab testing was conducted on a variety of synthetic equestrian surfaces provided by Equestrian Surfaces LTD. Initial tests were conducted on a batch of sample material that was made specifically by ES at their Sandbach factory for this project and had not been laid as a surface. The surface was made to match the original composition of the used surfaces which were to be examined. All used surfaces tested in this thesis were examples of the oldest, and most popular surface offered by ES: Sound Track. The relative mass percentages of the different components used in this surface are summarised in Table 10. In 2019 the surface composition was modified, hence, to establish an accurate baseline for comparison, a new batch of Sound Track surface, matching the original surface composition, was prepared for testing during this project; this will be referred to as the baseline surface (BS).

Surface Component	Relative Mass Percentage
Sand	91%
Wax	3.32%
Fibre	2.84%
Underlay	2.84%

Table 10. *Original surface composition of Sound Track surfaces studied in this project.*

2.2 Surface Sampling

The samples of used surface examined in this thesis were all provided by Equestrian Surfaces LTD and had been sourced from a range of customers in different locations. It is unclear how and where the different surfaces were sampled from the larger arenas, with this likely to influence the results recorded for each surface. This is something that must be considered when comparing results between surfaces. A sample of surface taken from a corner or edge of an arena is likely to have been subject to different usage compared to a sample taken from the centre of the arena, meaning the results may not accurately reflect the condition of the surface as a whole.

A summary of the relevant information for each used surface provided is shown in Table 11, with images of all examined surfaces shown in Figure 11. The images shown in Figure 11 were taken using a phone camera from a distance of 30 cm above the sample, with the samples themselves taken by hand from a larger supply. This is likely to impact the appearance of the surface since the relative percentage of materials present in the same is highly influenced by the sampling method used.

Surface	Location	Year Installed	Mass Provided
EOL1	Hampshire, UK	2012	6.0 kg
EOL4	Wiltshire, UK	2016	4.5 kg
EOL5	Warwickshire, UK	2016	2.8 kg
EOL6	Viborg, Denmark	2014	2.0 kg

Table 11. *Sourcing information for the different EOL surfaces studied.*

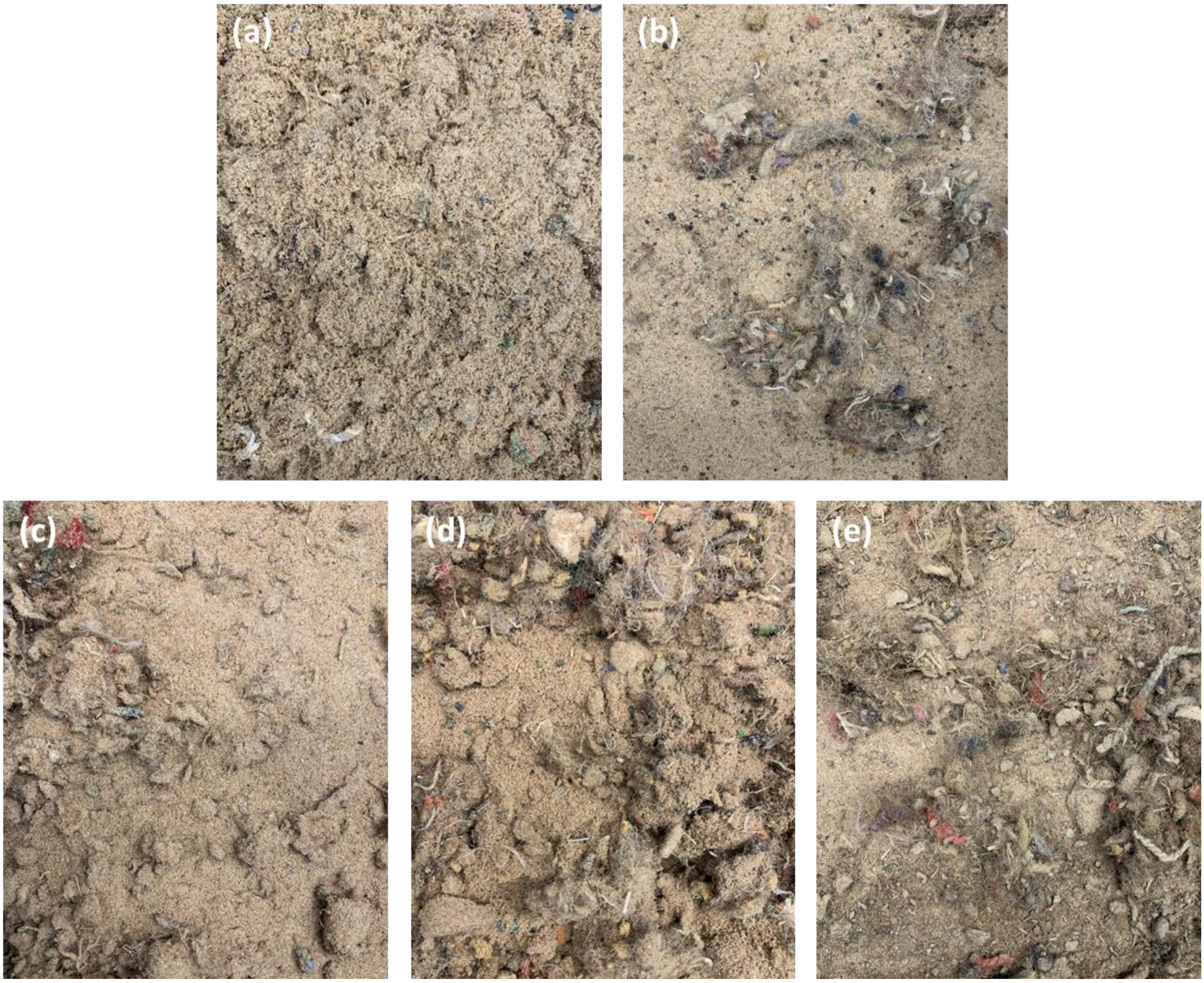


Figure 11. *Images of the different surfaces tested in this project: (a) Baseline Surface, (b)* ***EOL1****, (c)* ***EOL4****, (d)* ***EOL5****, and (e)* ***EOL6****.*

Inspection of the different surfaces revealed clear differences in both colour and consistency depending on the age/usage. The EOL surfaces show high variation, with the sand in **EOL1** and **EOL6** appearing duller and the fibres in these surfaces appearing less bound to sand relative to **EOL4** and **EOL5**. In contrast, the baseline surface appears well combined, with the sand and fibre blended thoroughly and bound together following coating with the wax binder.

2.3 Test Methods

Extensive testing was conducted on the different surfaces in order to isolate and characterise the individual components. This included both small scale lab testing as well as larger scale mechanical separation tests, both of which were heavily influenced by the sampling strategy employed.

2.3.1 Wax Extraction Tests

Initial tests focussed on extraction of wax from different samples of surface. This was done using both solvent and Soxhlet extraction techniques to establish the highest yielding method. Both methods were chosen because of their ability to extract organic soluble materials from solid samples using solvents. The extraction solvent was then varied to examine the effect this had on the yield of material recovered.

Extraction experiments were conducted on small samples of surface ranging from 50 to 250 grams due to the restrictions with equipment available in the laboratory. For each experiment, the sample of surface was taken from a larger stock supply, with each surface mixed thoroughly before sampling by hand. This sampling strategy was selected as the simplest and quickest method due to time constraints in the project. However, it is noted that this is not the most accurate method of sampling since the composition of the material removed is heavily influenced by where the sample was taken from the larger batch. It is also recognised that, by taking samples at random, the material composition of each sample is unlikely to match that of the original surface, hence this is also likely to impact the mass of material recovered. This sampling strategy was used consistently for all surfaces over all extraction experiments, with multiple repeat tests being performed, allowing more accurate average values to be determined.

2.3.2 Sieve Separation Tests

Sieve separation tests were performed using a series of stainless-steel net chroming body test MMLFX sieves purchased from AAOMA on Amazon. The grading of sieves purchased included 1 mm, 0.5 mm, 0.3 mm, and 0.125 mm.

2.3.2.1 Sand Grading Tests

Grading tests were performed on 50.0 g samples of sand sampled at random from larger batches. This included sampling material which had been subject to wax extraction, with this material left to dry in air for 2 weeks before testing. For dewaxed surface samples, larger fibrous material was removed before grading by passing the material through a 1.5 mm sieve.

For the testing itself, the material was passed through each sieve sequentially from largest pore size to smallest pore size, with the mass retained in each sieve recorded. This was then expressed as a percentage of the total mass of sand sampled to give the grading.

2.3.2.2 Surface Separation Tests

Similar to grading tests, samples of dewaxed and waxed surfaces were separated in using size separation techniques. The term ‘dewaxed’ refers to the sand and fibre isolated following removal of organic material from a surface by solvent extraction. In contrast, waxed refers to the true surface itself in its unmodified form as supplied by Equestrian Surfaces LTD.

These samples did not require any prior treatment; however, dewaxed samples were again left to dry in air for 2 weeks to remove any traces of solvent remaining. Tests were conducted on 100 g samples of surface, with multiple batches separated for each surface. Again, samples were taken by hand from larger batches of material, meaning the results reported are heavily influenced by human error when sampling. To minimise the impact of this on the results, tests were repeated at least twice for each surface, with the results reported in Chapter 4 being the average of all tests for that surface.

2.3.3 Trommel Separation Tests

Trommel separation was selected as a large-scale separation tool due to its cost effective and simple separation capabilities. Equestrian Surfaces LTD had highlighted this as a useful separation tool, with previous research carried out by the company verifying it as useful for the separation of solid material. In response to this, ES purchased a large trommel, removing the initial cost barrier towards using this in industry.

Trommel separation experiments were performed using a model trommel supplied by Equestrian Surfaces LTD. This was provided alongside a series of trommel drums with pore sizes including 6 mm, 5 mm, 4 mm, 1 mm, and 0.8 mm. Each drum was 1.5 metres long, with an internal diameter of 250 mm. Preliminary research revealed the 4 mm, 1 mm, and 0.8 mm drums as the most well-suited towards surface separation, hence these three drums formed the basis of all mechanical separation tests.

Separation tests were conducted using a range of different masses of surface, with each surface subject to a standardised separation procedure of 15 rotations per minute for 2 minutes at an inclination angle of 0 °.

The separation process is heavily restricted by the mass of each surface provided by ES. The larger capacity of the trommel enabled larger samples of surface to be separated, with sample sizes ranging from 2 kg to 6 kg. For all samples, the material was added to the trommel in sequential additions of ~ 500 g to prevent overloading. In this instance, the samples of used surface were added in their entirety to eliminate sampling bias, meaning these results are likely to be more representative than the small-scale sieve tests. However, it is important to recognise that the results are still likely to be affected by the initial sampling method employed by ES when sourcing the materials. In addition, the different sample sizes of materials provided means the impact of sampling varies between surfaces.

2.4 Materials and Reagents

Organic solvents chloroform, heptane, pentane, toluene, ethyl acetate, acetone, acetonitrile, and THF were all analytical grade >99% and were purchased from Fischer Scientific UK limited. GC-MS samples were prepared with HPLC grade chloroform that was purchased from Fisher Scientific UK Ltd. Column chromatography was performed using Silica 60 (40-63 microns) supplied by Fisher, Fluorochem, or Sigma unless otherwise stated. Celite 577 was supplied by Sigma.

2.5 Experimental Methods and Analytical Techniques

Initial analysis was performed on crude waxes to determine their chemical properties: chemical functionality by FTIR and NMR, molecular weight distribution by GPC and GC-MS, and identification of volatiles by GC-MS. Extracts and fractions containing impurities that were obtained by the extraction methods were analysed by FTIR, NMR, CHNS elemental analysis and GC-MS to determine chemical properties and identify contaminant components. Purified waxes were analysed by FTIR, NMR, and GC-MS to compare their properties with those of crude and sample waxes.

2.5.1 Soxhlet Extraction

Surface (50 g) was extracted with chloroform (150 mL) in a standard Soxhlet extraction apparatus for twelve hours. The recovered extracts were then evaporated to dryness in vacuo. To eliminate moisture and traces of residual solvent, extracts were air-dried at room temperature. The extracts were weighed periodically until constant weight was achieved.

2.5.2 Solvent Extraction

Surface (100 g) was extracted with 150 mL of the selected solvent by stirring at room temperature for 1 hour. The suspension was then immediately filtered, and the solids washed with solvent (2 x 20 mL) before the extracts were then evaporated to dryness in vacuo. To eliminate moisture and traces of residual solvent, extracts were air-dried at room temperature. The extracts were weighed periodically until constant weight was achieved.

2.5.3 Filtration of Extracted Wax

The filter aid used in this study was Celite 577. This is a pure, fully calcined DE, with a median particle size of 40 μm, consisting of 91.5% silica (SiO_2), 4% aluminium oxide (Al_2O_3) and 1.1% ferric oxide (Fe_2O_3).[86]

Surface (100 g) was extracted with 150 mL of chloroform by stirring at room temperature for 1 hour. The recovered extracts were immediately filtered over celite (50 g). The celite was rinsed with chloroform and the filtrate evaporated to dryness in vacuo. To eliminate moisture and traces of residual solvent, extracts were air-dried at room temperature. The extracts were weighed periodically until constant weight was achieved.

2.5.4 Hot Recrystallisation Extraction

Surface (100 g) was extracted with 150 mL of ethyl acetate by stirring at 75°C for 2 hours. The solution was then immediately filtered, and the filtrate left to cool for 2 hours. The resulting suspension was then filtered under vacuum and the solid collected. To eliminate moisture and traces of residual solvent, solid extracts were air-dried at room temperature for 3 days. The extracts were weighed periodically until constant weight was achieved.

2.5.5 Purification by Flash Chromatography

Silica column chromatography enabled the separation of wax samples into fractions based on their polarity by eluting through silica dry-packed into a sinter funnel with vacuum assistance. Samples were prepared by dissolving extracted wax (2.0 g) in pentane (100 mL). The sample solution was charged onto the column (3.5 cm diameter, 48 cm column, 30 g silica) and eluted with pentane (150 mL) to elute the non-polar fraction. Medium polarity compounds were eluted with DCM (150 mL). High polarity compounds were eluted with 9:1 DCM-MeOH (150 mL). The fractions were evaporated under reduced pressure affording three distinct fractions: non-polar, medium polarity and high polarity compounds.

2.5.6 Microemulsion Extraction

The microemulsion was prepared by adding under constant stirring the following components (% w/w): water, 86.2%; Triton X-100 , 10.7%; p-xylene, 1.8%; nonane, 1.3%. The system was equilibrated until an optically clear liquid was obtained. The number of solvents was chosen based on the calculations carried out by Baglioni and co-workers.[64] Triton X-100 is a non-ionic surfactant with a hydrophilic polyethylene oxide chain and an aromatic hydrocarbon hydrophobic group (Figure 7, page 32). This was purchased from Sigma (average molecular wt. 625 g mol^{-1}).

Surface (50 g) was extracted with 100 mL of microemulsion by stirring at room temperature for 1 hour. The resulting suspensions were immediately filtered under vacuum. The filter cake was then re-extracted with chloroform (100 mL) by stirring at room temperature for 1 hour. The solution was then filtered under vacuum, and the resulting solution was extracted with de-ionised water (50 mL) and $NaHCO_3$ (50 mL). The bi-phasic solutions were inverted, and pressure released periodically. The aqueous wash was repeated two times (2 x 50 mL) and the total aqueous solutions were combined and extracted with 2 x 20 mL of $CHCl_3$. The $CHCl_3$ washes were combined, dried ($MgSO_4$) and dried in vacuo.

To eliminate moisture and traces of residual solvent, extracts were air-dried at room temperature. The extracts were weighed periodically until constant weight was achieved. Microemulsion extraction yields were calculated based on previous chloroform extraction experiments. The difference in mass isolated following aqueous extraction was used to determine the microemulsion extraction yield.

2.6 Chemical Compositions and Analysis Procedures

2.6.1 Fourier Transform Infrared Spectroscopy

No sample preparation was necessary for infrared spectroscopy. After running a background, solid samples were gently smeared onto the crystal and the clamp was screwed down. For liquid samples, one drop was pipetted onto the crystal. All spectra were recorded using an Agilent Technologies Cary 630 FTIR instrument (Agilent Technologies Ltd., Cheadle, UK) at a resolution of 1 cm^{-1} with an average of 16 scans. Correlations provided by Williams and Fleming were used to assign peaks.[45]

2.6.2 Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR experiments were carried out on a Bruker AVANCE III 400 spectrometer. Samples were prepared by dissolving a known mass of wax in a measured volume of deuterated solvent. Deuterated chloroform was selected as a suitable solvent owing to its improved ability to dissolve the waxes over other solvents. Correlation tables provided by Williams and Fleming and experimental data from Sin et al. were used to assist in the assignment of peaks.[45]

2.6.3 Gas Chromatography-Mass Spectrometry

All GC-MS experiments were carried out on a Shimadzu GC-MS-TQ8040 instrument. Liquid injection was used to inject the samples dissolved in chloroform to characterise volatiles and semi-volatiles. Samples were prepared in HPLC grade chloroform at concentrations between 1 – 2 mg mL^{-1} .

Analysis was performed on a Restek Rxi-5Sil MS (30 m x 0.25 mm x 0.25 µm - 5m integrated guard) column in split mode with a split ratio of 1. The injection volume was 1 µL and the inlet temperature was 250 °C. The initial oven temperature was 60 °C with a hold time of 2 minutes and ramped at 10 °C min^{-1} to reach a final temperature of 330 °C with a hold time of 10 minutes and a total run time of 29.2 minutes. The ion source on the mass spectrometer was set to 250 °C. Peaks on the chromatogram were integrated automatically and compounds were identified by matching their mass fragment patterns and retention indices with those in the NIST library.

2.6.4 Differential Scanning Calorimetry

Samples were analysed using a Mettler Toledo STARe Calorimeter using airtight aluminium crucibles under an inert nitrogen atmosphere. Each sample was heated from 20 °C to 150 °C at 10 °C min^{-1} increments before being cooled to 20 °C. The heating/cooling cycle was repeated three times for each sample.

2.6.5 CHNS Elemental Analysis

Elemental analyses (C, H, N, and S) of sand samples, wax precipitates and their fractions were obtained with the use of a Perkin-Elmer 2400 Series II CHNS analyser. A combustion method was used to determine C, H, N, and S content. The homogenised gases were depressurised through a column where they were separated and detected as a function of their thermal conductivities. A known standard was first analysed to calibrate the analyser. The calibration factor calculated from this analysis was then used to determine unknowns. The system was specified for a precision of 0.3 wt % for each element.

2.6.6 Scanning Electron Microscopy

Sample preparation for SEM imaging considered of extracting materials from surfaces, placing them on an aluminium stud with double-sided black carbon tape. The samples were then sputtered with 5 nm of gold using a Quorum Q150RES sputter coater (Quorum Technologies Ltd) to dissipate heat from the focussed electron beam.[87] The structures were observed using a JEOL JSM 7800F scanning electron microscope (JEOL, Welwyn Garden City, UK) operating at 10–15 kV.

2.6.7 Energy Dispersive X-Ray Spectroscopy

For qualitative EDX analysis, the samples were sputter coated with a layer of gold (60 s, 20 mA, 8×10^{-2} mBar, ≈5 nm) using a Quorum Q150RES sputter coater (Quorum Technologies Ltd) and then investigated using a field-emission SEM JEOL JSM 7800F with an EDX system (X-Max50, Oxford Instruments, Abingdon, UK) at 10 mm working distance and 10 kV voltage mounted on a brass JEOL holder with 25 mm carbon tables (G3348N, Agar Scientific, Stansted, UK).

2.6.8 Tensile Strength Tests

Tensile strength tests were carried out according to the procedure described by Kunchi and co-workers.[88] Shredded polymer fibres from different surfaces were fixed to cardboard frames as shown below in Figure 12.

Figure 12. *Samples for tensile strength testing, with carpet fibres sandwiched between cardboard frames to enable gripping.*

Tests were then carried out using an Instron 3345 test machine equipped with 50 N load cell with gauge length of 20 mm and test speed of 10 mm/min until fracture (Figure 13).

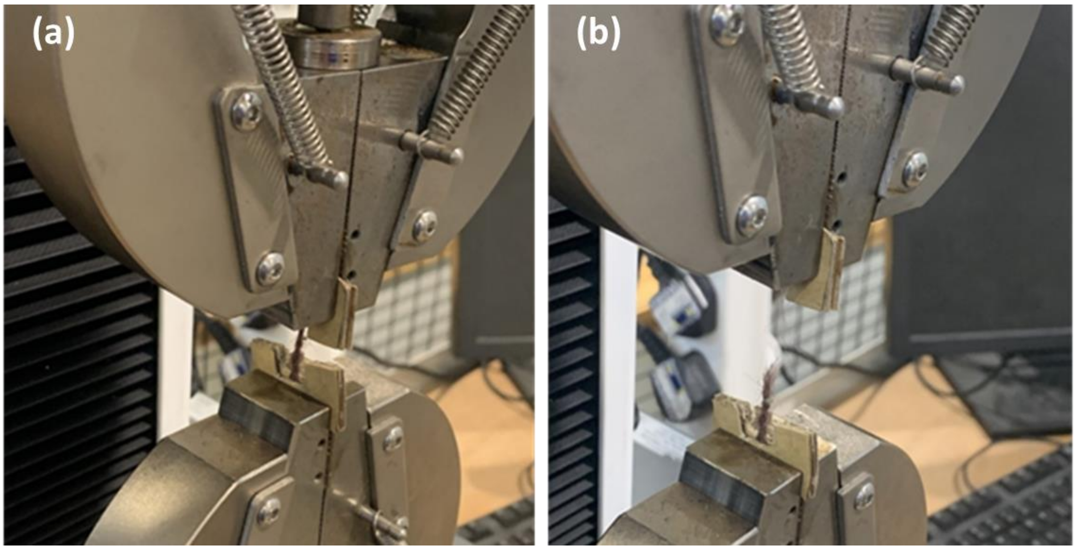


Figure 13. *Before (a) and after (b) tensile strength testing of carpet fibres.*

Chapter 3 – Results and Discussion – Wax Extraction and Characterisation

For synthetic equestrian surfaces to be suitably recycled, it is critical that the individual surface components are extracted, isolated, and characterised. Ideally, the properties of the materials should undergo minimal change following usage. As well as this, it is imperative that methods employed for surface separation are economically viable with minimal environmental impact. This chapter focusses on the separation of wax from different equestrian surfaces and presents an analysis of the extracted materials to establish recyclability.

Because the equine industry suffers from a lack of standardised procedures, the primary method used to define a surface as end-of-life currently relies solely on visual inspection. This is entirely subjective and as such means that different EOL surfaces can be expected to contain different ratios of the three major components. Furthermore, there are a wide range of equine surfaces on offer in the market, the majority of which differ in the proportion of wax, sand, and fibre. Thus, any results obtained for the surfaces examined in this study relate only to the specific surface type studied and should be carefully considered before comparison to other synthetic surfaces.

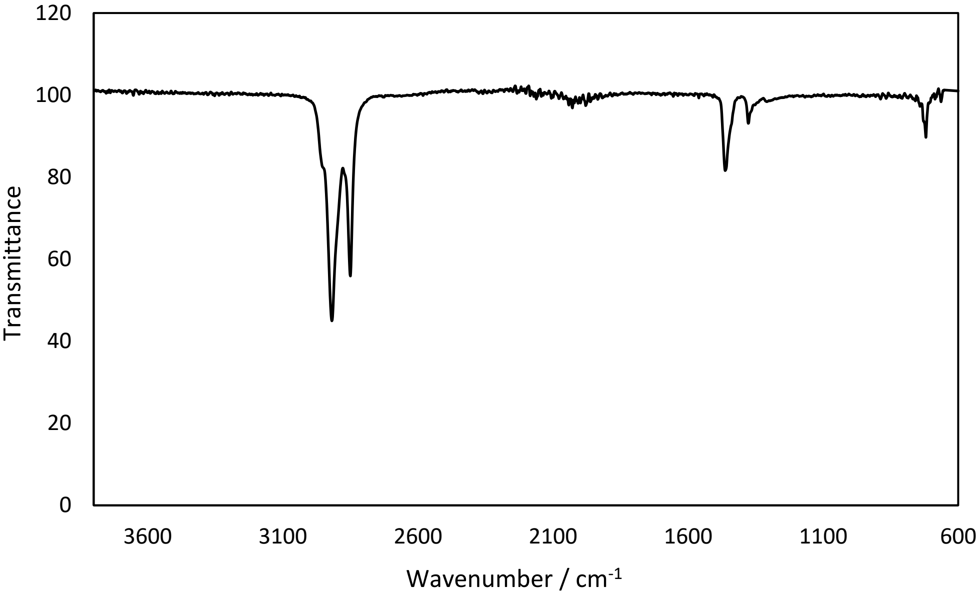
Experiments were conducted using surface samples of different ages. Each surface was studied individually, and the findings compared to determine if and how the properties change overtime. These surfaces were all Sound Track surfaces acquired from different customers in different locations (Section 2.2, page 42).

3.1 Supplier Wax Analysis

Before surface analysis could commence, it was necessary to determine the chemical composition of the wax used by ES during surface manufacturing. By doing this, any changes to the structure and purity of the wax could be easily identified. The wax used by ES is a slack paraffin wax. Typically, paraffin wax consists of a mixture of mostly straight chain *n*-alkanes, where both the melting point and heat of fusion of the material increase with increasing chain length.[89]

Samples of supplier wax were analysed using GC-MS, FTIR spectroscopy and NMR spectroscopy. Comparison of the IR spectra to known standards confirmed the wax to be paraffin wax (Figure 14), with only the five characteristic alkane chain peaks present. This was further confirmed by NMR analysis, with only simple aliphatic environments present in the ^1H and ^{13}C spectra (see Section 6.1.1).

Following confirmation of the wax as paraffin-based, the organic composition of the wax was analysed via GC-MS.[40] Initial testing using GPC indicated the wax contained short-chain alkanes, with all material occurring outside the limit of detection of the apparatus.[90] Hence, GC-MS was employed as an alternative as this is well-suited to the analysis of low melting point molecules.[91] This allowed the chain length distribution of the wax to be determined.



A	2916	CH_2 Asymmetric C-H stretch
B	2850	CH_2 Symmetric C-H stretch
C	1463	CH Bending
D	1377	CH_3 Umbrella mode
E	719	CH_2 Rock

Figure 14. *FTIR spectra of GT70 wax with assignment.*[77]

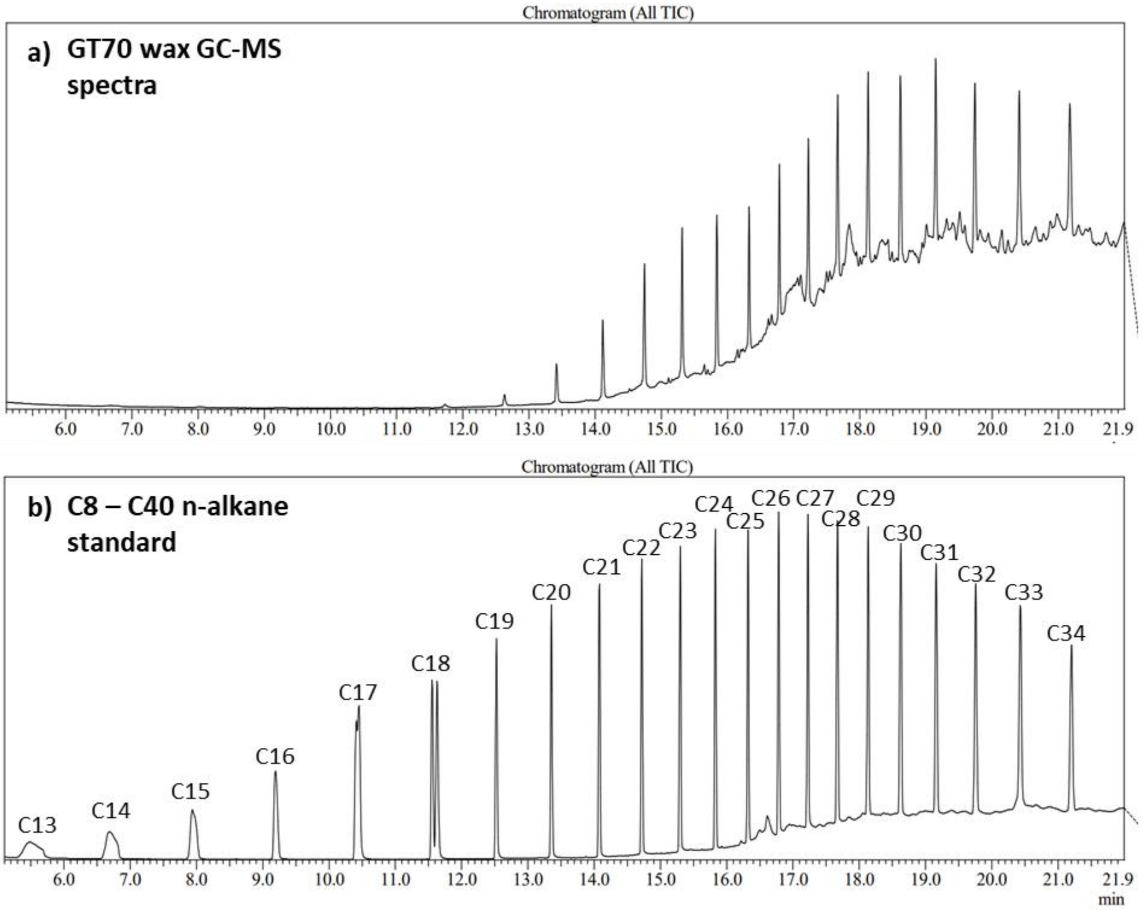


Figure 15. *GC–MS spectrum of feed PE wax and that of the C8-C40 calibration standard.*

Gas chromatographic analysis of wax was performed based on ASTM D5442 using a Shimadzu GC-MS-TQ8040 with flame ionisation detection.[92] Figure 15 presents the GC-MS spectra for the polyethylene wax along with the calibration spectra to indicate the chain length distribution. As evidenced in Table 12, the wax purchased by ES appears to be a polyethylene paraffin wax, with n-alkane chain length ranging from C_{18} to C_{34}.

Retention Time / minutes	Compound	Formula	Retention Time / minutes	Compound	Formula
5.48	Tridecane	$C_{13}H_{28}$	15.83	Tetracosane	$C_{24}H_{50}$
6.67	Tetradecane	$C_{14}H_{30}$	16.33	Pentacosane	$C_{25}H_{52}$
7.98	Pentadecane	$C_{15}H_{32}$	16.81	Hexacosane	$C_{26}H_{54}$
9.21	Hexadecane	$C_{16}H_{34}$	17.23	Heptacosane	$C_{27}H_{56}$
10.45	Heptadecane	$C_{17}H_{36}$	17.69	Octacosane	$C_{28}H_{58}$
11.63	Octadecane	$C_{18}H_{38}$	18.15	Nonacosane	$C_{29}H_{60}$
12.55	Nonadecane	$C_{19}H_{40}$	18.62	Triacontane	$C_{30}H_{62}$
13.35	Eicosane	$C_{20}H_{42}$	19.18	Hentriacontane	$C_{31}H_{64}$
14.08	Heneicsoane	$C_{21}H_{44}$	19.75	Dotriacontane	$C_{32}H_{66}$
14.73	Docosane	$C_{22}H_{46}$	20.44	Tritriacontane	$C_{33}H_{68}$
15.32	Tricosane	$C_{23}H_{48}$	21.22	Tetratriacontane	$C_{34}H_{70}$

Table 12. *GC-MS characterisation of C_8-C_{40} analytical standard.*

3.2 Baseline Surface Analysis

Initial experiments focused on analysing samples of the baseline surface. By doing this, a reference point from which the used samples can be compared to could be established. Preliminary research therefore focused on extracting wax from this surface and characterising any isolated material. This also involved screening a range of solvents for wax extraction in an attempt to maximise material recovery.

3.2.1 Wax Extraction

Traditionally lipids are extracted using low polarity organic solvents such as hexane, pentane, or toluene. With this in mind, a range of traditional organic solvents were screened for their capacity to extract wax from surfaces. The extractions were conducted at room temperature using the solvent extraction procedure described in Section 2.5.2. Yields were calculated based on the 3.32% (by weight) wax content for this surface as quoted by ES. Table 13 shows a comparison of the solvent properties and wax extraction yields recorded for a sample of baseline surface extracted with a range of organic solvents. #

As evidenced in Figure 16, the extraction yields vary depending on the solvent. Intrinsic properties of the wax can be determined based on the extraction yields recorded. For the high polarity solvents – acetone and acetonitrile – the extraction yields are extremely low, indicating low solubility of the wax in these solvents. This is consistent with what is expected for paraffin wax.[94]

Solvent	Boiling Point	Polarity Index	Yield of Organic Material
Pentane	36.1	0	82%
Pet Ether	40-60, 60-80	0.1	93%
Toluene	110.6	2.4	107%
THF	66.0	4.0	104%
Chloroform	61.1	4.1	119%
Ethanol	78.5	4.3	13%
Ethyl acetate	77.1	4.4	81%
Acetone	56.3	5.1	14%
Acetonitrile	81.6	5.8	1%

Table 13. *Table showing the boiling point, polarity index, and extraction yield of wax for a series of common organic solvents.*[93]

In contrast, the low polarity solvents – pentane and pet ether – show high yields of extracted material, due to high compatibility between the hydrophobic chains of the wax and the solvent. Medium polarity solvents, toluene, THF and chloroform give rise to the highest yields of organic material, with all three solvents recording yields over 100%. This suggests that these solvents extract other materials present in the surfaces, including organic soluble compounds present in the carpet fibres and underlay (see Table 15). Considering the turbid nature of the extracts, it is also possible that fine particles of sand were extracted from surfaces, with this additional mass contributing towards the >100% yields. Taking this into account, the total mass of wax extracted with chloroform is in good agreement with the known composition of the baseline surface, hence this solvent was employed for further extraction experiments.

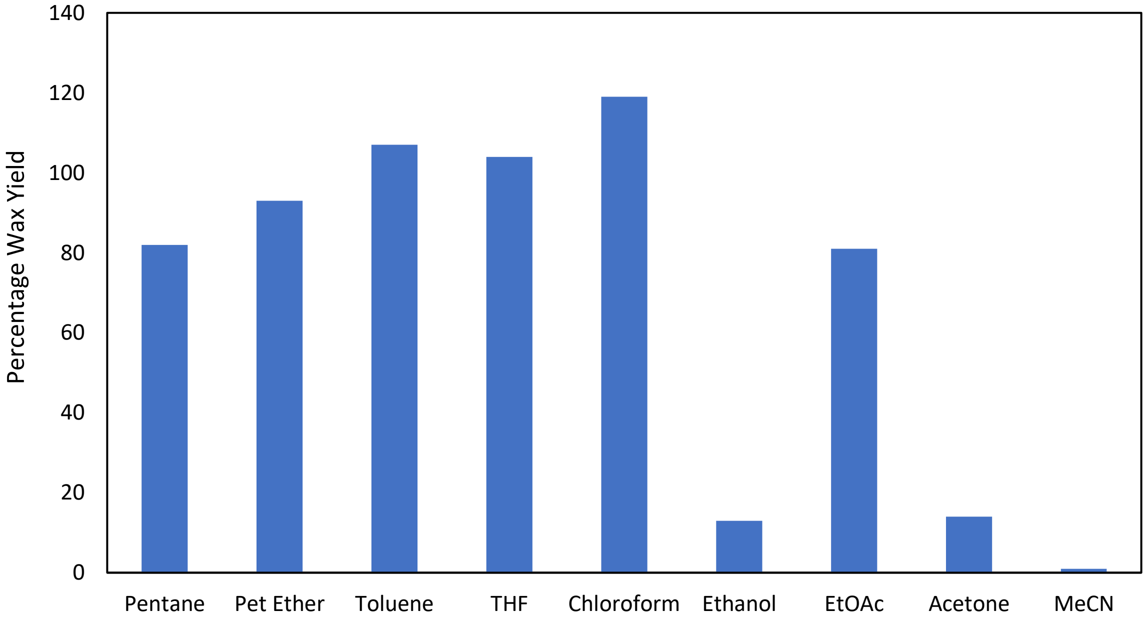
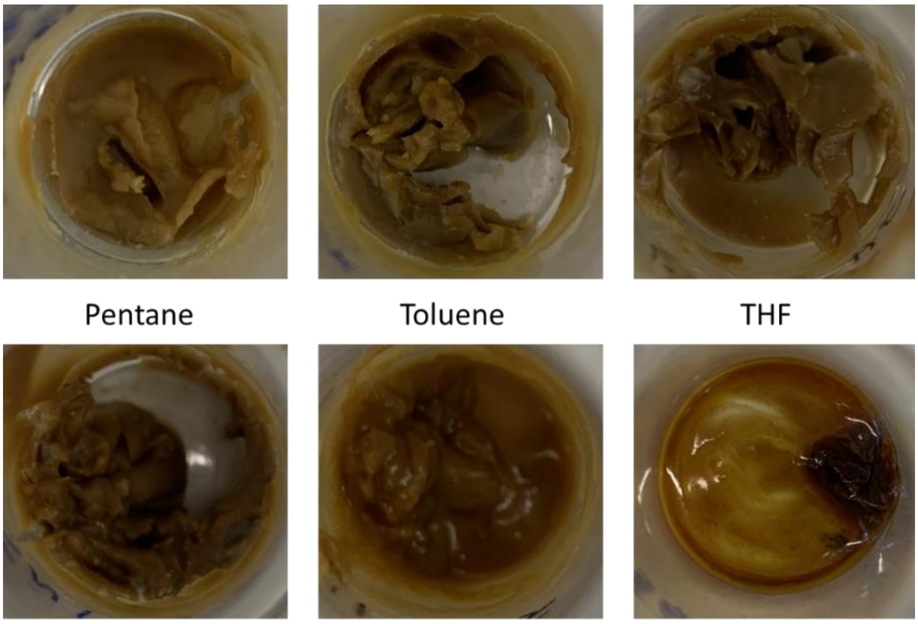


Figure 16. *Graph showing extraction yields with different organic solvents.*

Relative to the supplier GT70 wax, the appearance of the material extracted from the **BS** varied depending on the solvent, with material extracted using the high yielding solvents (chloroform, THF, and toluene) appearing as a dark amber waxy solid instead of a pale-yellow wax. The appearance of some of the isolated wax samples are shown in Figure 17 below.



Pentane Toluene THF

Chloroform Ethyl Acetate Acetone

Figure 17. *Appearance of waxes extracted from samples of the baseline surface with different solvents via solvent extraction.*

Although the results display large variation between solvents, the extraction yield recorded is also influenced by sampling. Surfaces are made on a large ton scale, with the wax sprayed onto a rotating mixture of sand and fibre. This is not homogenous and so it is likely that different samples of surface contain different amounts of wax. Additionally, the samples for solvent extraction were taken by hand from a larger stock of material, meaning each sample is likely to differ in material content, with this also having an impact on the mass of wax extracted. Both sampling issues apply to all extraction experiments with the baseline surface, meaning the results should be carefully considered before comparing to other surfaces.

3.2.2 Soxhlet Extraction

As well as solvent extraction, Soxhlet extraction was also explored for wax removal. This method uses heat and condensation to continuously wash a sample with organic solvent, allowing organic-soluble material to dissolve into the solvent and be separated. The Soxhlet extraction process was carried out according to the procedure described in Section 2.5.1, with toluene used as the extraction solvent.[46]

A comparison of the yields observed for Soxhlet, and solvent extraction are shown in Table 14. Although the yields observed for both processes are similar, the material isolated following Soxhlet extraction was isolated as a green waxy solid, which contrasts to the orange waxy solid isolated via solvent extraction. This bears less resemblance to the supplier wax used to create the surfaces, an amber waxy solid, suggesting higher contamination. This can be attributed to the greater leaching of organic-soluble material from the fibre and underlay that occurs because of the prolonged extraction time and increased reaction temperature during Soxhlet extraction.

The yield of material recovered from Soxhlet extraction is lower than that of solvent extraction. This could arise due to the smaller pore size of the Soxhlet thimble which likely reduces contamination of the wax extract with fine sand particles. This further indicates that particulate sand contributes towards the >100% yields observed using solvent extraction.

Extraction Method	Extraction Yield	Appearance
Solvent Extraction	107%	Orange waxy solid
Soxhlet Extraction	100%	Green waxy solid

Table 14. *Comparison of toluene extraction yields observed for Soxhlet and solvent extraction techniques.*

In summary, both the Soxhlet and solvent extraction methods proved effective for extracting wax from equine surfaces. The yields isolated for both techniques are similar, with the main difference between the two techniques being the visual appearance of the isolated material (Figure 18). Solvent extraction was selected as the extraction method to be explored in this project as this gave a higher wax yield and the material isolated more closely resembled the supplier wax. Furthermore, solvent extraction occurs at room temperature, avoiding the need for high heating and energy costs, making it a more practical extraction tool for use in industry.

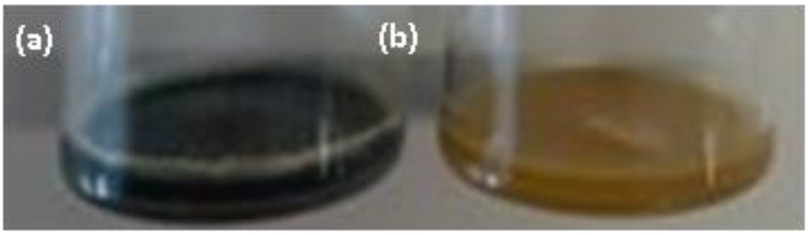


Figure 18. *Waxes extracted from the baseline surface via (a) Soxhlet and (b) solvent extraction techniques.*

3.2.3 Wax Analysis

Following extraction, the wax extracted from the baseline surface (**BS**) was characterised via IR spectroscopy. This confirmed extraction to be effective, with the spectrum appearing almost identical to that of the supplier wax (Figure 19). Despite this, the high yields of material isolated appeared to suggest the presence of some impurities within the wax. This is evidenced in IR via the existence of a minor peak at 1700 cm^{-1} which is indicative of carbonyl presence. This likely arises due to the presence of carbonyl-containing plasticisers, extracted from fibres within the surface.

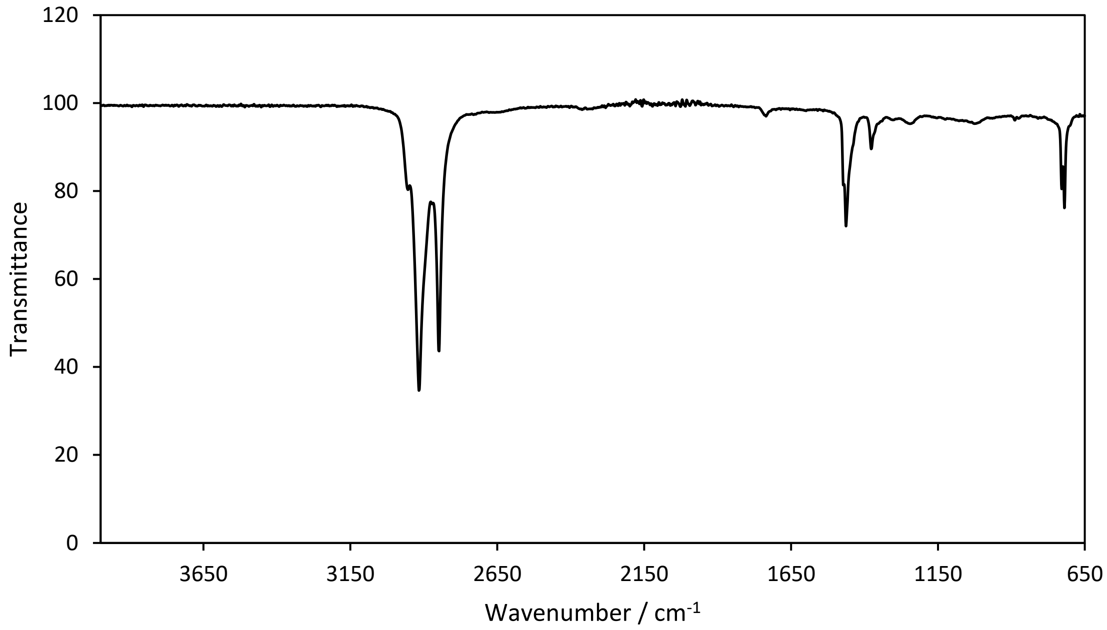


Figure 19. *FTIR spectrum of the* ***BS*** *wax.*

To confirm this, the wax was analysed via GC-MS. A comparison of the spectra observed for the **BS** wax, as well as the supplier wax (**GT70**) is shown in Figure 20. The spectra appear similar, with the straight chain alkane nature of the wax evident in both samples. The chain length distribution is also similar, with a small reduction observed for the **BS** wax, decreasing from C_{18}-C_{34} to C_{20}-C_{34}.

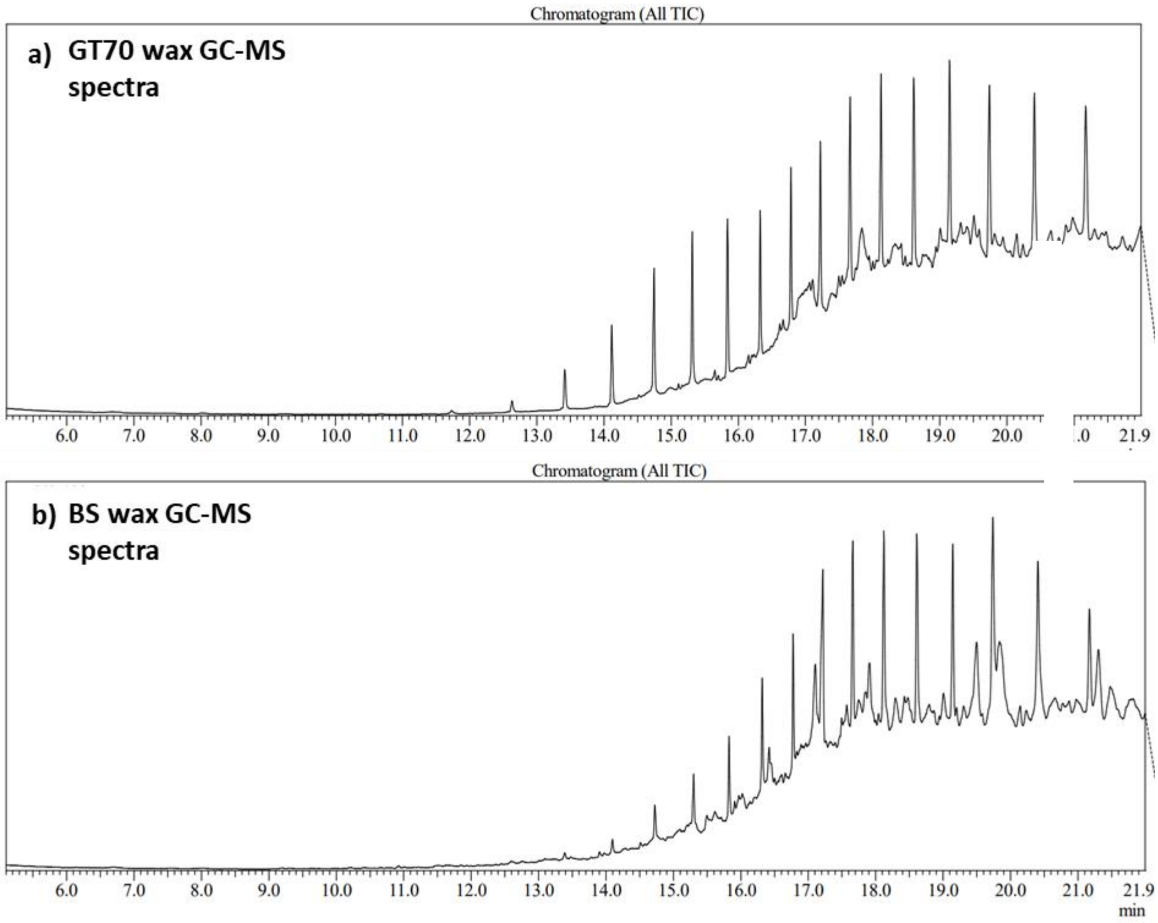


Figure 20. *GC–MS spectrum of supplier GT70 wax, and wax extracted from the baseline surface.*

GC-MS results revealed the presence of impurities within the **BS** wax, with the main impurity identified as phthalic acid, di(2-propylphenyl) ester. Phthalates like this are widely used as plasticisers; substances added to polymers to increase their flexibility[95]; hence this is likely a leachate from the carpet fibres that is extracted along with wax. It is the extraction of such organic soluble materials from the fibres that results in the high extraction yield recorded for the **BS**.

To further investigate this, samples of shredded fibre were extracted with chloroform according to the procedure described in Section 2.5.2. This involved the extraction of both post-industrial and post-consumer carpet fibres, as well as underlay. The percentage recovery by mass for each sample is shown in Table 15. These results confirm the presence of organic soluble compounds in the fibrous material, validating this as an additional source of mass during solvent extraction.

Surface	$CHCl_3$ Extraction Mass Recovery %	Extract Appearance
Post-industrial Fibre	2.4%	Green waxy solid
Post-consumer Fibre	2.5%	Dark-grey waxy solid
Underlay	10.4%	Dark-orange oil

Table 15. *Mass recovery percentages for samples of fibre and underlay extracted with chloroform.*

3.3 EOL Surface Wax Extraction

Following extraction of the baseline surface and identification of suitable extraction solvents, it was necessary to extract organic material from samples of used surfaces. For these experiments, four different samples of used surfaces were procured by ES. The sampling and sourcing information for these surfaces is detailed in Section 2.2.

3.3.1 Solvent Extraction

To identify the extent of wax breakdown, the EOL surfaces were, extracted using the solvent extraction method described in Section 2.5.2 with chloroform chosen as the extraction solvent. As evidenced in Table 16, the yields observed for the EOL surfaces are highly variable, ranging from 50% recovery to 136% recovery.

Surface	$CHCl_3$ Extraction Yield	Extract Appearance
BS	119%	Orange waxy solid
EOL1	50%	Dark brown waxy solid
EOL4	96%	Dark brown waxy solid
EOL5	136%	Dark brown waxy solid
EOL6	78%	Dark brown waxy solid

Table 16. *Average chloroform extraction yields observed for the different surfaces.*

Interestingly, the extraction yield observed for **EOL5** is higher than that recorded for the baseline surface. The extreme cloudiness of the extraction solution for **EOL5** suggested high contamination of the extract with fine particles, which likely contribute towards the high yield recorded. In comparison, the results observed for **EOL1** show a significant reduction in wax content relative to the **BS**, suggesting removal of wax as the surface is used.[44]

As well as high variation in extraction yield, there is also a major change to the appearance of the extracted material following usage, with the wax changing from an orange waxy solid to a dark brown waxy solid. A comparison of the visual appearance of the supplier wax and the wax extracted from the **BS** and **EOL1** surface is shown in Figure 21. This further highlights modification of the wax – with the change in appearance likely occurring due to a combination of the presence of organic and inorganic impurities within the extracts and because of chemical changes to the structure of the wax polymer itself.

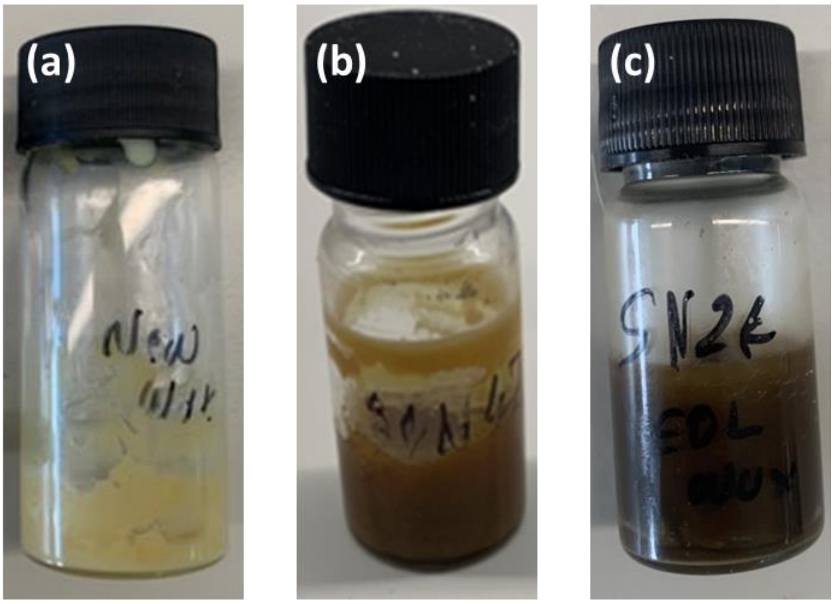


Figure 21. *Comparison of wax samples: (a) GT70 supplier wax, (b) wax extracted from the baseline surface, and (c) wax extracted from* ***EOL1*** *surface.*

3.3.2 Fine Filtration Extraction

Although the wax can be extracted from used surfaces using solvent extraction, the isolated material varied highly in purity, with the crude material isolated as a dark brown solid in all cases. Because the initial extract solution appeared cloudy, it was hypothesised that the source of impurities within the wax was likely due to the extraction of insoluble fine particles from surfaces which permeate the filter and contaminate the isolated wax solutions, leading to a change in the appearance of the material. Typically, industry employs filter-aid filtration techniques to remove such particles from solutions, with a major example of this being celite filtration. Celite is a material composed primarily of silica, which is well-suited as a filtration medium due to its high porosity.[96]

With this in mind, extraction experiments were repeated, utilising celite filtration in an attempt to remove insoluble particles from the extracts. This had minimal impact on the extraction yield observed for the **BS**; however, for the EOL surfaces the extraction yield was significantly reduced in all cases (Table 17).

Surface	Solvent Extraction Yield	Celite Extraction Yield
BS	119%	112%
EOL1	50%	29%
EOL4	96%	56%
EOL5	136%	76%
EOL6	78%	32%

Table 17. *Comparison of the chloroform extraction yields observed for the initial solvent extraction and celite extraction methods.*

These results are now more consistent with what is expected, with all EOL surfaces showing a reduction in wax yield relative to the **BS**. This is strong evidence of wax breakdown during surface usage; consistent with the findings of Bridge and co-workers.[44] Nonetheless, there is still large discrepancy between the different EOL surfaces, with yields ranging from 29% to 76%. This can be used to infer information about the true EOL state of a surface, with lower extraction yields corresponding to a greater EOL state.

The results observed therefore suggest that **EOL1** is at the greatest EOL state, closely followed by **EOL6**. This is consistent with the appearance of the surfaces as shown in Figure 11 (Section 2.2), with the sand and fibre in these surfaces appearing as largely separate components. In contrast, **EOL4** and **EOL5** surfaces record higher wax coatings, indicating these surfaces are not yet in a full EOL state.

Despite the removal of fine particles from the wax samples, the appearance of the extracted material did not change, with all EOL surfaces again yielding brown waxy solids. This major change in appearance relative to the initial **GT70** wax suggests alteration to the composition of the wax, arising from chemical change to the wax itself or due to the presence of impurities within the extracted material. This therefore indicates that fine filtration is not entirely effective for removal of impurities from the wax samples, and that, for reusable wax to be isolated, further purification is necessary.

3.3.3 Summary

In summary, extraction experiments have shown that for some surfaces the wax binder is lost in significant proportions during usage, suggesting significant wax breakdown (**EOL1**), whilst other surfaces record high yields of organic material, indicating high contamination of the surface with organic and/or inorganic compounds (**EOL5**).

Fine filtration tests have confirmed the presence of particulate matter within the extract solutions. This can be suitably removed using celite filtration, reducing the observed extraction yields to well below 100% in all cases. Nevertheless, the radical change in appearance of the extracted waxes indicates modification of the wax composition relative to the supplier wax, questioning the suitability of the extracted wax for reuse.

Although the results of fine filtration experiments proved promising, time constraints of the project meant it was not possible to carry out full analysis on the waxes isolated from these tests. Hence, going forward, the majority of results presented are for wax samples isolated via simple solvent extraction methods without fine filtration unless stated otherwise. Fine filtration of samples was only carried out where this was a requirement for the apparatus, with GC-MS being a prime example.

3.4 Wax Analysis

Although the appearance of the wax changes significantly following usage, the effect of this change on the basic physical and chemical properties of the wax is unknown. If this does not appear to impact the properties of the wax, then the material is likely suitable to be reincorporated into new surfaces without the need for further purification; however, if the properties of the wax change significantly, then alternative reuse streams for the wax may be required.

The different waxes extracted from the EOL surfaces were analysed using a range of analytical tools to assess if and how the purity of the material changes relative to the wax extracted from the **BS** and the initial supplier wax.

3.4.1 IR Analysis

Chemical changes to the wax can be easily identified using IR spectroscopy. By recording IR spectra for the different EOL waxes, new chemical functionality could be identified.[44] The FTIR results recorded for the EOL and **BS** waxes are shown in Figure 22. The EOL samples show an increase in the number of peaks present, with a range of broad peaks observed for all EOL waxes. These results clearly reveal change to the composition of the wax. This could be attributed to oxidation of the wax, or to contamination of the wax with other organic soluble materials present in the surface.[44]

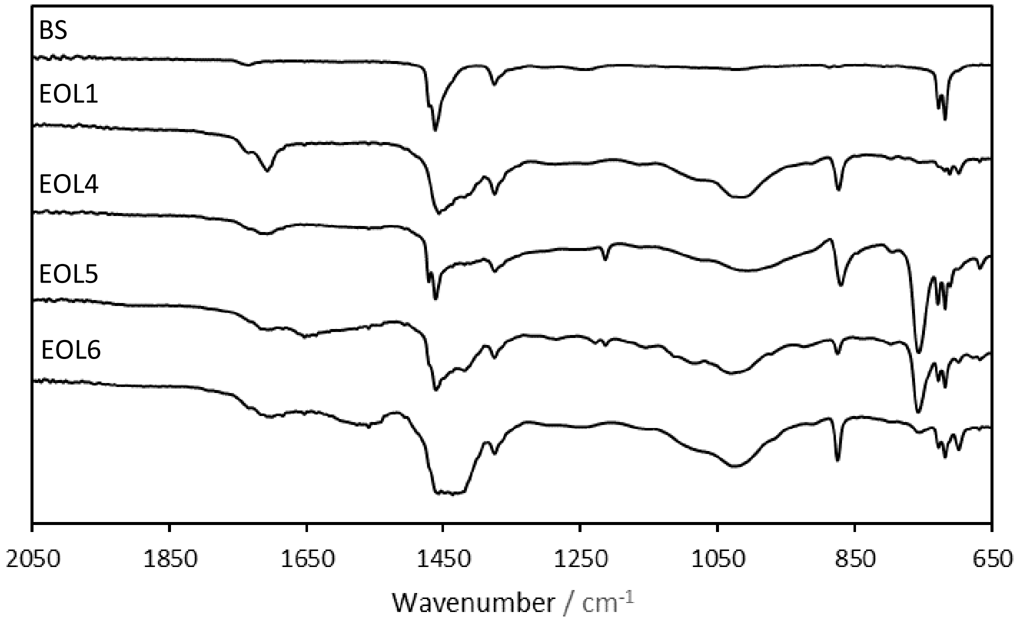


Figure 22. *Stacked IR spectra showing the variation between the* ***BS*** *and EOL waxes.*

For the EOL extracted waxes, the spectra are similar, with analogous peaks present in all samples, including a sharp peak around 875 cm^{-1} and a broad absorbance in the 1250-1450 cm^{-1} range. These peaks can be attributed to the out-of-plane bending of calcium carbonate and the asymmetric CO_3^{2-} carbonate stretching, respectively.[97] This is used as a filling material in the backing of carpets and could have been extracted as fine particulate during extraction. For reference, the spectrum of calcium carbonate is shown in Figure 23 below.

Figure 23. *FTIR spectra of calcium carbonate.*

The broad and crowded nature of the spectra recorded for the EOL samples makes it difficult to verify if the additional peaks arise because of chemical change to the wax itself or because of impurities. To further assess this, samples of EOL waxes were purified using PTFE (polytetrafluoroethylene) membrane filters. The PTFE structure uses the inherent hydrophobic and non-stick nature of PTFE to facilitate removal of particulate matter and polar impurities from solutions.[98]

All EOL-extracted waxes were passed through PTFE filters before being re-examined via FTIR spectroscopy. This significantly improved the quality of the spectra ($CaCO_3$ removed), with only one additional peak now present in the 1700-1720 cm^{-1} region (Figure 24). This wavenumber region corresponds to the carbonyl (C=O) functional groups present in oxidized hydrocarbon compounds that typically include aldehydes, ketones, and carboxylic acids.[44]

The presence of this carbonyl functionality in all EOL-extracted samples could be evidence that the paraffin wax is subject to oxidation during usage. This is consistent with the observations of Bridge and co-workers who observed growing wax oxidation with increasing surface age (Section 1.5.3, page 25).[7, 44] However, it is also possible that this peak arises due to the presence of phthalate plasticisers extracted from the carpet fibres during solvent extraction.

While chemical change may occur to the wax binder, the impact this has on the physical and mechanical properties of the wax is currently unknown. Oxidation of the paraffin structure would introduce polar functionality into the material. Polar groups such as carboxylic acids and ketones can modify the cohesive properties of the binder; with an oxidized, more polar binder reducing the hydrophobic properties of the wax, allowing increased water absorption and thereby decreasing the drainage capacity of a surface.[44]

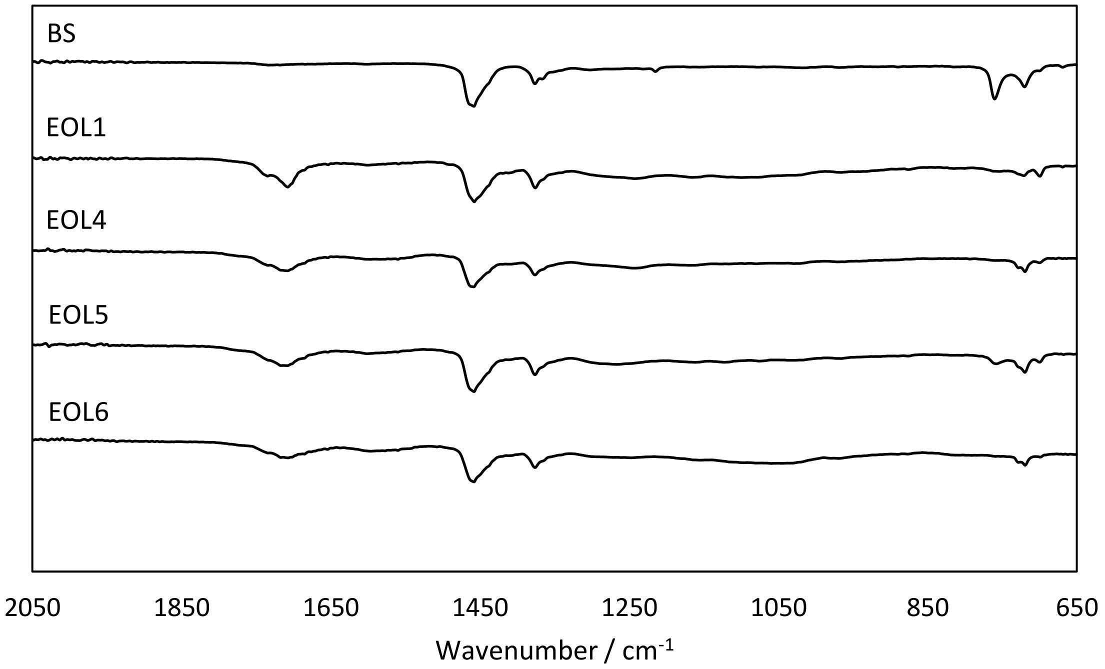


Figure 24. *Stacked IR spectra showing the variation between the* ***BS*** *and EOL PTFE-filtered waxes.*

The effects of these chemical changes to the wax on the properties and behaviour of the wax have a significant influence on the reusability of the material. Hence, to establish if chemical change to the wax has occurred, the wax was subject to further analytical testing.

3.4.2 GC-MS Analysis

Gas chromatographic tests showed high variability between EOL wax samples. Prior to analysis, samples were dissolved in chloroform, and passed through a PTFE membrane filter to remove any insoluble material that would damage the instrument.[40]

Figure 25 shows the GC spectra of wax extracted from the **BS** (a) and wax extracted from **EOL4** (b) and **EOL5** (c) surfaces. Relative to the **BS** wax, there is a noticeable loss of the lighter hydrocarbon molecules for the EOL waxes, with the range of alkanes detected in **EOL4** and **EOL5** identified as C_{24}-C_{34}. The prominent peak at 16.50 minutes in **EOL5** was identified as bis(2-ethylhexyl) phthalate (DEPH) which is most likely a leachate from polymer fibres during solvent extraction.[40]

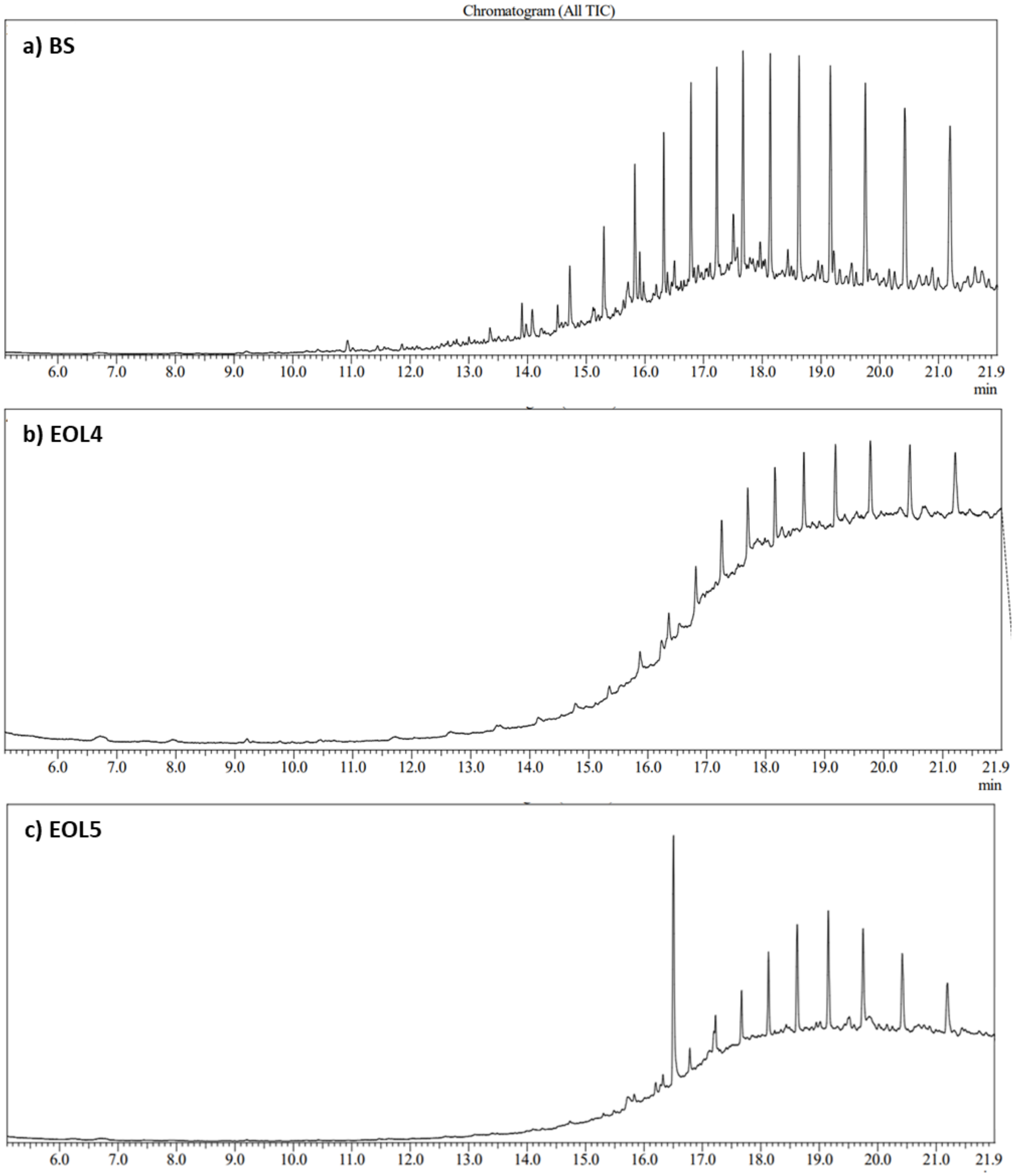


Figure 25. GC-FID wax binder comparisons of **BS** (a), **EOL4** (b), and **EOL5** (c) waxes.

In contrast, the chromatograms recorded for the PTFE-filtered **EOL1** and **EOL6** waxes show no major peaks present (Figure 26). This suggests that the extracted material does not contain substantial mass of the original paraffin wax and that the majority of the material is non-volatile and hence not analysable by GC-MS. Previous extraction experiments revealed these surfaces to be at the greatest EOL state (see Table 17) with low wax recovery recorded for both surfaces. This is therefore the likely reason behind the lack of functionality observed here.

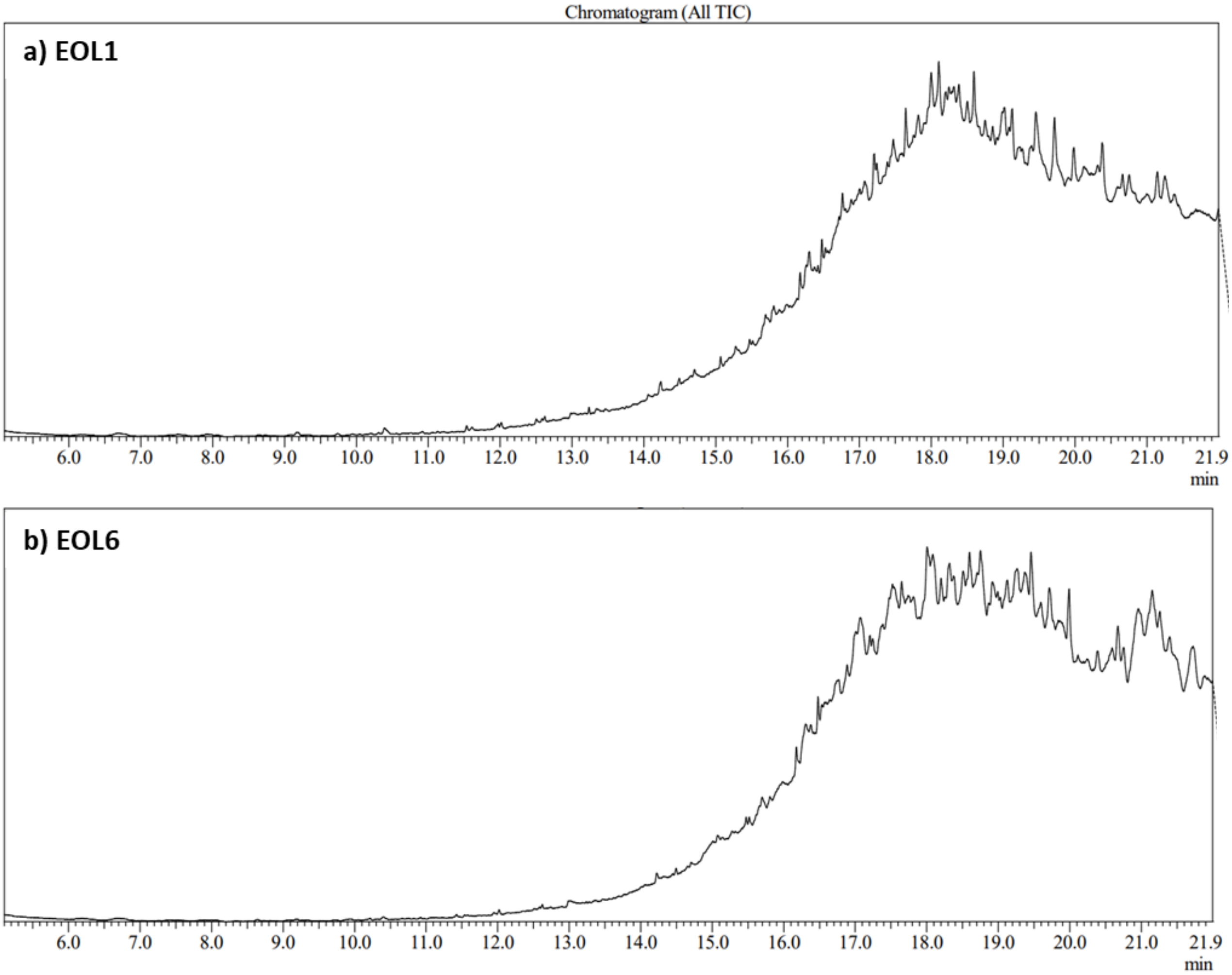


Figure 26. GC-FID wax binder comparisons of **EOL1** (a), and **EOL6** (b) waxes.

Further analysis of all EOL waxes revealed common contaminants present across the EOL waxes. As well as DEPH, butylated hydroxytoluene, tris(1-chloro-2-propyl) phosphate (TCPP), and bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate were all detected in multiple wax samples. The structure of these molecules is presented in Figure 27.

Chlorinated phosphates like those shown in Figure 27 are used as flame retardants in carpets, while butylated hydroxytoluene is often used as a chemical preservative in plastics and can be found in carpet backings and pads.[99] Finally, DEPH is a common plasticiser used in carpet manufacturing to tune fibre properties.[100] In this case, all major identified impurities observed in the GC-MS chromatograms can be assigned as leachates from the polymer fibres during solvent extraction.

Due to the structure of the chlorinated phosphates identified in the GC-MS experiments, concerns around their potential as POPs arose. However, they are not listed under the Stockholm Conventions POPs list and as such are not classified as POPs.[101] This is consistent with preliminary research authorized by ES which focussed on identifying POPs in carpet fibre extracts. GC-MS tests identified a range of compounds, including napthalenes, chlorinated organophosphates, melamines, and azulenes. Spectra were scanned for specific m/z peaks corresponding to fragments of POPs according to literature values with no matches found.

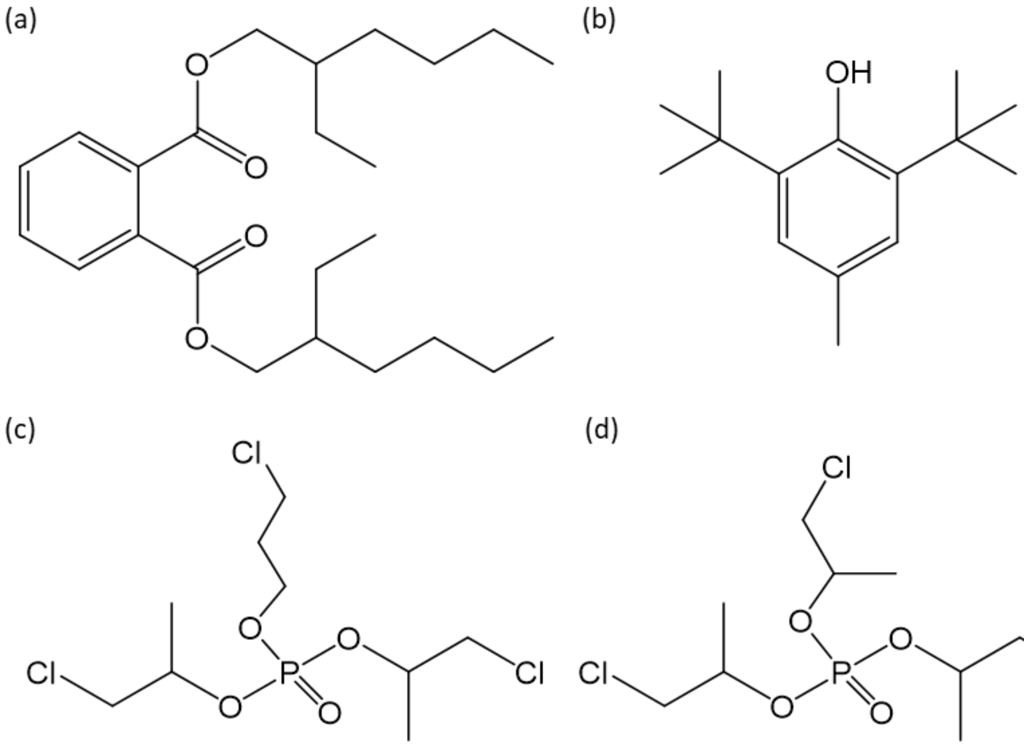


Figure 27. Chemical structure of impurities identified in wax samples extracted from EOL surfaces. (a) bis(2-ethylhexyl) phthalate, (b) butylated hydroxytoluene, (c) bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate, and (d) tris(1-chloro-2-propyl) phosphate.

In summary, GC-MS analysis revealed molecular changes to the structure of the wax molecules, with some sample showing a reduced alkane range (**EOL4** and **EOL5**) and others showing no signs of paraffin wax presence (**EOL1** and **EOL6**). Either way, the results further confirm modification of the wax binder following prolonged surface usage.

3.4.3 Elemental Analysis

To further investigate the composition of the EOL waxes, the waxes were analysed using a CHNS elemental analyser.[102] Samples were prepared directly, with no filtration of the waxes prior to analysis.

The recorded carbon, hydrogen, nitrogen, and sulphur contents are shown in Figure 28 and Table 18 below. Since the supplier wax is paraffin based, the majority of the mass of this material is expected to be carbon, with the % of N and S expected to be negligible. This is the case for the supplier (**GT70**) and **BS** waxes, where C and H make-up the bulk of the material (Figure 28).Generally, the amount of nitrogen and sulphur is low, with all surfaces showing negligible sulphur content, and a nitrogen content in the range of 0.1-1%.

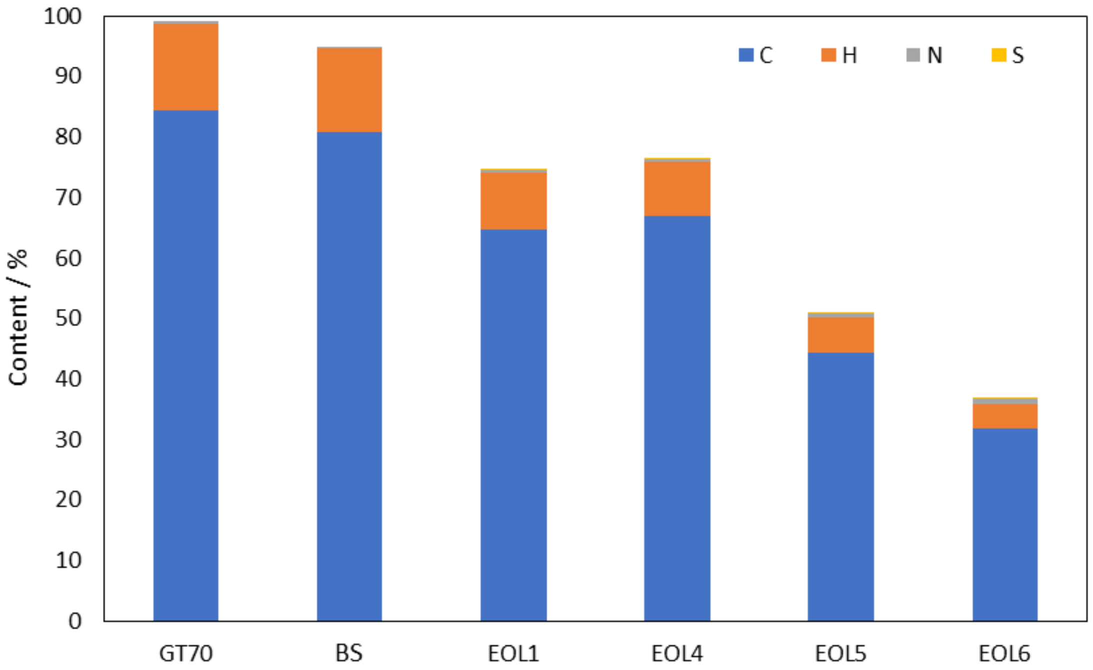


Figure 28. *Elemental analysis of wax extracts.*

Wax Sample	C (Wt %)	H (Wt %)	N (Wt %)	S (Wt %)	C/H
GT70	84.39	14.41	0.41	0.00	5.86
BS Wax	80.87	13.81	0.17	0.00	5.85
EOL1	64.65	9.48	0.50	0.05	6.82
EOL4	67.00	8.78	0.49	0.01	7.63
EOL5	44.21	5.86	0.64	0.34	7.55
EOL6	31.88	3.88	0.95	0.01	8.21

Table 18. *Elemental analysis (CHNS) results for all extracted wax samples.*

For the EOL surfaces, the carbon content is visibly reduced compared to the **GT70** and **BS** waxes. This likely arises due to a combination of oxidative degradation to the wax itself, and contamination of the wax with other inorganic impurities, with fine sand and calcium carbonate particles being major examples. Hence, for more accurate conclusions to be made, elemental analysis tests should be repeated with celite filtered wax samples in order to ascertain the impact of fine particulate matter on the results.

3.4.4 DSC Analysis

The melting behaviour of a wax sample is highly dependent on its intrinsic chemical properties, hence any change to the structure of the wax will impact the thermal properties of the material. Because the wax is applied as a liquid during surface manufacture, the melting point of the material is an important property to be considered when determining reusability.

DSC measures heat flow into and out of a material as a function of time or temperature. This technique provides quantitative characterization about physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity, hence it can be used to determine the melting point of waxes.[91]

DSC results for the EOL and BS waxes show variability in melting enthalpy between samples (Figure 29), with the supplier and BS waxes showing a thermal transition corresponding to the melting point of the wax in the 67-70 °C range. For the EOL samples, the thermograms show no major peak in this region, indicating loss or degradation of the paraffin wax binder. The **EOL4** wax shows a broad peak from 50-60 °C. This likely also corresponds to the wax binder, however the melting range is lowered due to the presence of impurities within the sample which disrupt the crystal structure of the material. This is further evidence that particulate matter is extracted alongside wax during the solvent extraction process.

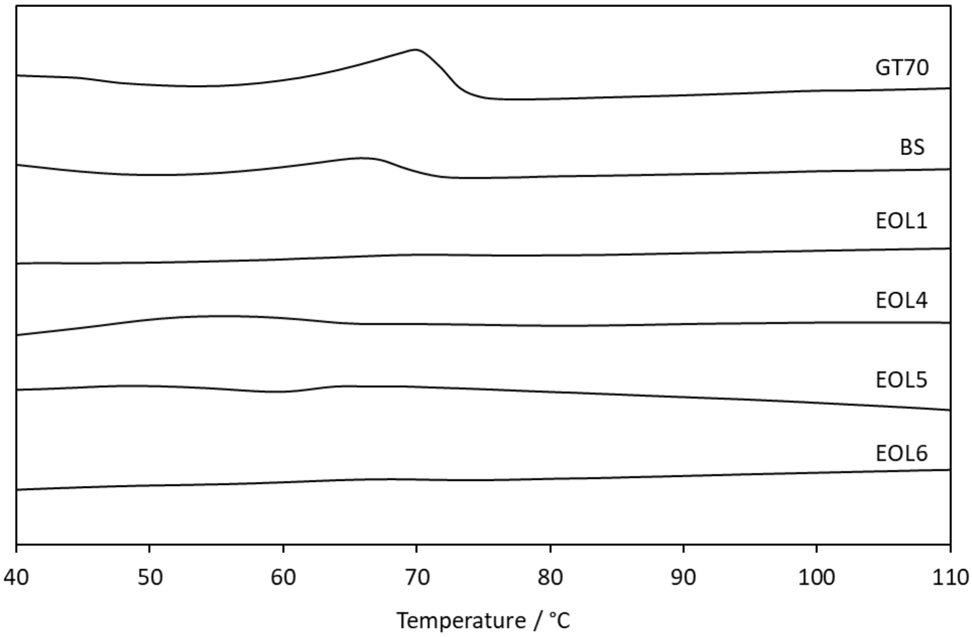


Figure 29. Stacked DSC thermograms of the supplier and extracted waxes.

3.4.5 Summary

During surface usage, a significant portion of the wax binder is lost as shown by the low yields obtained from solvent extraction of EOL surfaces. FTIR analysis, with supporting GC-MS, CHNS, and DSC data shows that the remaining wax is subject to complex chemical changes that impact both the appearance and properties of the material. These changes likely occur due to direct exposure of the surface to air (oxygen) and natural weathering processes including UV radiation and ozonolysis.[44] This, as well as significant contamination of the wax with organic soluble and fine particulate impurities affects the properties and reusability of the extracted material. The extent of contamination observed is dependent on the extraction method chosen, with the solvent extraction method employed in this project resulting in significant particulate contamination. Alternative extraction methods could be explored which may reduce the effect of this, with Soxhlet and supercritical CO_2 extraction highlighted as potential alternatives.[45]

Additional effects may be evident in the manner in which the surface interacts with moisture. An oxidized, more polar binder will reduce the hydrophobic nature of the surface, decreasing the drainage ability of a surface. Hence addition of a fresh, non-polar wax would be required to reduce the relative amounts of oxidized binder and ensure the surface retains its hydrophobic properties.[44] These changes in the wax may be a factor in synthetic tracks with drainage problems and with the overall perception of decreased surface performance over time. Understanding these changes is critical before the reuse capacity of the wax can be established.

The effects of these changes to the wax on the mechanical behaviour of the surface would be expected to be evident in tests such as the triaxial shear test.[44] In this instance, budget and time constraints meant it was not possible to explore the performance properties of different EOL surfaces, however this is something that ES are currently exploring in more depth.

In summary, solvent extraction has proved effective for the removal and isolation of material from equine surfaces, however, the purity of the material varies significantly between samples, with waxes extracted from EOL surfaces appearing heavily contaminated. Hence, for this material to be suitable for reuse, alternative extraction or purification methods need to be explored.

3.5 Green Extraction Strategies

Although wax extraction from equine surfaces proved successful, the large variability in yield and purity observed for the EOL surfaces complicates the scaling of extraction to industry. In addition, extraction experiments thus far have focussed on optimising yields using common organic solvents including toluene and chloroform. These flammable and problematic organic solvents cause adverse health and environmental effects and hence the use of these on large scale does not align with the circular economy aims of this project.[103] Because of this, alternative extraction techniques were explored, with the main focus on use of green solvent substitutes.

3.5.1 Green Solvent Extraction

Safety, environmental, and health concerns have increased the interest in alternatives to organic solvents to reduce emissions of volatile organic compounds into the atmosphere. Due to new emphasis on environmental protection and the development of green chemistry, such solvent use is to be avoided where possible.[104] To attain sustainability, the best solution is to substitute the classic organic solvent-based methodologies with green and cleaner alternatives. For example, bio-based solvents have attractive advantages including biodegradability, low vapour pressure and reduced toxicity. Various bio-based solvents, including ethyl lactate and Cyrene have been commercialised in recent years meaning the cost of these solvents is now more in line with common organic solvents.[105]

Given the success of solvent extraction for wax removal from equine surfaces, a series of greener solvents were screened for their wax extraction performance. Initially, tests focussed on extracting wax using the bio-based solvent Cyrene.[54] The physical properties and structure of Cyrene are described in Table 19. As a polar aprotic solvent, Cyrene has properties similar to that of THF. As THF recorded a high wax recovery yield with the baseline surface (104%) it was reasoned that Cyrene would also be well-suited to wax extraction.

Solvent	Structure	Density	Boiling Point
Cyrene		1.25 g/mL	227 °C

Table 19. *Physical properties of Cyrene.*[105]

Extraction experiments were conducted on samples of baseline surface according to the procedure described in Section 2.5.2. The high boiling point of Cyrene makes it difficult to remove the solvent under reduced pressure, hence an alternative work-up procedure was necessary.[54] The high miscibility of Cyrene in water meant aqueous work-up techniques were employed for wax recovery.

The yield and appearance of wax isolated following Cyrene extraction are described in Table 20. The high yield recorded indicates good solubility of the wax in Cyrene, however this yield is significantly higher than those observed for the classic organic solvents detailed in Section 3.2.1. This is due to difficulties removing all the Cyrene from the extracts, with the aqueous work-up procedure proving unsuccessful for achieving complete solvent removal.

Solvent	Yield of Organic Material	Appearance
Cyrene	133%	Orange waxy solid

Table 20. *Wax recovery data for Cyrene extraction of* ***BS****.*

In response to this, dimethyl carbonate (DMC) was selected as an alternative, lower boiling point, green extraction solvent. Previous research identified DMC as a suitable green substitute for highly toxic halo-hydrocarbon solvents including chloroform and dichloromethane.[106] Despite this, DMC proved ineffective for wax extraction with a poor yield of just 15% recorded for the **BS**.

Although green solvents like DMC and Cyrene seem theoretically suitable for wax extraction, their use is inherently complicated by their intrinsic properties including polarity and boiling point.[103] Moreover, most green extraction solvents are limited in terms of availability due to the high production and removal costs associated with their use. Because of this, alternative green wax extraction techniques were explored.

3.5.2 Ethyl Acetate Extraction

Previous extraction experiments revealed chloroform and toluene to be the highest yielding solvents for wax extraction. However, ethyl acetate also proved effective with a yield of 81% recorded for the **BS**. Relative to other widely available organic solvents, ethyl acetate is often regarded as greener. In terms of health and safety issues, ethyl acetate is one of the best non-harmful organic solvents.[107] Although it is primarily produced using fossil-based processes, it can be sourced renewably, with research into the production of sustainable ethyl acetate from bioethanol gaining traction in recent years.[108]

In light of this, ethyl acetate was employed as an extraction solvent for application to EOL surfaces. The results observed are highlighted below in Table 21. Again, the extraction yields varied considerably between surfaces, with **EOL1** recording the lowest wax recovery, and **EOL5** showing high recovery of organic matter. Relative to the chloroform extraction yields detailed in Section 3.3.1, ethyl acetate generally records yields around 15% lower. This may impact the applicability of this solvent to industry since the mass of recoverable and potentially reusable material would be reduced. However, the lower yields observed are counteracted by the greener properties of ethyl acetate, meaning both factors need to be carefully considered before selecting a suitable solvent.

Surface	EtOAc Extraction Yield	Extract Appearance
EOL1	36%	Dark brown waxy solid
EOL4	78%	Dark brown waxy solid
EOL5	119%	Dark brown waxy solid
EOL6	58%	Dark brown waxy solid

Table 21. *Average EtOAc extraction yields observed for the different EOL surfaces using solvent extraction.*

Although ethyl acetate proved promising as a green solvent alternative, the extracted material still appeared highly impure, with all waxes isolated from the EOL surfaces as dark brown solids. This means wax purification is still required to enable material reuse; a step that reduces the cost and time efficiency of any industrial process.

3.5.3 Recrystallisation Extraction

In attempt to increase the purity of the material isolated following ethyl acetate extraction, the extraction experiments were repeated, modifying the procedure to include extraction under heat. By heating the extraction mixture, it was hypothesised that, following extraction and filtration of solid material, the dissolved wax would crash out in solution. This could then be isolated by filtration, with the organic-soluble impurities remaining in solution, enabling the isolation of pure wax from surfaces.

To test this hypothesis, extraction of the **BS** was carried out at 75°C according to the method described in Section 2.5.4. Following hot filtration of the surface, the solution was left to cool, with the wax crashing out in solution as a pale-amber solid. This was isolated by filtration in a 61% yield. NMR and IR tests revealed the wax to be pure, with only paraffin functionality detected in both spectra.

Following this, extraction of **EOL1** surface using the same procedure was explored, with the wax crashing out in solution as a dark grey solid in a low 16% yield. A visual comparison of the solid material isolated from the baseline and **EOL1** surfaces following recrystallisation extraction is shown in Figure 30.

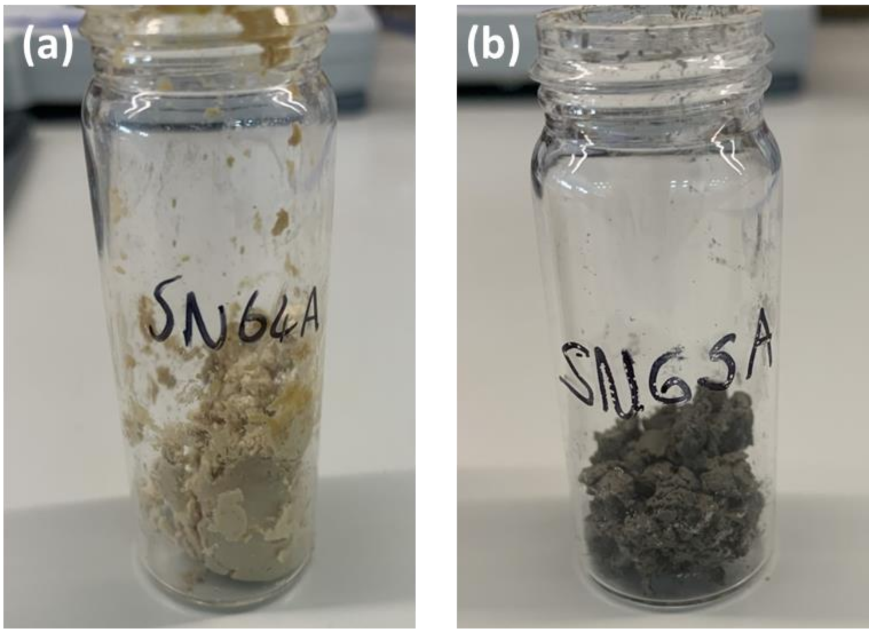


Figure 30. *Wax samples isolated following hot extraction of (a) baseline and (b)* ***EOL1*** *surfaces.*

A comparison of the yields of material isolated for room temperature EtOAc extraction, and hot EtOAc recrystallisation extraction are shown in Table 22. This highlights the significant reduction in yield observed for the hot recrystallisation extraction process. The low 16% yield recorded for the **EOL1** surface means that this process is unlikely to be viable in industry due to a combination of low yield and the additional heating costs. Furthermore, although the material isolated from the **BS** using this method proved cleaner, the material isolated from the **EOL1** surface remained heavily contaminated, meaning further optimisation and purification is needed before reusable wax could be isolated.

Extraction Method	Surface Type	Yield	Appearance
RT solvent extraction	Baseline	82%	Orange waxy solid
	EOL1	40%	Dark brown waxy solid
Hot recrystallisation extraction.	Baseline	61%	Pale-amber solid
	EOL1	16%	Dark grey dry solid

Table 22. *Comparison of the EtOAc extraction yields for the standard solvent extraction procedure and the hot recrystallisation extraction procedure.*

3.5.4 Microemulsion Extraction

As well as green solvent extraction, aqueous extraction techniques were also explored for wax extraction. In comparison to organic solvent extraction, aqueous solution extraction is a cleaner method with less or no usage of volatile solvents. This involves the addition of surfactants, which are amphiphilic organic molecules of variable size, to water. The principal method of solvation sees the surfactant reduce the surface tension between the polar water molecules and the non-polar solute, forming an emulsion.[109]

Generally, a microemulsion is a four-component system prepared by emulsifying organic material in aqueous solution with the help of surfactant and co-surfactant. The co-surfactants are generally intermediate chain length alcohols such as pentanol or butanol.[60] A representation of an oil-in-water microemulsion droplet is shown below in Figure 31.

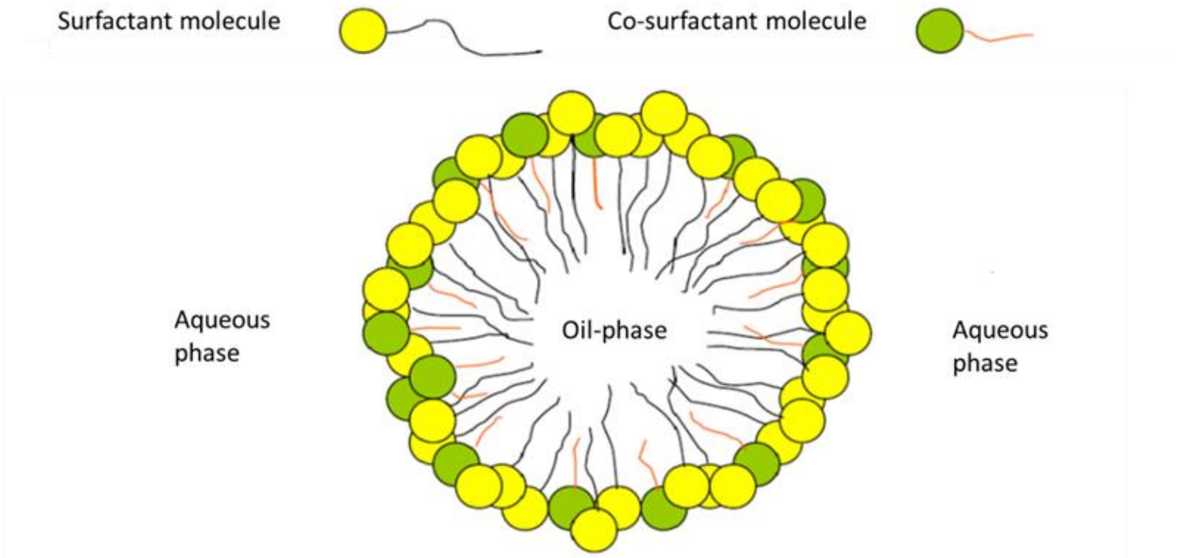


Figure 31. *Cross sectional representation of a spherical oil-in-water microemulsion droplet.*

Many surfactants can be used for microemulsion formulation. The materials should be biocompatible, non-hazardous, and safe. With this in mind, the microemulsion technique used in this study employed TritonX-100 as the non-ionic surfactant component, and *p*-xylene and *n*-octane as the co-surfactants. The capacity of these compounds for microemulsion formation and subsequent wax extraction had previously been reported by Baglioni and co-workers in 2018.[64] The authors demonstrated the ability of this microemulsion to remove hydrophobic matter from works of art.

This method was then applied to the extraction of wax from equine surfaces, with microemulsion preparation and extraction carried out according to the procedure described in Section 2.5.6. Due to issues surrounding recovery of organic material from the microemulsion, successful extraction was inferred by re-extracting the surface material with chloroform following aqueous extraction. Chloroform was selected as references, as it was identified as the most efficient solvent for extraction of organic material from surfaces.

Microemulsion extraction of the baseline surface proved moderately effective, with the yield of material extracted from the **BS** with chloroform reduced from 119% to 37%. This method was then applied to the removal of wax from EOL surfaces, with the results observed for **EOL4**, **EOL5**, and **EOL6** surfaces, as well as the previous $CHCl_3$ extraction yields shown in Table 23. This further verified microemulsion extraction as successful for wax removal, with a significant mass of material being removed from the EOL surfaces by the microemulsion wash.

Surface	$CHCl_3$ Extraction Yield	Post-aqueous Extraction $CHCl_3$ Yield
BS	119%	37%
EOL4	96%	17%
EOL5	136%	19%
EOL6	78%	11%

Table 23. *Comparison of the extraction yields observed for chloroform solvent extraction and chloroform extraction following microemulsion extraction.*

Although this method has proved effective, its applicability to industry is currently restricted by the issues with recovering reusable material from the aqueous solution. Typically, centrifugation is used instead of evaporation to recover organic material following microemulsion extraction. This uses centrifugal acceleration to separate materials based on density. Once separated the different liquids can be isolated by decanting.[60] This provides a lower cost, sustainable method for separation and recovery of wax from equine surfaces. However, for this to be used in industry, further investigation into the recovery of material as well as an analysis of the microemulsion-extracted waxes is necessary to establish if purification of the wax is required before reuse as this will impact the applicability of this technique to industry.

In summary, microemulsion extraction has proved effective for removal of organic material from equestrian surfaces, providing a green alternative to organic extraction which could be used in industry. Compared to conventional solvent extraction techniques this method avoids the use of large volumes of hazardous organic solvents whilst operating under ambient conditions and requiring low surfactant concentrations for high extraction efficiencies.

3.5.5 Summary

Replacement of conventional organic solvents with emerging green alternatives, such as bio-based solvents and non-ionic surfactants, has proved effective for the extraction and isolation of organic material from equine surfaces. However, green extraction technologies are not without their own shortcomings; high capital investment, high operating costs, high maintenance costs, and complex configuration are major limitations restricting the large-scale application of these techniques to industry.[93] Taking all these factors into account, ethyl acetate extraction appears to be the most promising green extraction method and the most suitable for large scale wax recovery from equine surfaces.

Nevertheless, extraction of wax from EOL surfaces is again limited by issues surrounding the purity of the extracted material, with the wax isolated from all used surfaces appearing as a dark brown solid. Analysis of this material has repeatedly shown this to be heavily impure, meaning purification is required before reusable material can be isolated.

3.6 Wax Purification

Initial research employed fine filtration techniques for purification (Section 3.3.2, page 58). Although this proved effective for removing fine particulate from the extracts, the appearance of the wax was not altered by this process, indicating some soluble impurities remained. Instead, silica gel column chromatography was employed as an alternative to separate the lipid extract into different classes based on polarity.[110]

Chromatographic separation is based on the relative attraction of analyte compounds to either the stationary phase that makes up the column (in this case silica gel) or the mobile phase passing through the column (in this case a series of solvents and solvent mixtures of increasing polarity).[111] The solvent scheme for elution of different compound classes can vary based on the target compounds. Because the initial **GT70** wax was confirmed as *n*-alkane paraffin wax, pentane was selected for elution as a non-polar hydrophobic solvent.[110]

The four EOL wax samples were purified via column chromatography, with the low-polarity fraction mass recovery percentages and extract appearance presented in Table 24. A sample of GT70 wax was purified in the same way, with the results also highlighted in Table 24. In all cases, samples of wax were dissolved in pentane and dry loaded onto the column. The column was then run according to the procedure detailed in Section 2.5.5.

Wax Sample	Wax Recovery Percentage	Appearance
GT70	84%	Yellow waxy solid
EOL1	19%	Yellow waxy solid
EOL4	39%	Yellow waxy solid
EOL5	27%	Yellow waxy solid
EOL6	20%	Yellow waxy solid

Table 24. *Mass recovery percentages for silica gel chromatographic separation of unfiltered 2.0 g samples of **GT70** wax and waxes isolated from four EOL surfaces. Wax was isolated following elution with 150 mL of pentane.*

In all cases, the product was isolated as a yellow waxy solid. For the EOL wax this shows a drastic change in appearance from the dark brown material isolated following solvent extraction. This was taken as indication of successful removal of impurities from the waxes, with the appearance of the material now matching that of the supplier wax.

^{13}C NMR analysis of the isolated waxes confirmed the material as paraffin wax, with only the 5 characteristic paraffin environments present in all spectra (Figure 32). In addition, this was further confirmed by FTIR analysis, with all spectra appearing identical to that of the supplier **GT70** wax (Figure 33).

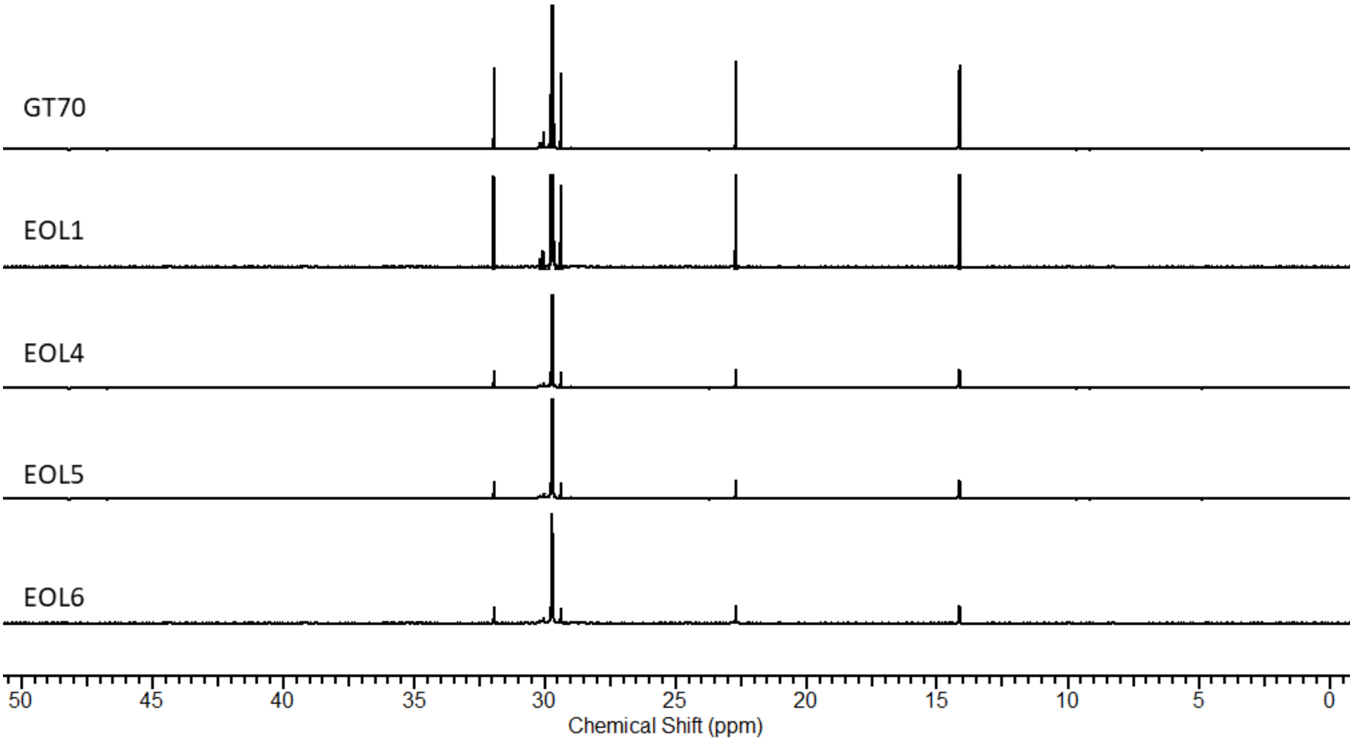


Figure 32. Stacked *^{13}C NMR spectra for the pentane fractions isolated following column purification of different wax samples.*

Unlike with fine filtration (Section 3.3.2, page 58) the IR spectra for the column-purified wax samples are identical to the supplier wax, with no indication of wax oxidation. This is as any oxidized wax will remain on the column for a longer duration due to the polar nature of the carbonyl bond increasing the polarity of the oxidised wax. In contrast, the saturated paraffin wax is highly non-polar and hence has low affinity for the polar silica stationary phase. Instead, it moves along the column with the non-polar mobile phase, eluting as clean paraffin wax. This indicates that not all wax is subject to oxidation and confirms that it is possible to recover reusable straight chain paraffin wax following surface usage.

On comparing the properties of extracted and purified wax it is evident that column chromatography is a suitable technique for the removal of impurities from EOL surface extracted waxes. However, the recovery percentages of material for the EOL waxes are low, with all EOL samples recording recovery percentages below 40% (Table 24). Furthermore, additional analysis of the isolated EOL wax samples is necessary before reuse is deemed suitable. This includes analysis of samples by GC-MS to ascertain the purity and chain length distribution of the columned waxes, and analysis by DSC to verify the thermal properties of the materials.

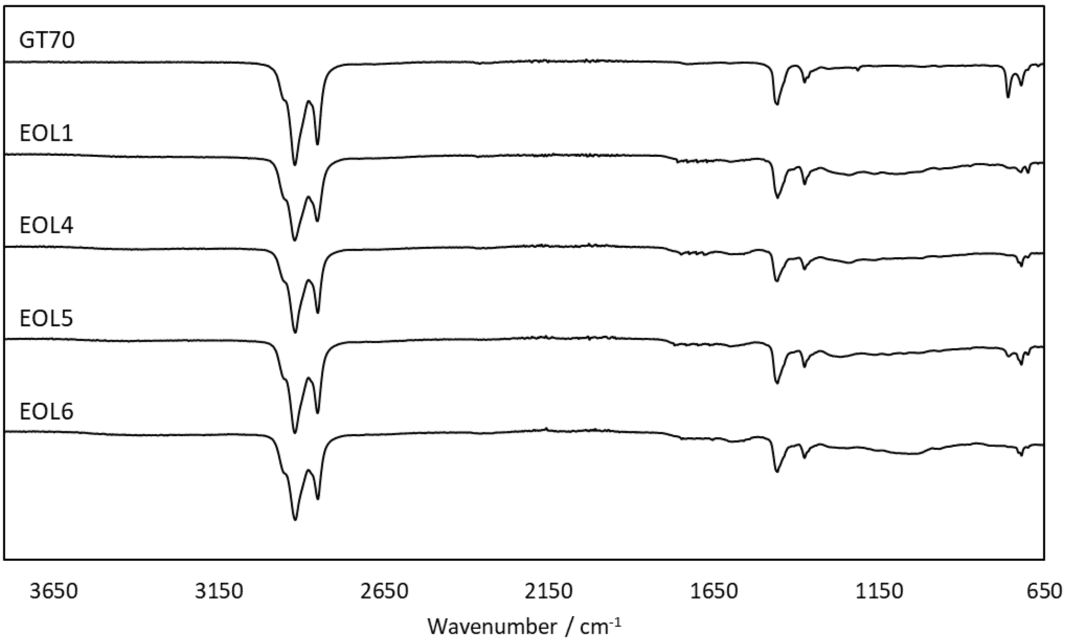


Figure 33. *Stacked FTIR spectra for the pentane fractions isolated following column purification of different wax samples.*

The true yield of paraffin wax is also impacted by the initial solvent extraction yield. For example, **EOL1** recorded an average $CHCl_3$ extraction yield of 50%, hence the 19% recovery observed here is 19% of a 50% recovery. The adjusted extraction yields, relating to the mass of recoverable pure paraffin wax as determined by column chromatography are highlighted in Table 25. These results further highlight the low yields of pure wax recoverable from EOL surfaces.

Surface	$CHCl_3$ Extraction Yield	Column Recovery Percentage	Adjusted Wax Recovery Percentage
EOL1	50%	19%	**9.5%**
EOL4	96%	39%	**37%**
EOL5	136%	27%	**37%**
EOL6	78%	20%	**16%**

Table 25. *Table showing the initial $CHCl_3$ extraction yields, mass of reusable material recovered following column purification, and the adjusted wax recovery yields for a series of EOL surfaces.*

Although the material recovered from the column appears pure, the adjusted recovery yields are low, meaning ES would be required to combine any isolated wax with fresh wax when making new surfaces. This questions the applicability of this to industry since large-scale column purification requires considerable investment in equipment, materials, and manpower, making this unfavourable in terms of value but also in relation to a circular economy as the process also generates substantial volumes of waste. In addition, this process requires the use of toxic, unfavourable hydrocarbon solvents, which are not desired in industry.[112]

Taking all this into account, although effective, wax purification is unlikely to align with the aims of this project (or at least would need significant research devoted to large scale wax purification that could not be investigated here due to time constraints): to create a circular economy for equine surfaces whilst reducing the emissions associated with the current waste disposal processes in place.

3.7 Conclusions

Initial research focussed on the extraction and characterisation of wax from equestrian surfaces. This confirmed solvent extraction as a suitable method to extract organic material from surfaces, with toluene and chloroform identified as the most effective solvents. Although high yielding, the applicability of these solvents to industry is hindered by their inherent toxicity. Hence, to keep in line with circular economy principles, alternative, green extraction routes needed to be explored instead.[112]

Wax extraction experiments with used surfaces revealed the high variability in yield for the different EOL surfaces, with some surfaces recording yields higher than those observed for the **BS**. This was attributed to the extraction of organic and inorganic impurities present in the samples, as well as to the presence of fine particulate materials in the extracts. The presence of such impurities within the materials has a significant impact on the appearance of the extracts, with the material extracted from used surfaces repeatedly isolated as a dark born waxy solid instead of an amber wax.

A range of analytical techniques have been explored to examine the extent of contamination, with IR and GC-MS tests confirming the presence of plasticisers and fine particulate materials ($CaCO_3$ and sand) within the EOL wax samples. In addition, IR tests also appear to suggest that the wax may undergo chemical change during usage, with PTFE-filtered wax samples showing strong signs of oxidation due to the presence of carbonyl functionality in the spectra around 1700 cm^{-1}. Both factors hinder the reusability of the material in this form, as it is unlikely to provide the same benefits to a surface in terms of performance and safety without further treatment.

In response to this, extraction was modified, employing celite filtration to remove the fine particulate material from the extract solutions. This reduced the extraction yields observed, with all surfaces now recording yields lower than the **BS**. This is strong evidence that the wax coating is removed from surfaces during usage, with the extent of wax removal varying dependent on the age and usage frequency of the surface. A summary of the chloroform extraction yields for the EOL surfaces, as well as the baseline surface is shown in Table 26. This highlights the difference in yield recorded for the surfaces when using the different extraction methods. The celite filtration tests give a more accurate representation of the wax coverage of the surfaces, with further testing required to validate how the purity of the material extracted via celite extraction compares to that of the solvent extracted samples.

Surface	Extraction Method	Solvent Extraction Yield
Baseline Surface	Solvent Extraction	119%
EOL1	Solvent Extraction	50%
EOL4	Solvent Extraction	96%
EOL5	Solvent Extraction	136%
EOL6	Solvent Extraction	78%
Baseline Surface	Fine Filtration Extraction	112%
EOL1	Fine Filtration Extraction	29%
EOL4	Fine Filtration Extraction	56%
EOL5	Fine Filtration Extraction	76%
EOL6	Fine Filtration Extraction	32%

Table 26. *Wax extraction yields observed for different surfaces extracted with $CHCl_3$ via solvent and fine filtration extraction methods.*

Due to the issues with wax purity, purification techniques were utilized to determine if material that was comparable to the supplier wax both in terms of purity and appearance could be recovered. This was verified using chromatographic methods, with column chromatography proving effective for isolating clean wax from the EOL surface waxes. Although successful, the mass of reusable material isolated following purification is very low, making this a costly and time-consuming method of wax recovery. With this in mind, wax purification does not align with the aims of this project as the method employed here requires a range of other chemicals including silica and pentane which have their own hazards and complications associated with them.

In line with the circular economy objectives of this project, green extraction techniques have also been studied for their capacity to extract wax from surfaces. A range of different green methods have been explored, with microemulsion and ethyl acetate extraction highlighted as two suitable alternatives to chloroform extraction. However, both methods are again complicated by issues surrounding wax purity and recovery, meaning further investigation and method optimisation is required before these methods can be used in industry. For instances where removal of wax from surfaces is necessary for reuse of the other surface materials to be viable, microemulsion extraction is the most promising solution based on both efficiency and sustainability factors.

In summary, a range of solvents and extraction methods have been explored for their ability to remove wax from both used and unused surfaces. Analysis of the EOL surface extracts revealed the materials to be highly impure, with wax reuse not possible without considerable purification or treatment. This fundamentally does not align with the circular economy principles of this project since both the extraction and purification processes are likely to involve considerable investment, material, and emission costs. With this in mind, wax extraction and therefore wax reuse was deemed an unsuitable reuse pathway, with the remainder of the project focussing on alternative, more sustainable solutions for equestrian surface recycling.

Chapter 4 – Results and Discussion – Mechanical Separation Tests

Initial research focused on the removal and recovery of wax from surfaces, however, the results presented in Chapter 3 demonstrate how the material extracted from used surfaces is not suitable for reuse without substantial purification. This is a costly, time consuming and unsustainable process, hence, to keep in line with the aims of the project, it was decided that alternative strategies for surface recycling should be explored, with a key example including the separation of surfaces using mechanical separation techniques.

Preliminary experiments utilised small-scale sieve tests to assess the feasibility of size separation with samples of dewaxed surfaces. In this way, the reusability of the sand and fibres isolated from surfaces could be determined.

4.1 Preliminary Sieve Separation Tests

A series of laboratory standard test sieves were purchased with pore sizes ranging from 1.0 mm to 0.125 mm. Samples of dewaxed surfaces were passed through the 1 mm sieve, with the large fibrous material remaining in the sieve, and the small sand grains passing through the pores. The isolated sand was then passed through a 0.5 mm sieve in an attempt to recover pure sand. This permitted the removal of impurities and small fibres from the sand. The recovered masses as well as visual images of the fractions isolated for a sample of dewaxed baseline surface (**BS**) are shown in Table 27. The separation proved effective, with the sand and fibre isolated appearing pure and in good yield.

Sieve Grading	Mass Recovery %	Appearance
> 1 mm	7.9	
1 mm > x > 0.5 mm	3.1	
< 0.5 mm	89	

Table 27. *Mass recovery percentages recorded for sieve separation of 60.0 g of dewaxed* ***BS****.*

Following testing on the baseline surface, samples of dewaxed **EOL1** surface were separated in the same way. The results appeared similar, with the sand isolated in good yield. However, relative to the baseline surface, the mass of material > 1 mm recovered was significantly reduced. This was attributed to the breakdown of fibrous material during usage, which creates microplastics that can be blown off the surface and into the environment. Any microplastics which remain in the surface are reduced in size and can pass through the 1 mm sieve, contaminating the other fractions. This was observed here, with the sand now appearing contaminated with microplastic fibres (Table 28).

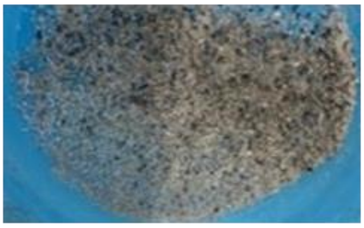
Sieve Grading	Mass Recovery %	Appearance
> 1 mm	2.3	
1 mm > x > 0.5 mm	2.0	
< 0.5 mm	95	

Table 28. *Mass recovery percentages recorded for sieve separation of 60.0 g of dewaxed* ***EOL1*** *surface.*

In summary, preliminary sieve separation tests proved effective for the isolation of sand and fibre from dewaxed surfaces. Tests revealed the importance of a two-step sieving process for separation of surfaces, with impurities isolated in the intermediate sized fraction. In contrast to the **BS**, the purity of the isolated fractions is slightly reduced for the **EOL1** surface, with the sand showing minor contamination with microplastics. Despite this, the yield of material recovered using this method is strong, reinforcing this method as a trivial and scalable method for use in industry.

4.2 Mechanical Separation of Waxed Surfaces

EOL surface extraction experiments repeatedly recorded high variation in wax recovery, with some surfaces showing remaining wax contents less than 40% (following fine filtration extraction, see Section 3.3.2). This suggests that, at a true EOL state, a significant proportion of wax is lost from surfaces and hence it may be possible to separate sand and fibres easily without the need to remove wax from surfaces.

Since preliminary sieve separation tests proved effective for the separation of dewaxed fibre and sand, the same method was applied towards the separation of waxed surfaces. If successful, this would allow for the direct separation of sand and fibre without the need to remove wax from surfaces, eliminating a difficult and resource-intensive step from the surface recycling process.

4.2.1 Waxed Surface Separation

Samples of waxed EOL surface were separated using the two-step sieve method described in Section 3.4.1. The results varied depending on the EOL surface, with the surfaces generally showing good recovery of sand (Table 29). **EOL1** and **EOL6** surfaces show strong sand recovery with mass recovery percentages over 85% recorded. This is consistent with the low wax extraction yields observed for these surfaces, further confirming that the remaining wax content on these surfaces is low.

Sieve Grading	EOL1	EOL4	EOL5	EOL6
> 1 mm	7%	16%	13%	8%
1 mm > x > 0.5 mm	5%	10%	9%	6%
< 0.5 mm	88%	74%	78%	86%

Table 29. *Mass recovery percentages recorded for sieve separation of 100 g of waxed EOL surfaces.*

In contrast, the sand recovery percentages for the **EOL4** and **EOL5** surfaces are significantly lower. This is due to the higher remaining wax coverage on these surfaces which causes the sand and fibre to stick together, preventing optimal separation. Nevertheless, sand recovery is still good, with the sand isolated displaying minimal microplastic contamination.

A comparison of the sand recovery (<0.5 mm) percentages for the waxed and dewaxed forms of the EOL surfaces is shown in Figure 34. For the dewaxed surfaces, the percentages were calculated for the dewaxed sand and fibre only whereas, for the waxed surfaces, the mass of surface includes the remining wax coating as well as the sand and fibre, hence this may affect the mass distribution recorded.

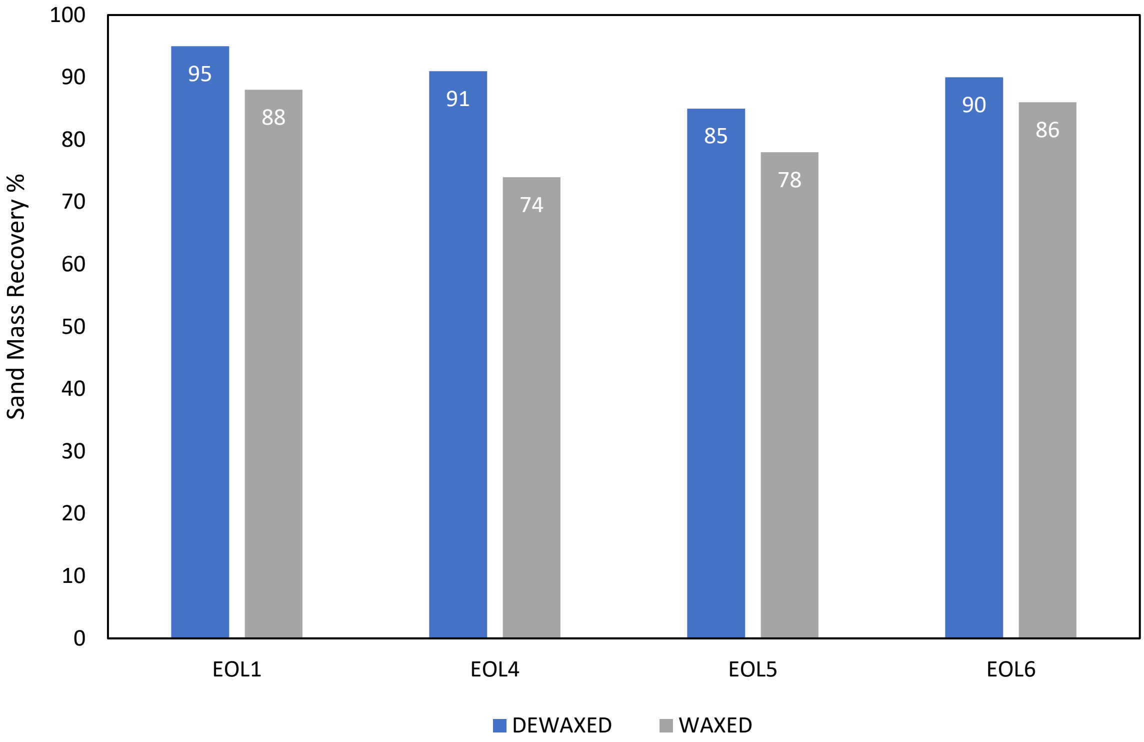


Figure 34. *Graph showing the reduction in sand recovery for waxed EOL surfaces compared to dewaxed EOL surfaces.*

In summary, the separation of waxed surfaces directly has proved effective for the isolation of fibre-free sand from surfaces. Although the yields are slightly reduced relative to the dewaxed equivalents, this method enables surfaces to be separated without the need for wax removal, hence it is substantially greener in terms of both costs and emissions, as well as being more practical.

Furthermore, the results of these tests can be used to infer information about the remaining wax content of a surface. Surfaces with low remaining wax content undergo trivial separation, whereas surfaces with higher wax content record lower sand recovery percentages. This is due to the influence of wax on the size and cohesion of surface components.

Although small-scale tests have proved promising, sampling issues and the small sample sizes used mean these results should not be used alone to confirm separation efficiency. Hence, for this method to be used in industry, the scale of testing was increased to determine how the purity of the three fractions varies with increasing scale.

4.2.2 Trommel Separation

Following the success of the small-scale sieve tests for facilitating surface separation, the scale of separation was increased. This involved the development of a model trommel, with the capacity to separate around 1 kg of surface at a time. In addition to this, a series of trommel drums were procured, with pore sizes ranging from 6 mm to 0.8 mm. By assessing separation using a range of pore sizes, it was anticipated that the optimum separation conditions could be established. As well as pore size, the angle of inclination and rotational speed of the trommel also contribute towards the separation efficiency.[67]

Previous tests, described in Section 4.1, revealed the necessity of a two-step separation method for isolating pure material from surfaces, hence, initial trommel experiments focussed on evaluating the viability of the two-step method on a larger scale. Given the range of drums available (6 mm, 5 mm, 4 mm, and 0.8 mm), 4 mm and 0.8 mm drums were selected for the trommel separation of a one-kilogram sample of **EOL1** surface.

Material was added to the 4 mm drum, before being subject to the standardised separation procedure described in Section 2.3.3. The isolated material was then collected, and the material < 4 mm re-processed in the trommel at 0.8 mm. The results, as well as a schematic representation of the two-step separation process, are shown in Table 30 and Figure 35, respectively.

Sieve Grading	Mass Recovery %	Appearance
> 4 mm	3.6	
4 mm > x > 0.8 mm	3.4	
< 0.8 mm	93	

Table 30. *Percentage mass recovery for a 1 kg sample of **EOL1** surface, processed in the trommel at 4 mm and then at 0.8 mm.*

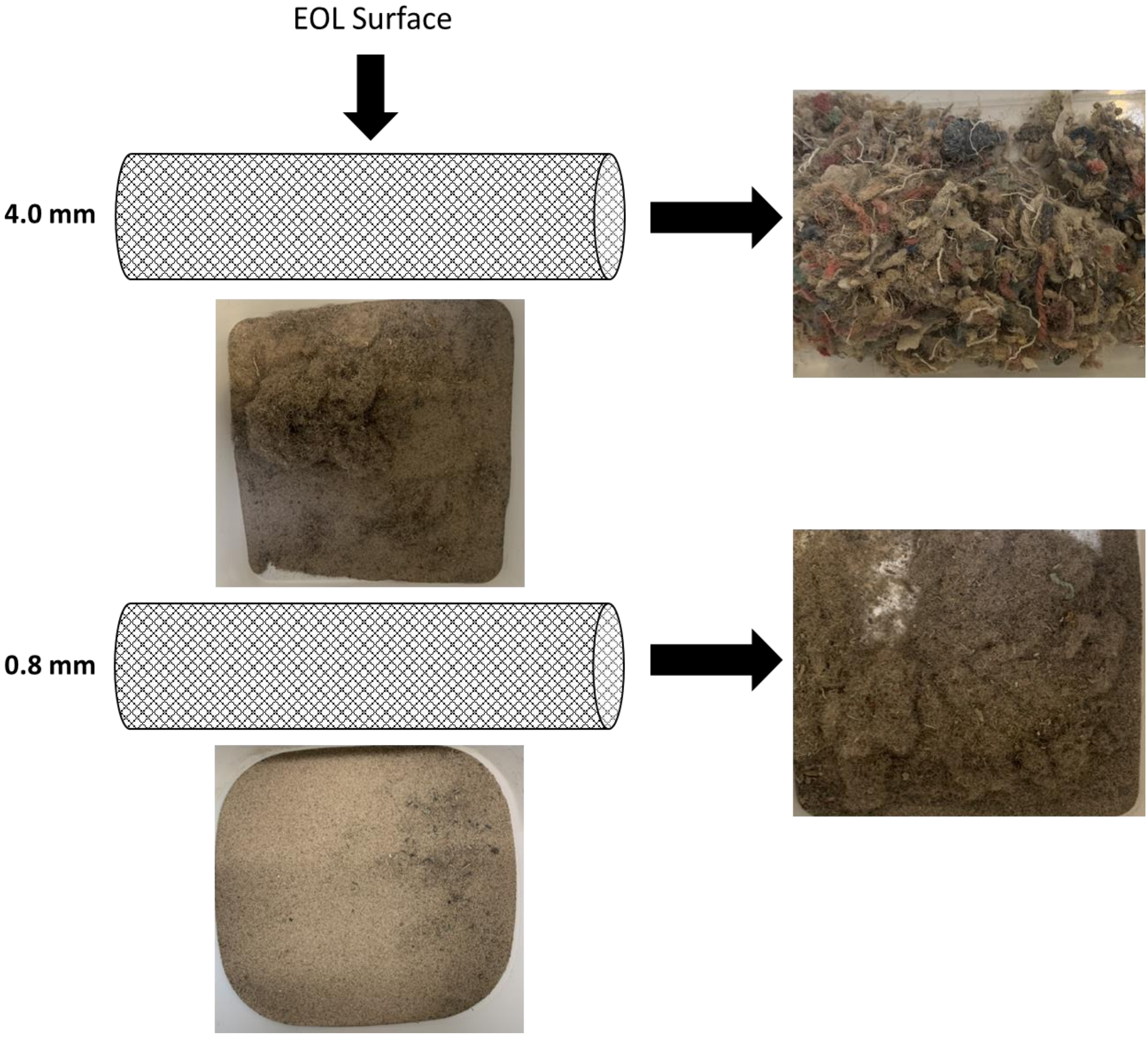


Figure 35. *Schematic representation of the two-step trommel separation method.*

The results show good recovery of material, with the majority of surface mass isolated as sand, consistent with the small-scale sieve tests. Again, the mass of fibre recovered is reduced relative to the initial composition (5.68%), indicating significant loss of large fibrous material during usage. This arises due to a combination of fibre breakdown (and subsequent microplastic formation), and fibre loss as the wax coating breaks down and fibrous material rises to the surface, where it is subsequently blown away.

As evidenced in Figure 35, the sand that passes through the 4 mm drum appears heavily contaminated with microplastics. The majority of these MPs can be removed by re-processing the material in the trommel at 0.8 mm, enabling isolation of cleaner sand which is more suitable for re-incorporation into new surfaces.

Following separation of the **EOL1** surface, testing was expanded to determine the success of trommel separation with other EOL surfaces. The surfaces were separated in the same way using the two-step method, with the recorded mass recovery percentages for all EOL surfaces shown in Table 31. Compared to **EOL1**, the sand recovery for the other EOL surfaces is slightly reduced relative to the small-scale sieve tests (see Table 29). The larger sample size used for these tests means these results more accurately represent the true separation capacity of these EOL surfaces, with the results being less impacted by sampling issues.

Surface Sample	> 4 mm	4 mm > x > 0.8 mm	< 0.8 mm
EOL1	3.6%	3.4%	93%
EOL4	25%	5%	70%
EOL5	21%	11%	68%
EOL6	10%	9%	81%

Table 31. *Mass recovery percentages for 1 kg samples of EOL surface, processed in the trommel at 4 mm and then at 0.8 mm.*

The higher organic content of the **EOL4** and **EOL5** surfaces reduces the recoverable mass of sand from the trommel, with the fibre (> 4 mm) and microplastics (4 mm > x > 0.8 mm) fractions appearing contaminated with sand. Despite this, visual inspection of the sands recovered from the trommel revealed them to be high purity, with minimal microplastic contamination observed in all cases (Figure 36).

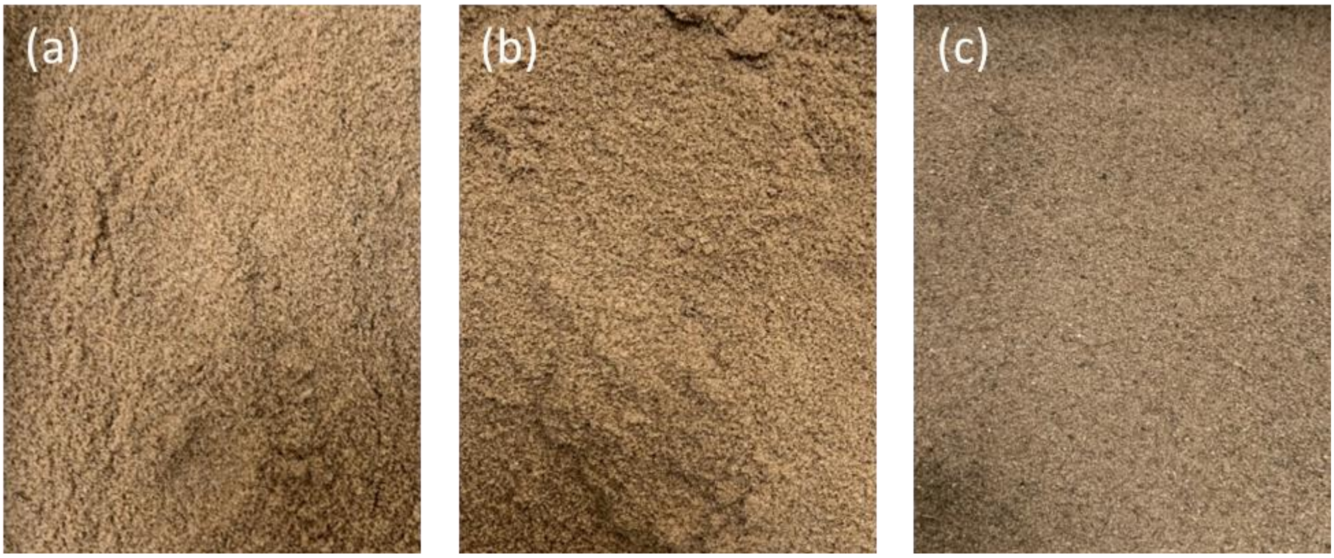


Figure 36. *EOL sands isolated from the 0.8 mm trommel:* ***EOL4*** *(a),* ***EOL5*** *(b), and* ***EOL6*** *(c).*

To further establish the scalability of separation, a large sample (4.0 kg) of **EOL4** surface was separated in the same way. The material was added to the trommel in approximately 500 g increments, with the larger material removed from the trommel drum following each separation cycle. The results, as well as images showing the isolated fractions, are shown in Table 32.

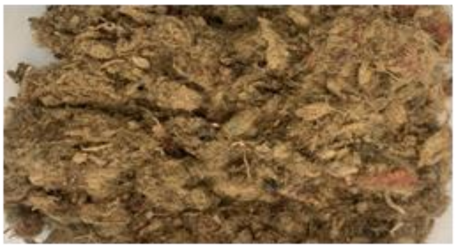
Sieve Grading	Mass Recovery %	Appearance
> 4 mm	17%	
4 mm > x > 0.8 mm	21%	
< 0.8 mm	62%	

Table 32. *Percentage mass recovery for a 4.0 kg sample of* ***EOL4*** *surface, processed in the trommel at 4 mm and then at 0.8 mm.*

Interestingly, increasing the scale of separation further had a significant impact on the recorded mass recovery percentages. The mass of material isolated in the intermediate fraction increased considerably, from 5% on a 1 kg scale, to 21% on a 4 kg scale. Conversely, the mass of sand recovered decreased, with significant mass of sand now isolated in the intermediate sized fraction. This suggested poor separation of material, indicating the 0.8 mm drum may not be the optimal pore size for maximum sand recovery.

With this in mind, a 1 mm drum was procured and tested for separation capacity. Although this did increase the mass of sand recovered from 62% to 70%, the sand now appeared visibly contaminated with microplastics. This is an issue in terms of sand recycling as clean sand is desired for re-incorporation into new surfaces. These results show how optimisation of mechanical separation involves a balance between the yield and purity of the material, with ES having the final say on both factors based on their quality and performance objectives for any recycled surfaces.

In summary, the two-step separation method appears well-suited to trommel separation of waxed EOL surfaces as it successfully permits the isolation and removal of microplastics from surfaces; whilst also facilitating the separation of potentially reusable fibre and sand from surfaces. The recovery of material is highly variable between EOL samples, with the remaining wax content having a significant influence on the isolated masses of material. Surfaces with minimal wax coating give high sand recovery, but those with greater remaining wax content show reduced sand recovery. Although the 4 mm and 0.8 mm drums have proved effective for surface separation, the yields of material for certain surfaces are not optimal, meaning methods for recovery optimisation need to be explored.

4.2.3 Trommel Optimisation Strategies

Instead of extracting wax from EOL surfaces, trommel modification strategies can be employed to enhance material recovery. A key example of this includes modification of the trommel drums with brushes. This is a strategy commonly used in industry to boost separation by ensuring the pores of the drum remain unblocked during each separation cycle.[68] Time constraints and budget limitations for this project meant it was not possible to explore this, however it is recognised that this is likely to help enhance separation and therefore ES should consider this before using the trommel on large scale.

Re-addition of material to the trommel is another strategy which can be used to enhance separation. This technique was applied to the large-scale separation of the **EOL4** surface reported above in Table 32. The material isolated in the large (> 4 mm) and intermediate (4 mm > x > 0.8 mm) sized fractions was re-processed through the trommel at 4 mm and 0.8 mm, respectively. This was found to improve sand recovery, with the mass of material isolated in the < 0.8 mm fraction increasing by 19% (Table 33). This is a considerable increase in yield, especially when considering the ton scale that this is likely to occur on if used in industry.

Sieve Grading	Initial Mass Recovery %	Adjusted Mass Recovery %
> 4 mm	17%	12%
4 mm > x > 0.8 mm	21%	7%
< 0.8 mm	62%	81%

Table 33. *Percentage mass recovery for a 4.0 kg sample of **EOL4** surface, separated using trommel separation at 4 mm and then at 0.8 mm, and adjusted mass recovery percentages following re-processing of material through trommel.*

Moreover, the purity of the sand recovered did not appear to be affected by this, with the majority of microplastics remaining in the intermediate sized fraction. These results therefore reinforce re-processing of larger material as an appropriate method to further enhance sand recovery, providing a trivial and low-cost strategy which can be employed on large scale in industry.

4.2.4 Summary

The EOL state of the equestrian surfaces tested in this project varies between samples, with the different surfaces recording different remaining wax coverages. Trommel separation studies have revealed how the mass of sand recovered from surfaces decreases with increasing wax coverage because of the effect the coating has on the sand particulate size and cohesion, meaning surfaces with high remaining wax coverage give low sand recovery. This complicates the separation of used surfaces as, although sand can be isolated following trommel separation, the yield of sand recovered is reduced for surfaces with higher remaining wax coverage (**EOL4** and **EOL5**, Table 34), meaning alternative separation methods may be needed to optimise material recovery. In this instance, trommel modification strategies can be deployed to enhance separation, with re-addition of material to the trommel proving an effective method to enhance sand recovery.

The wide range of synthetic surfaces available in the market means the strategy adopted for developing an end-of-life surface recycling solution needs to be straightforward and flexible. Different EOL surfaces acquired by ES may contain different materials in different relative percentages; hence, separation techniques need to be easily adjustable to account for this. As a simple and modifiable separation tool, trommel separation has proved effective for the direct separation of a range of waxed EOL surfaces, with visually clean sand isolated from all surfaces. This therefore provides a sustainable and low-cost method which can be used in industry for the isolation of fibrous material and sand from used equestrian surfaces.

Surface Sample	Sand Recovery % by Mass
EOL1	93%
EOL4	70%
EOL5	68%
EOL6	81%

Table 34. *Sand recovery percentages (<0.8 mm) for 1 kg samples of EOL surface, processed in the trommel at 4 mm and then at 0.8 mm.*

Before trommel separation can be used in industry, the reusability of the materials isolated following trommel separation needs to be established. If the properties of the sand and fibre isolated following trommel separation differ considerably to the original materials, this may hinder their reusability; hence the final part of this thesis will examine the condition of both materials to determine their capacity for reuse.

4.3 Sand Analysis

For the sand to be re-incorporated into new surfaces following separation, the properties of the EOL sands need to be established and compared to the supplier sand. Any major changes to the grading or purity of the sand will impact the performance and safety of a surface, hence this needs to be established before reuse can be considered. If the sand displays substantial change in purity, it is unlikely to be suitable for reuse and alternative recycling pathways may need to be explored.

4.3.1 Sand Grading Tests

To investigate variation in grading following usage, samples of dewaxed EOL sands were passed through a range of test sieves of different gradings, with the mass retained in each sieve recorded. By comparing this to the supplier sand (MOIST60) any major changes in grading could be identified. It was necessary to test dewaxed sands since the presence of a wax coating on the material would affect the material separation. Samples of dewaxed sand were obtained following the chloroform solvent extraction of surfaces discussed in Section 3.3.1, since this appeared to effectively remove the wax coating from surfaces.

Prior to testing, fibrous material was removed from the dewaxed surface samples by passing them through a 1.5 mm sieve. The isolated sands were then dried in an oven at 160 °C to remove any excess solvent or moisture. Sand grading tests were then performed on small samples of dewaxed sands according to the procedure described in Section 2.3.2.1. The observed particle size distribution for each EOL surface, as well as the supplier sand, is shown in Table 35.

Particle Size Category	Sieve range (mm)	Supplier Sand (%)	EOL1 (%)	EOL4 (%)	EOL5 (%)	EOL6 (%)
Very coarse sand	> 1	0.2	0.03	0.05	0.18	0.46
Coarse sand	0.5 – 1	2.0	3.0	2.5	4.1	4.6
Medium sand	0.3 – 0.5	16	25	21	24	22
Fine sand	< 0.3	82	72	76	72	73

Table 35. *Particle size distribution (%) of each EOL surface calculated using a 50 g sample of dewaxed sand that had been separated from binding polymer and fibre.*

The results observed for the EOL sands are relatively similar, with the majority of sand isolated being below 0.5 mm in size. In all cases the amount of very coarse and coarse sand is minimal. This is largely consistent with the results observed for the supplier sand, indicating minimal change to the grading and size of the sand grains following surface usage.

4.3.2 SEM-EDX Analysis

In response to sand grading tests, the purity of the isolated sands was further established using SEM-EDX analysis. SEM combined with EDX enables the analysis of large numbers of individual particles in a fast, automated way, providing detailed information about their elemental composition, size distribution and surface morphology.[85]

Initial tests focussed on examining the morphology of the supplier and **BS** sands, since these show the two extremities of no wax coating (supplier sand), and full wax coating (**BS** sand). Samples were prepared according to the procedure described in Section 2.6.6.[87] SEM images of the supplier and **BS** sands taken at different magnifications and locations across the samples are shown in Figure 37 and 38, respectively.

Samples of EOL sand were isolated following trommel separation, with the sand being obtained from the < 0.8 mm fraction. The samples were then characterised by SEM-EDX analysis.

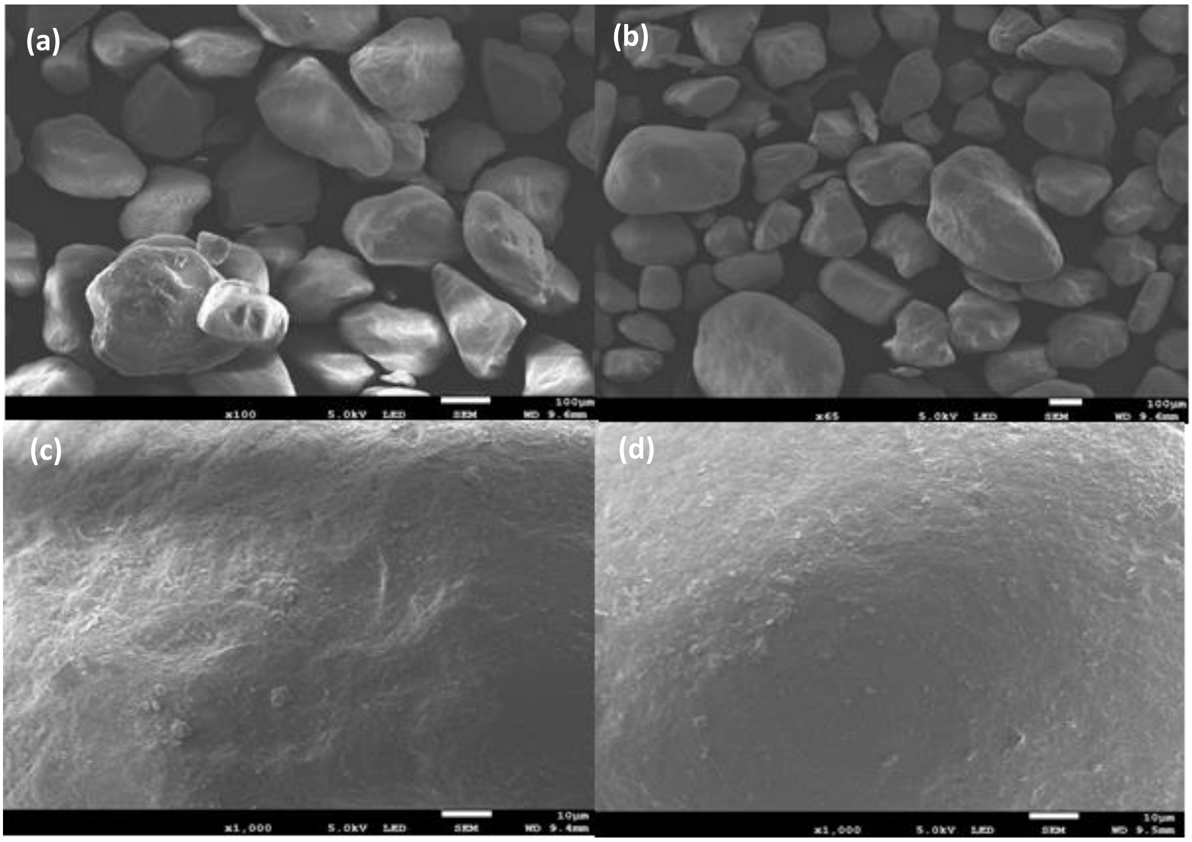


Figure 37. *SEM images of supplier sand taken at different magnifications: (a) X100, (b) X65, (c) X1000, (d) X1000.*

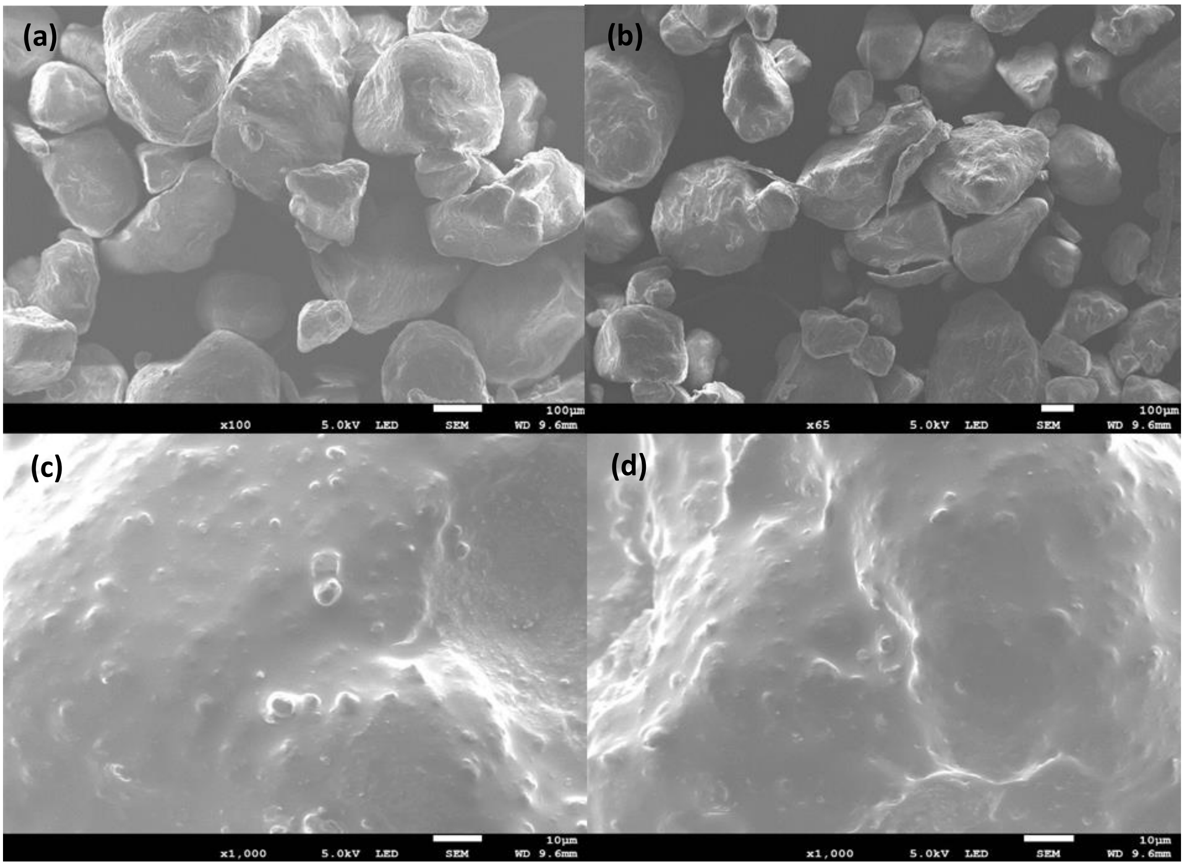


Figure 38. *SEM images of sand isolated from the* ***BS*** *taken at different magnifications: (a) X65, (b) X100, (c) X1000, (d) X1000.*

SEM images of the supplier sand highlight the smooth appearance of the grains, with the high magnification images revealing the grains to be dull in appearance (Figure 37). In contrast, the BS sand appears glossy, with the presence of the wax coating now evident on the surface of the grains (Figure 38). This demonstrates how the presence of wax coating on the surface of sand can be easily visualized using SEM, highlighting this as a useful tool for examining the extent of wax coverage on used surfaces.

SEM images of the waxed EOL sands show no major differences in terms of the sand grain size distribution and morphology (Figure 39). However, the images reveal contamination of the sands with microplastic fibres, with **EOL1** sand showing the most significant microplastic contamination. This indicates that the trommel-processed sand is not fully clean and that the 0.8 mm drum is not entirely effective for removing all microplastic fibres.

High magnification images also reveal differences in the morphology of the EOL sands, with the wax content appearing to vary between samples (Figure 40). The **EOL1** surface sand shows minimal wax content, with the surface appearing relatively smooth (Figure 40a). In contrast, **EOL4** sand shows a highly irregular surface morphology consistent with greater wax coverage (Figure 40b).

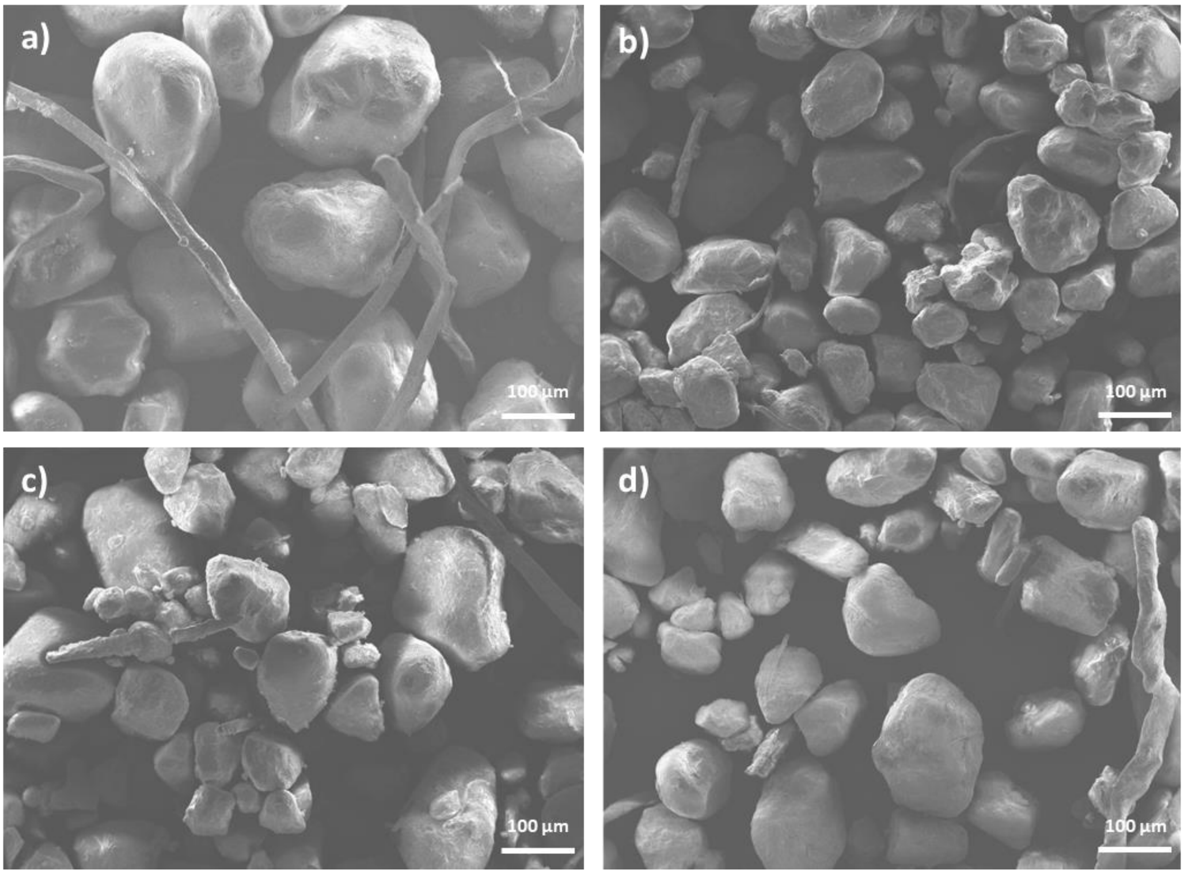


Figure 39. *SEM images of the waxed EOL sand samples isolated from the 0.8 mm trommel:* ***EOL1*** *(a),* ***EOL4*** *(b),* ***EOL5*** *(c), and* ***EOL6*** *(d). X60 magnification.*

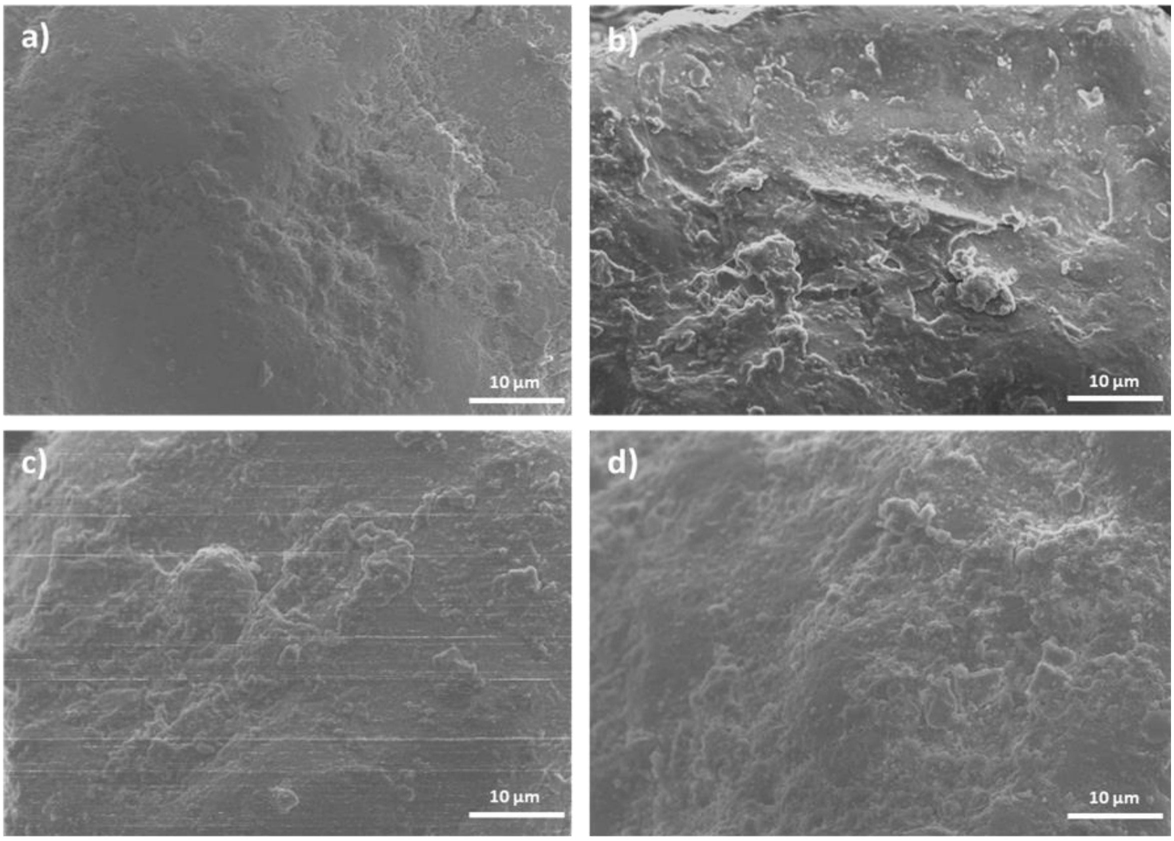
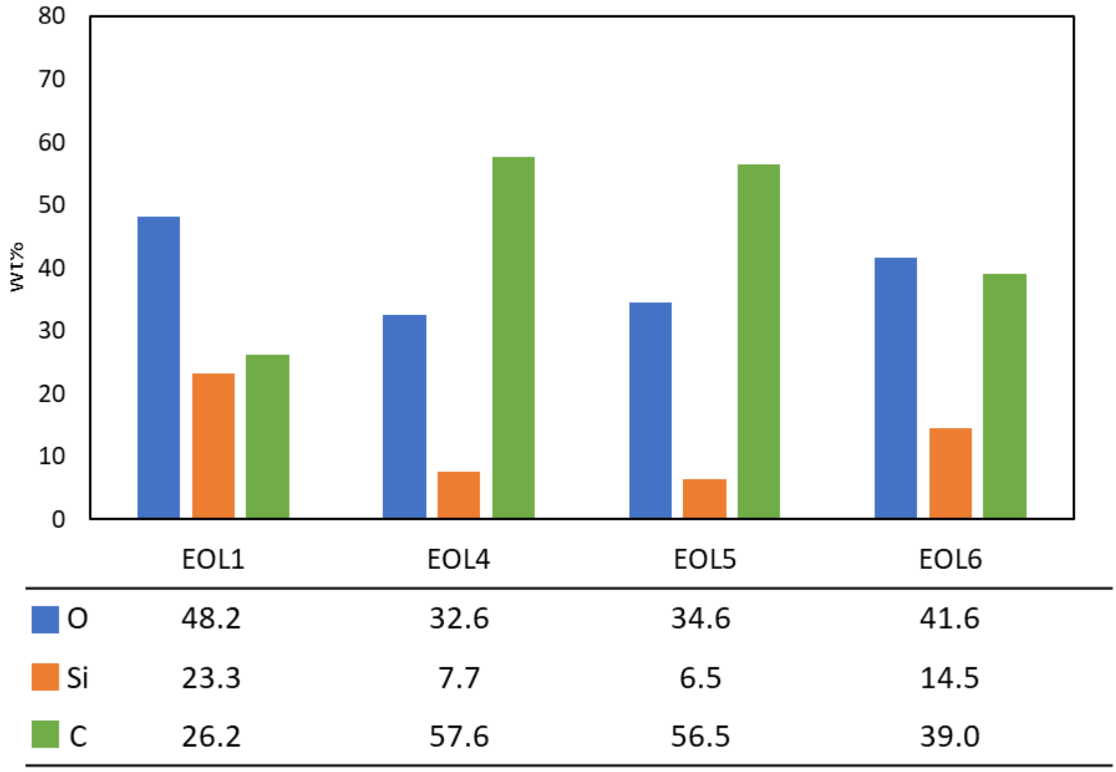


Figure 40. *SEM images of the waxed EOL sand samples isolated from the 0.8 mm trommel:* ***EOL1*** *(a),* ***EOL4*** *(b),* ***EOL5*** *(c), and* ***EOL6*** *(d). X600 magnification.*

The elemental structure of the EOL sand samples was then investigated via EDX analysis. Testing was performed according to the procedure described in section 2.6.7. This revealed the elemental composition of the high magnification images shown above in Figure 40. The weight percentage of the main elements were detected as shown in Figure 41.

Interestingly, **EOL1** sand shows a low carbon content. This is consistent with the extraction experiments described in Section 3.3.1, where this surface recorded a low yield of wax. This again indicates substantial removal of wax from this surface. In comparison, the carbon contents for the **EOL4** and **EOL5** sands are much higher, indicating higher remaining wax coverage. This is also consistent with the extraction and separation experiments where these surfaces showed poorer separation resulting from the greater remaining wax coverage.



	EOL1	EOL4	EOL5	EOL6
🟦 O	48.2	32.6	34.6	41.6
🟧 Si	23.3	7.7	6.5	14.5
🟩 C	26.2	57.6	56.5	39.0

Figure 41. *EDX analysis of the waxed EOL sand samples isolated from the 0.8 mm trommel:* ***EOL1*** *(a),* ***EOL4*** *(b),* ***EOL5*** *(c), and* ***EOL6*** *(d). X600 magnification.*

Additionally, EDX analysis data can also be used to confirm the presence of other elements within the sand samples. This can then be compared to the supplier sand to identify any major impurities. A comparison of the EDX results for the supplier sand, **BS** sand, and the EOL surface sands is shown in Table 36. For the EOL and baseline surfaces, sand was isolated following separation using the 0.8 mm trommel drum.

Sand Sample	O (Wt%)	Si (Wt%)	C (Wt%)	Al (Wt%)	Ca (Wt%)
Supplier	54.8	35	9.1	0.4	0.1
BS	22	8.2	70	0.2	0.4
EOL1	48.2	23.3	26.2	0.3	1.6
EOL4	32.6	7.7	57.6	0.3	1
EOL5	34.6	6.5	56.5	0.3	1.7
EOL6	41.6	14.5	39	1	2.4

Table 36. *EDX weight percentages for different prepared sand samples based on SEM images taken at X600 magnification.*

Sand isolated from the baseline surface shows a high carbon content. This reflects the hydrocarbon nature of the paraffin wax coating. It is the presence of this wax coating on the surface of the grains which reduces the silicon and oxygen weight percentages as they are blocked out by the wax coating.

In contrast, the supplier sand shows a very low carbon content, reflecting the fact that this material has not been coated in wax. Instead, this sand has a high oxygen and silicon content due to the chemical composition of sand (silicon dioxide). It is expected that the carbon wt% for the supplier sand should be negligible as it principally contains SiO_2, hence it is likely that the 9.1 wt% carbon recorded here arises due to the double-sided black carbon tape used to prepare the SEM/EDX samples.

For the EOL sands, the carbon content is highly variable, again highlighting the irregularity between surface samples. In all cases, the calcium content increases for the EOL sands. This arises due to the presence of calcium carbonate within the samples which likely comes from the backing of the shredded carpet fibres used in surfaces.

The extent of wax coverage can be further visualised via EDX elemental mapping. This method visualizes the distribution of elements in the sample by two-dimensionally displaying the characteristic X-ray intensities of the elements in colour coded images.[113] The intensity maps produced qualitatively show where the elements are most abundant. In relation to the EOL sands, this helps visualize the extent of wax coverage, with the carbon, silicon and oxygen signals appearing in different areas. EDX elemental maps, along with the original SEM image, for a sample of waxed **EOL1** sand are shown in Figure 42.

The SEM image shows a pale substance on the surface of the **EOL1** sand. EDX mapping confirmed this as wax, with this area giving a strong carbon signal (red) which blocks out the silicon (purple) and oxygen (green) signals. Comparatively, the wax-free surface of the sand registers minimal carbon signal, with high intensity signals for silicon and oxygen, indicating complete removal of the wax binder from this part of the surface. This is therefore further evidence of wax removal during surface usage.

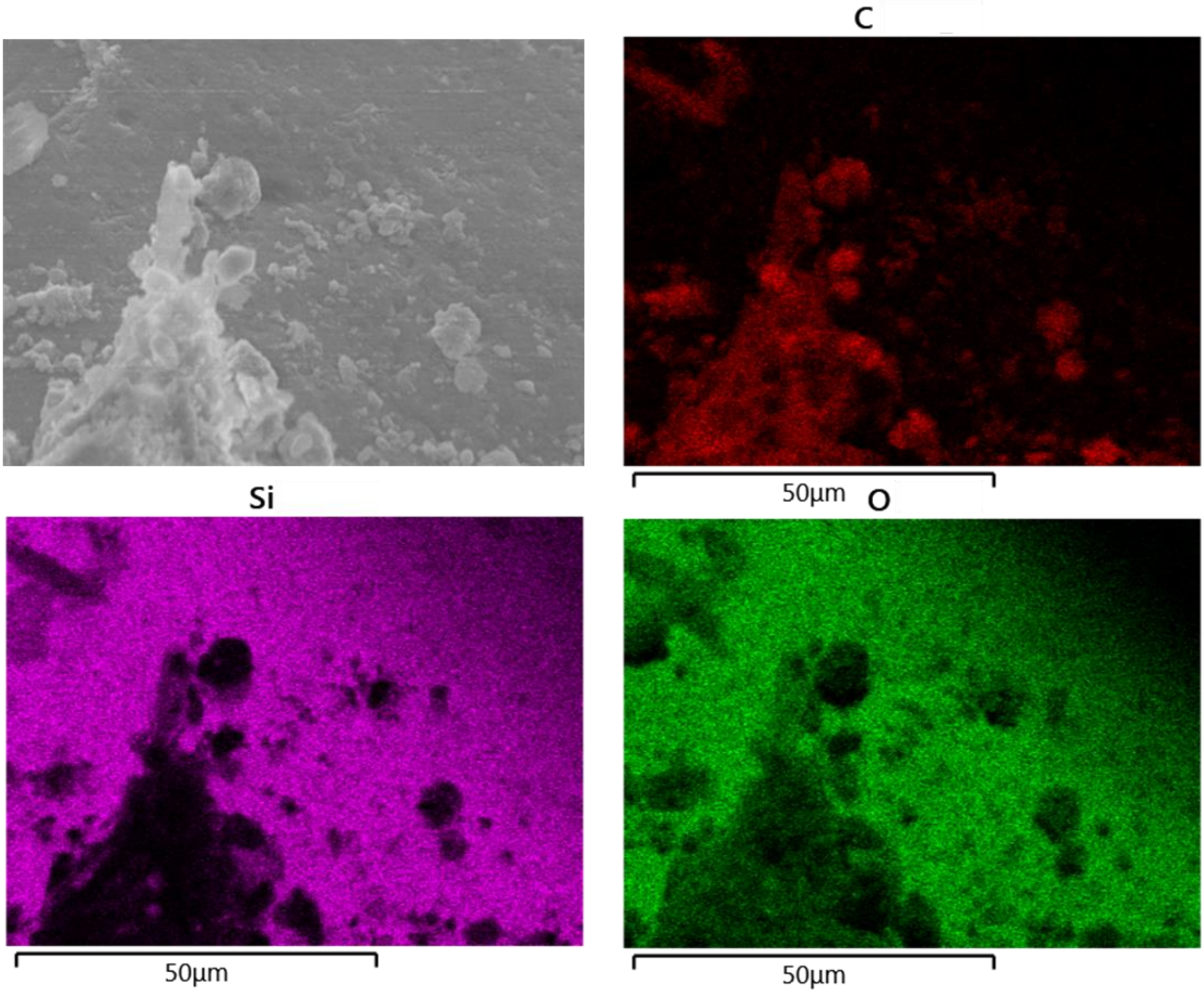


Figure 42. *SEM image and EDX elemental maps (C, Si, and O) recorded for a sample of **EOL1** waxed sand. X600 magnification.*

Additionally, the elemental mapping for a sample of **EOL4** sand confirms the greater remaining wax content of this surface, with strong carbon signals recorded across the sample (Figure 43). The high intensity carbon signal results in low intensity oxygen and silicon signals, with these mainly occurring in areas where the wax binder appears to be removed. This is consistent with the high wax extraction yields recorded for this surface.

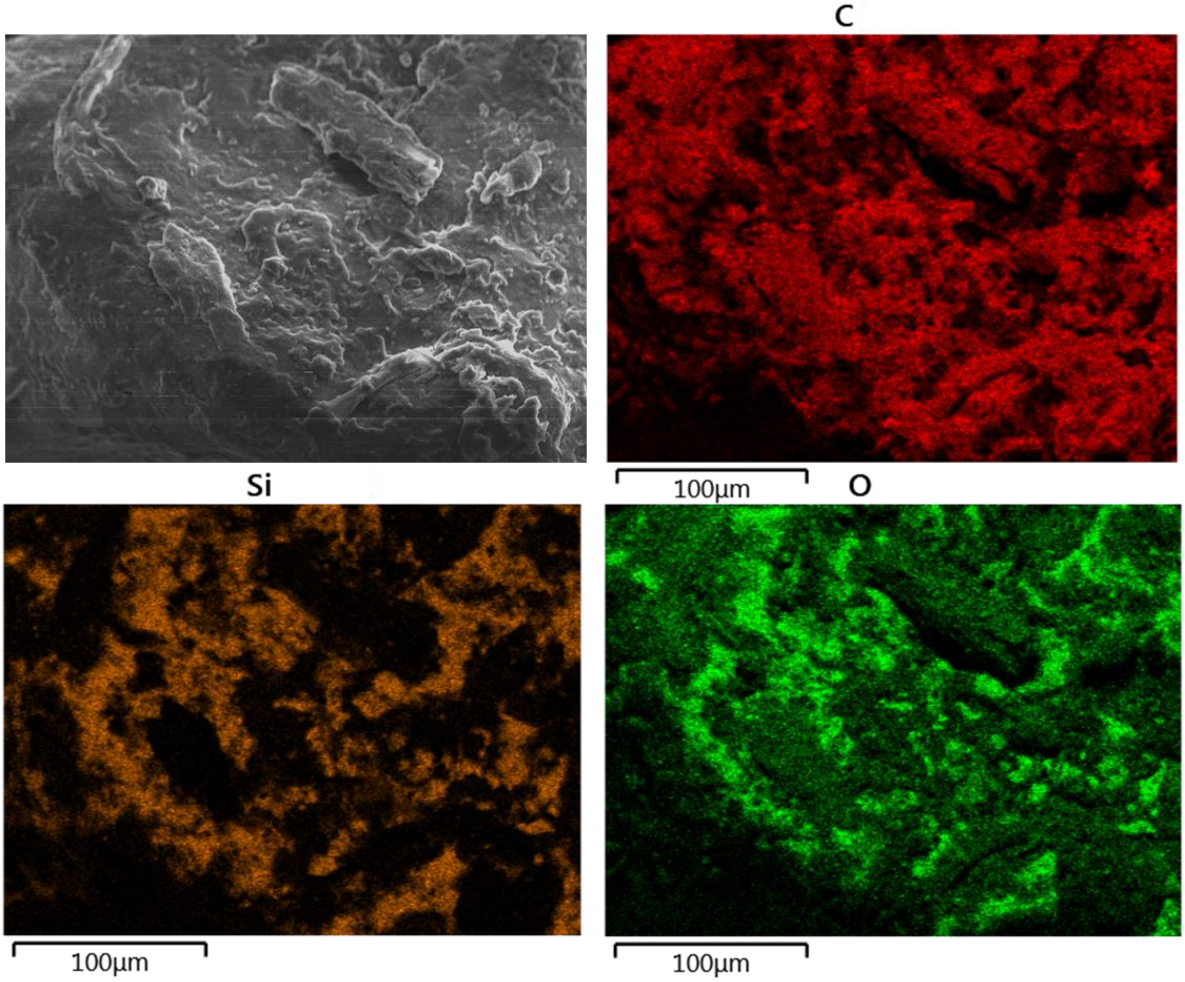


Figure 43. *SEM image and EDX elemental maps (C, Si, and O) recorded for a sample of **EOL4** waxed sand. X600 magnification.*

EDX mapping graphs for **EOL5** and **EOL6** surface sands are shown in Figures 44 and 45, respectively. These again highlight the extent of wax coverage remaining, with the **EOL5** sand showing a higher intensity carbon signal than **EOL6**. This aligns with the extraction data discussed in Section 3.3.1, where the **EOL5** surface recorded the second highest extraction yield, behind **EOL4**.

As well as revealing the extent of wax coverage, EDX mapping also reveals the abundance of other elements in the samples. This can be used to assess the purity of the sand samples. This revealed some minor impurities within the samples, with elements including sodium, potassium, and magnesium identified in all samples (See Section 6.3.1).

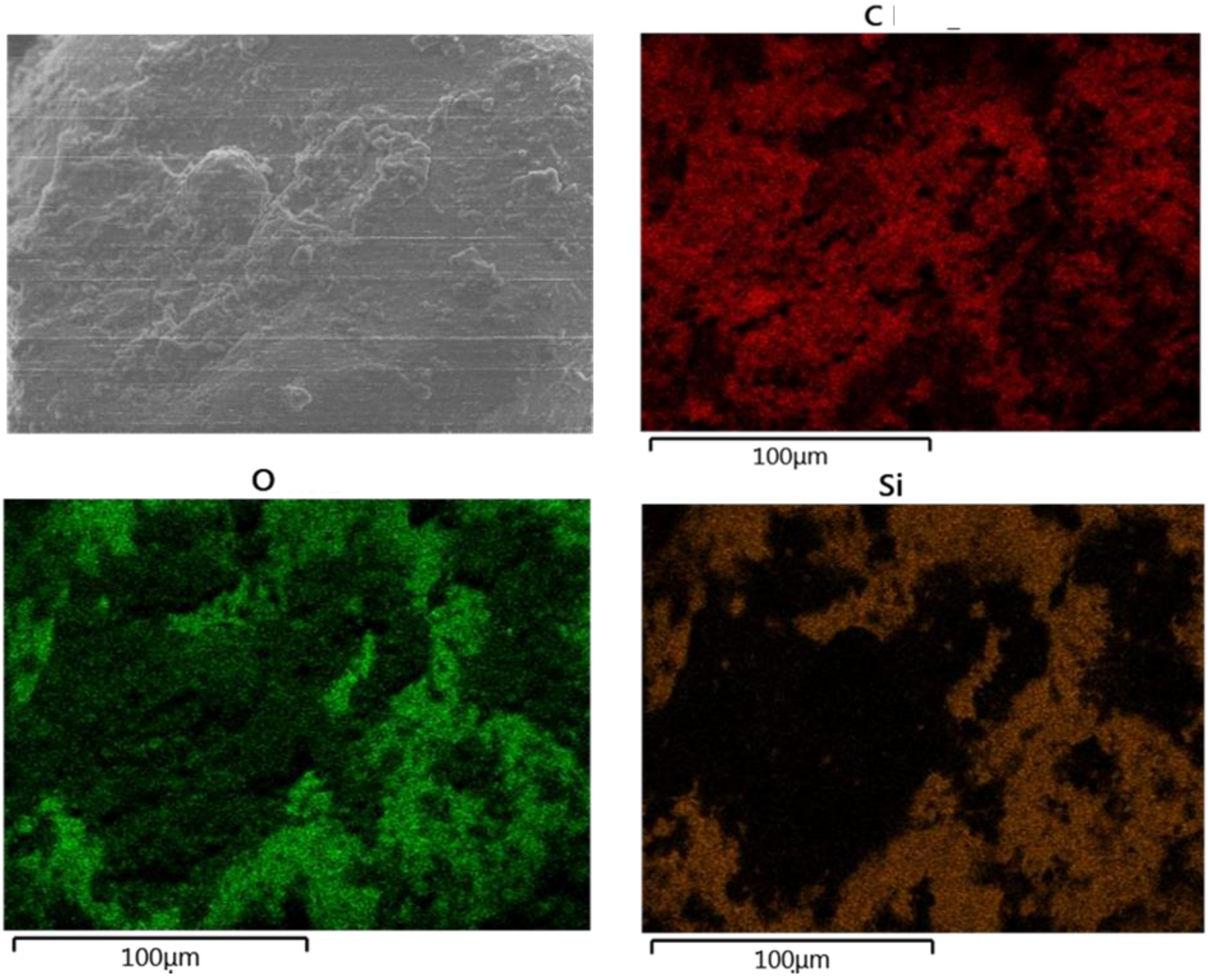


Figure 44. *SEM image and EDX elemental maps (C, Si, and O) recorded for a sample of* ***EOL5*** *waxed sand. X600 magnification.*

In summary, SEM/EDX analysis has been shown to provide useful data on the waxed state of different EOL sands. In particular, SEM/EDX can be used to assess the wax coverage of different sands, with elemental mapping proving a useful tool to easily highlight wax coverage. Moreover, EDX analysis has proved invaluable for assessing the purity of EOL sands, with only minor calcium carbonate contamination detected for all EOL samples.

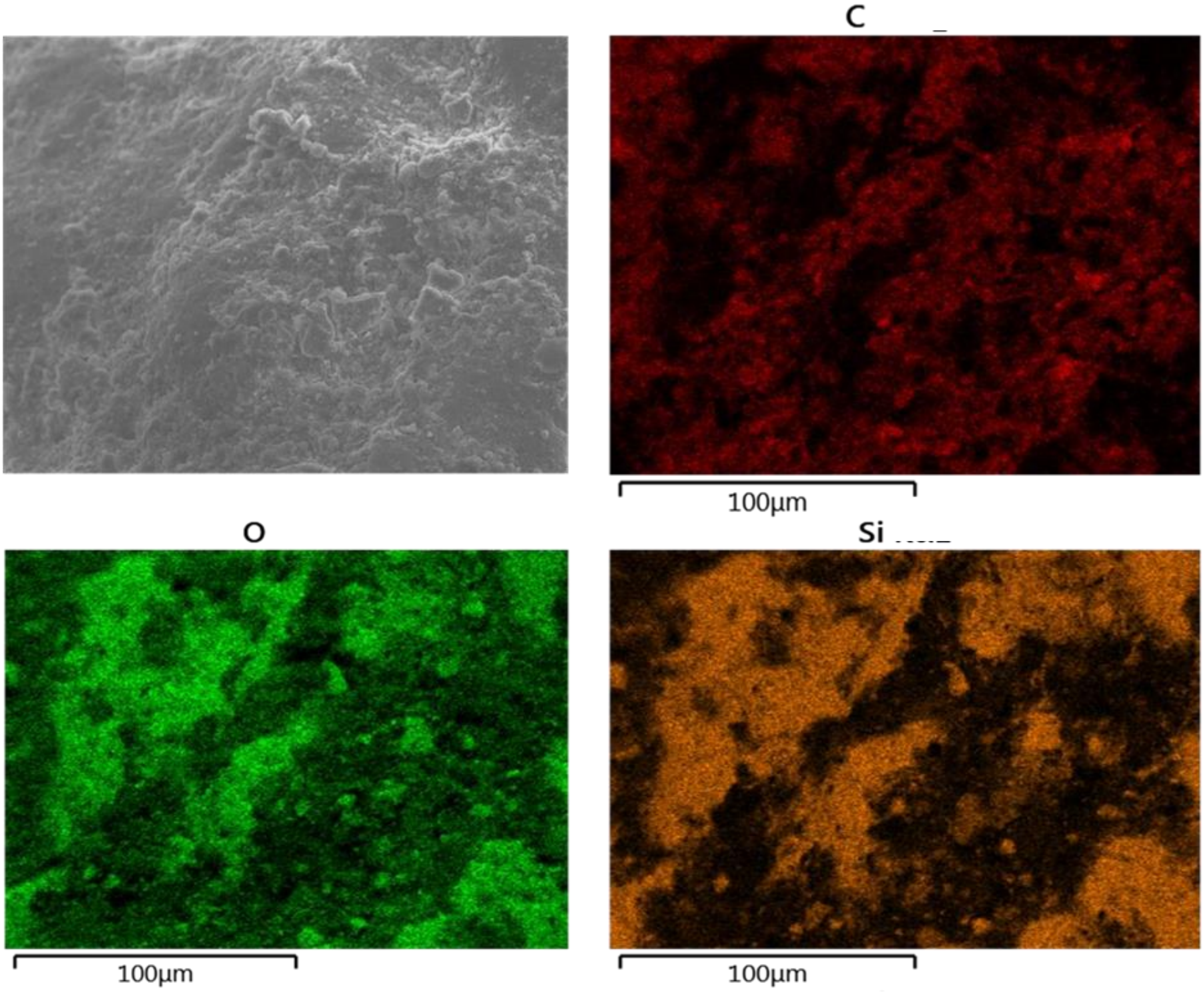


Figure 45. *SEM image and EDX elemental maps (C, Si, and O) recorded for a sample of* ***EOL6*** *waxed sand. X600 magnification.*

4.3.3 Elemental Analysis

CHNS elemental analysis can also be used to examine the elemental composition of the EOL sands, with the capacity to examine the whole sample as opposed to just the surface.[102] Samples of EOL and **BS** sand were again isolated following 0.8 mm trommel separation, with elemental analysis performed according to the procedure described in Section 2.6.5. The carbon, hydrogen, nitrogen, and sulphur contents for the four EOL sands, as well as the corresponding values for the supplier and baseline surface sands, are shown below in Table 37.

While the elemental composition is low in all cases, there remains variability in carbon content across the samples. The carbon content for the supplier sand is minimal, this is consistent with what is expected since this sand has no wax coating. In contrast, the **BS** sand records a higher carbon content, due to the presence of a full wax coating. The EOL sands are varied, with **EOL1** and **EOL6** showing lower carbon contents, and **EOL4** and **EOL5** showing higher values.

Sand Sample	C (Wt %)	H (Wt %)	N (Wt %)	S (Wt %)	C:H
Supplier	0.30	0.49	0.72	0	0.61
BS	2.97	0.55	0.54	0	5.40
EOL1	1.18	0.27	0.25	0	4.37
EOL4	2.28	0.51	0.41	0	4.47
EOL5	3.08	0.52	0.36	0	5.92
EOL6	1.78	0.56	0.56	0.01	3.18

Table 37. *CHNS weight percentages for different prepared sand samples.*

The carbon content recorded for **EOL5** is higher than that of the **BS** sand. This appears to suggest contamination of the sand with other carbon-containing compounds. This may arise due to the presence of calcium carbonate in the sample or could be due to the presence of other carbon-containing organic or inorganic impurities. Nevertheless, the high carbon content recorded for the **EOL4** and **EOL5** sands is additional indication of high remaining wax coverage.

This can be further visualised by plotting the carbon content (as determined by CHNS analysis) against the filtered extraction yields for each EOL surface (Figure 46). The high R^2 value observed indicates a positive correlation between the extraction yield and carbon content. This therefore provides a useful tool which could be used in industry to estimate the end-of-life state of different surfaces.

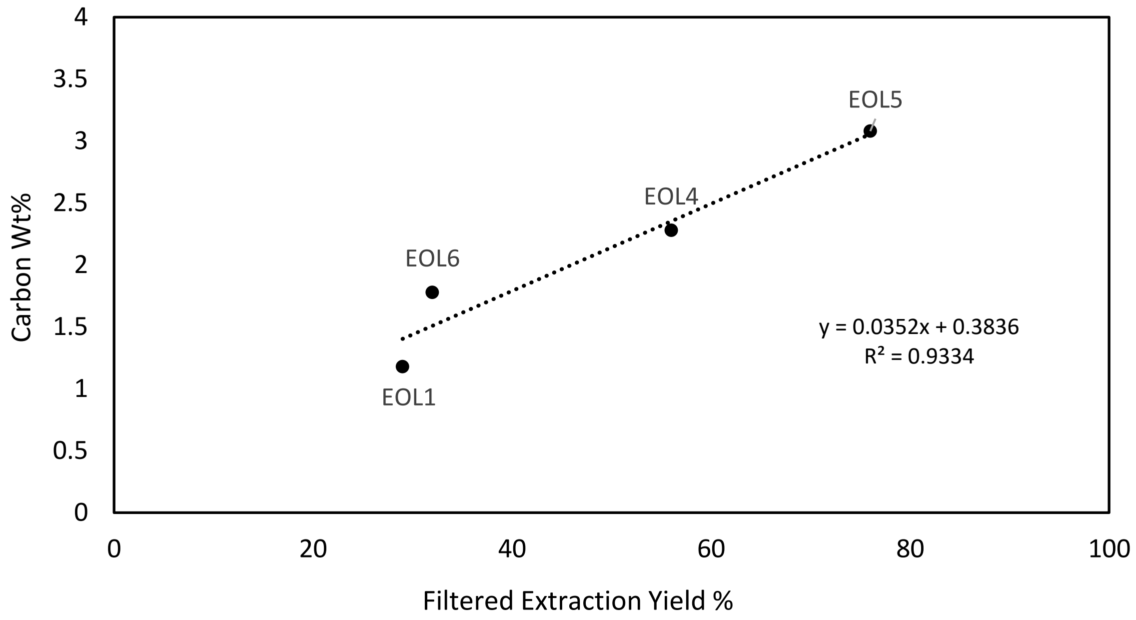


Figure 46. *Plot showing the filtered $CHCl_3$ extraction yields for EOL surfaces vs the carbon content recorded for waxed samples determined by CHNS analysis.*

Aside from the variation in carbon content, the values of nitrogen and sulphur are consistently low, with only minor differences between samples. Since there is no major increase in the presence of these elements for the EOL sands, it can be concluded that the sands are not contaminated with materials containing these elements. This is further indication that the waxed sands are likely suitable for reuse.

Elemental analysis can also be used to establish the extent of wax coating on sand samples by monitoring the change in carbon content. By analysing both waxed and dewaxed samples of sand, the difference in carbon content can be established. Dewaxed samples of sand were isolated following solvent extraction of surfaces with chloroform (Section 3.3.1). The results recorded for the waxed and dewaxed samples of EOL sands are shown in Figure 47.

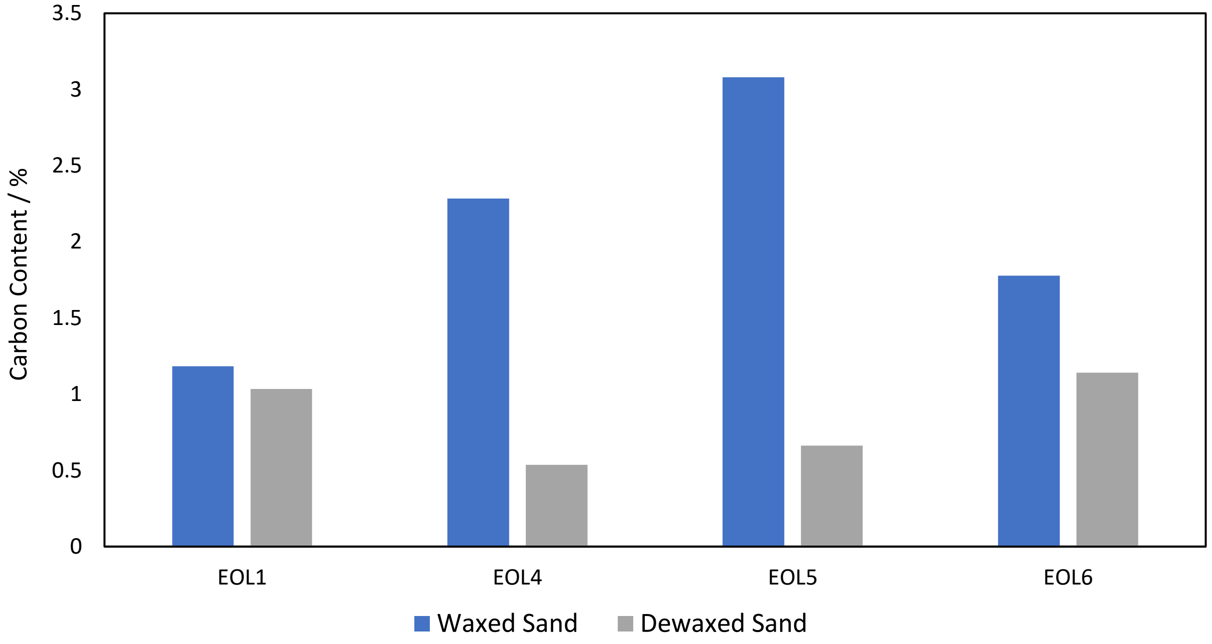


Figure 47. *Graph showing the difference in carbon content recorded for the waxed and dewaxed forms of EOL surfaces.*

As expected, the carbon content for the waxed sands is higher than the dewaxed form for all surfaces; however, the variation between waxed and dewaxed is different for different surfaces. **EOL4** and **EOL5** sands show a significant difference in carbon content between the waxed and dewaxed forms. This further indicates that these surfaces have a higher remaining wax coverage relative to **EOL1** and **EOL6**. This is an important factor to consider for industry since the wax coverage affects the separation efficiency of a surface, with low wax coverage leading to high sand recovery. Furthermore, since these surfaces are at different stages of their life, elemental analysis can in theory be used to inform customers about the EOL-state of their surface. This would enable ES to determine which surfaces can be classified as fully EOL and are therefore suitable for direct large-scale separation using trommel methods.

However, before this is suitable for use, further investigation and method optimisation is required to avoid false conclusions from being made. For example, the carbon contents of **EOL1** and **EOL6** remain high even for the dewaxed sands. This suggests that, either wax removal has not been fully successful, or that the sands contain significant mass of carbon-containing impurities such as microplastic fibres or $CaCO_3$. Methods to distinguish between the different carbon-sources are therefore required before this tool can be used in industry.

4.3.4 Summary

In summary, the purity of the waxed sands isolated from used surfaces following trommel separation appears to vary depending on the surface itself, with SEM-EDX and CHNS elemental analysis proving to be useful tools for assessing the extent of wax coverage remaining. The results presented above are further indication that the **EOL4** and **EOL5** surfaces examined in this project are not fully EOL and have a significant portion of the wax binder remaining. This is consistent with the trommel separation results discussed in Section 4.2.2 and the wax extraction results reported in Section 3.3.1.

Furthermore, SEM images have highlighted issues with the separation process itself, with the used sands appearing contaminated with microplastic fibres. The presence of these fibres does not currently prohibit the reuse of the EOL sands; however, it may alter the appearance of any recycled surfaces and so this should be considered when applying this to industry. Nevertheless, microplastic contamination appears to be the only major factor affecting the reusability of the used sands, with the purity and grading of the materials appearing to be similar to that of the supplier sand. This is strong indication that the sand is suitable for reuse without the need for wax removal, providing the surface itself is in a sufficiently EOL state. This aligns with the aims of this project since the sand makes up the bulk of synthetic surfaces and the capacity to reuse this without needing to remove the wax or treat the surface in any way offers a green solution in line with the circular economy principles of the project.

4.4 Fibre Testing

Much like with sand, for the fibres to be reused in surfaces, the properties of the isolated material need to be tested and compared to pre-surface fibres to establish any major changes. If the properties of the fibres undergo drastic changes, then it is unlikely they can be reused since the strength and cushioning provided by these fibres to the surface would not be the same. Interestingly, the fibres incorporated into equestrian surfaces are currently acquired from both post-industrial and post-consumer carpet waste, meaning a substantial portion of fibres have already been exposed to prolonged usage.

Visual inspection of fibres isolated following solvent extraction revealed stark differences between EOL and **BS** fibres, with the EOL fibres generally appearing duller and darker in colour (Figure 48). Furthermore, the EOL fibres contained other materials, with stones and horse hairs isolated alongside fibre. Generally, the size of the EOL fibres is reduced, with fibrous material appearing thinner, a result of fibre breakdown during surface usage. Further tests on dewaxed EOL samples allowed larger samples of EOL fibres to be isolated, which further highlighted the duller and distressed appearance of these fibres (Figure 49).

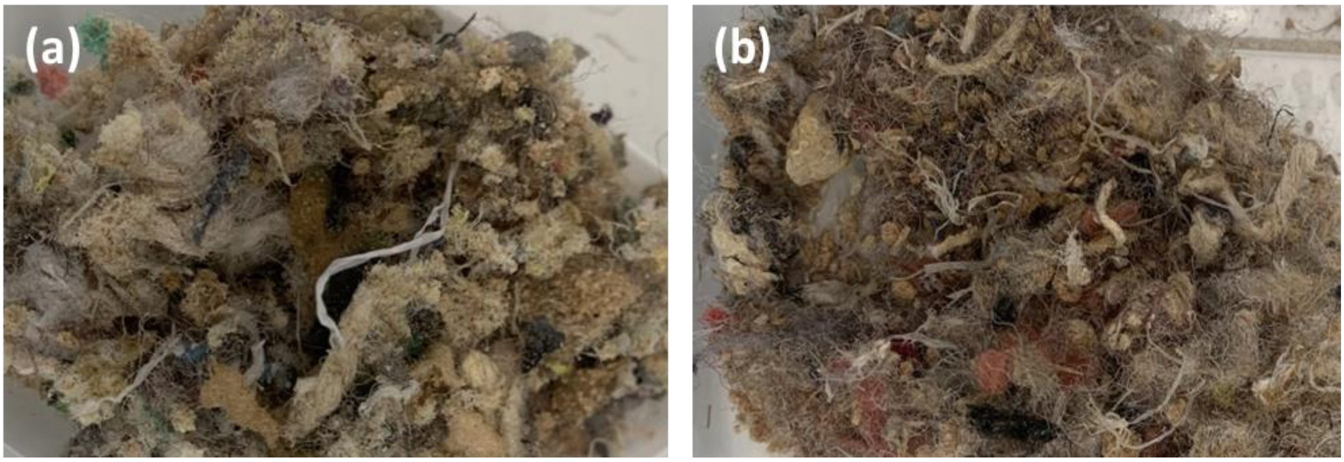


Figure 48. *Appearance of fibres isolated from dewaxed baseline (a) and **EOL1** (b) surfaces following sieving at 4 mm.*

The change to appearance, unity, and composition of the fibres suggests that they may not be suitable for reuse in this form as they are unlikely to provide the required level of cushioning to surfaces. To further confirm this, individual fibres were taken from the **EOL1** surface and subject to tensile strength tests.

Figure 49. *Fibres isolated from **EOL4** surface following trommel separation at 4 mm.*

4.4.1 Tensile Strength Tests

Fibres are added to surfaces to aid comfort and improve the load bearing capacity and durability of a surface. The fibres generally act as tensile reinforcing units that transfer shear stresses that develop in the surface into tensile resistance in the fibre via fibre/sand interactions; hence the tensile strength of the fibres is an important property which effects surface performance and safety.[114]

The tensile strength of a material is the maximum force that can be applied before it breaks or fails.[88] During any tensile test there are parameters which can be measured including tensile strain and elongation. To investigate the impact of surface usage on the tensile strength of carpet fibres, tensile strength tests were performed on samples of pre-surface fibres and fibres isolated from the **EOL1** surface. Samples were prepared and tested according to the procedure described in Section 2.6.8 .[88] Tests were carried out using an Instron 3345 test machine with a test speed of 10 mm/min until the fracture was recorded. Four samples of fibre were isolated from each surface, with the average fracture point shown in Table 38 below.

Fibre Type	Average Fracture Point / N
Pre-surface	48.5
EOL1 Surface	11.9

Table 38 . *Average fracture points recorded for a series of different synthetic fibres.*

The results show a general decrease to the tensile strength of the fibres following prolonged usage. This suggests that during surface usage, fibres are exposed to conditions which alter their properties and decrease their tensile strength. This questions the reusability of EOL-surfaces fibres as the decreased tensile strength of these fibres may impact the performance and safety of any recycled surfaces made.

It is important to note that these results are only preliminary, with the results likely to be heavily influenced by issues with sampling and sample preparation. There are a variety of synthetic fibres used in equestrian surfaces, with polymer types including polypropylene, nylon, and PET. Each different polymer has different intrinsic properties which will influence the fracture point observed. The polymer structure was not taken into account during these tests meaning this is likely to have influenced the results recorded. In addition, the small size of the fibres caused issues with the machine gripping the samples, hence it was necessary to glue the fibres onto cardboard frames before testing. This likely also affects the results recorded, reducing confidence in the trend observed. With this in mind, further testing is necessary before tensile strength data can be used to determine the reusability of fibres.

4.4.2 SEM Tests

As well as mechanical properties, the surface properties of fibres can be investigated to identify any post-usage modifications. SEM tests were run on three samples of pre-surface shredded carpet fibres provided by ES. Samples were prepared according to the procedure described in Section 2.6.6.

Microscopic evaluation revealed the surface morphology of the fibres, with the surface of the fibres appearing clean (Figure 50). High magnification images of the fibres revealed minor contamination of fibres, with small particles detected on the surface (Figure 47c). These small particles likely arise due to the presence of dust within the fibres or because of calcium carbonate from the carpet backing material.

SEM analysis of fibres isolated from the **EOL1** surface was then conducted. Fibres were isolated following the small-scale sieve separation of dewaxed **EOL1** surface described in Section 4.1. Again, three fibres were isolated and prepared as above.

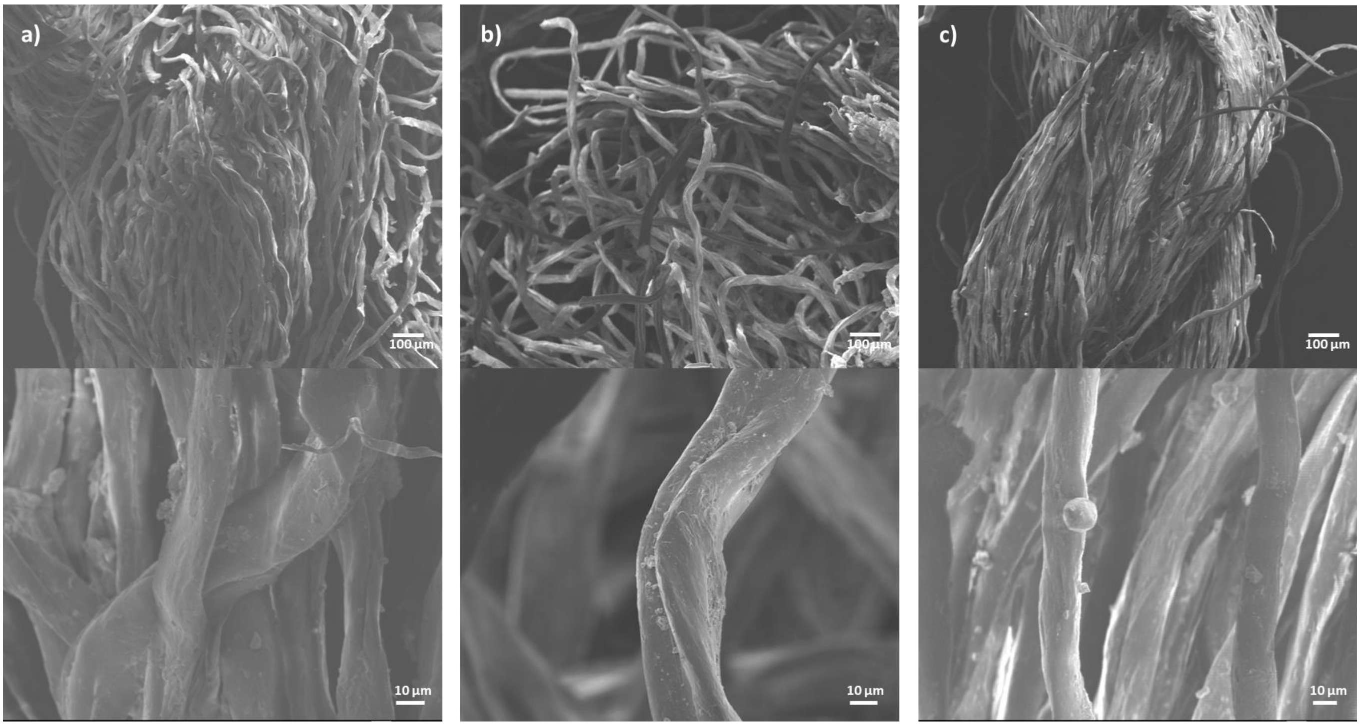


Figure 50. *SEM images of shredded pre-surface carpet fibres acquired by ES. Three fibres were tested (a), (b), and (c) (Appendix, Section 6.4.2). Images recorded at X50 and X500 magnification.*

SEM analysis revealed a significant change in surface morphology compared to the pre-surface fibres, with the EOL fibres appearing highly contaminated (Figure 51). High magnification images revealed the presence of large clumps within the fibres which appear to contain both wax and sand from the surface. This affects the reusability of the fibres since these impurities will contribute towards the total mass of fibres added to the surface, which in turn disturbs the ratios of material incorporated into the surface.

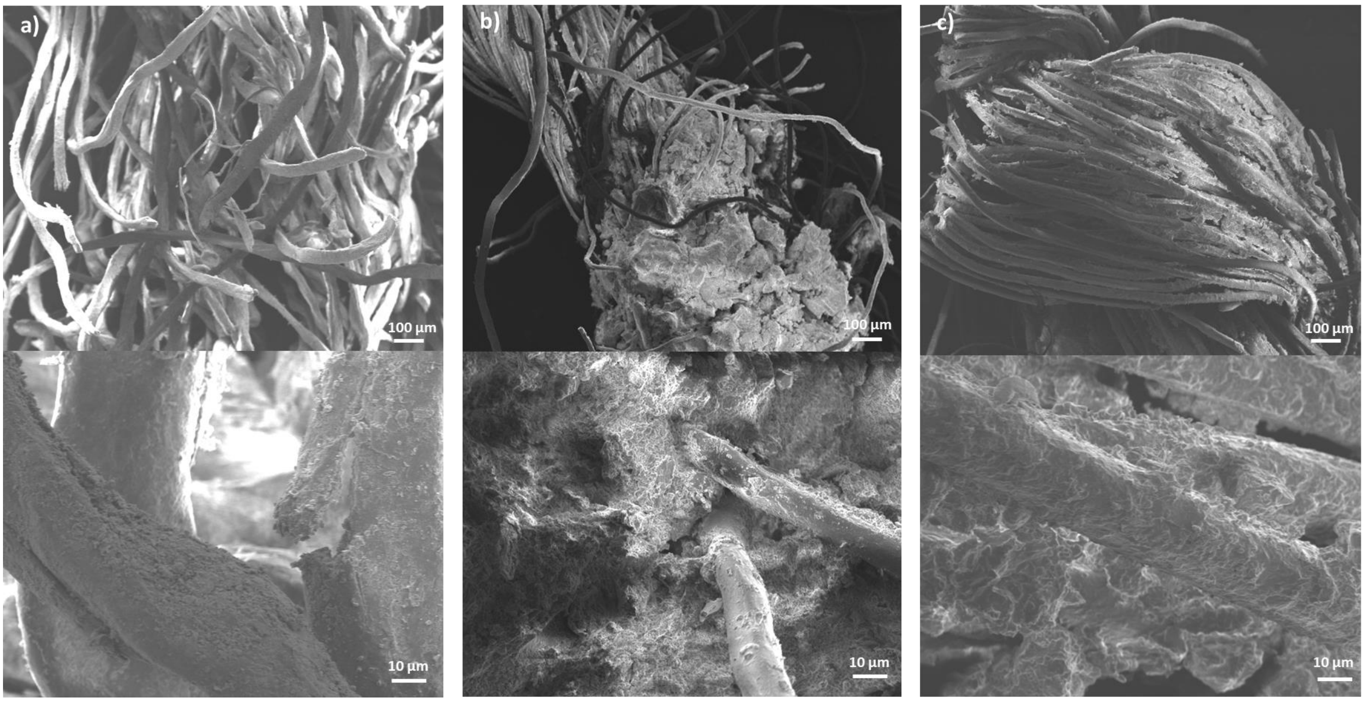


Figure 51. *SEM images of carpet fibres isolated from dewaxed **EOL1** surface. Three fibres were tested (a), (b), and (c) (Appendix, Section 6.4.2). Images recorded at X50 and X500 magnification.*

Furthermore, since these fibres were tested in the dewaxed form it was expected that the sand contamination would be minimal as the binder holding these two materials together should have theoretically been removed following extraction. This does not appear to be the case; with the sands retaining significant mass of sand. For the waxed surface fibres this is only likely to be aggravated by the presence of the wax coating, further reducing the reusability of these materials.

4.4.3 Summary

Carpet tests have highlighted issues with fibre reuse, with preliminary tensile strength tests revealing a reduction in the tensile strength of fibres with increasing surface age. Additionally, SEM analysis has confirmed the contaminated nature of used surface fibres, with the materials retaining substantial mass of sand even after wax extraction. The equestrian industry currently acts as a major recycling route for used carpet waste, meaning there is an abundance of material available to be used in new surfaces. This questions the need to reincorporate potentially impure and poor-quality material into new surfaces.

The agglomerated nature of the EOL-surface isolated fibres hinders their suitability for reuse. Instead, alternative reuse streams may need to be explored. This is complicated for fibres isolated from EOL surfaces in the waxed form since these materials contain significant amounts of wax and sand as well as other impurities. The presence of such materials makes it difficult to repurpose these fibres directly. Instead, it is likely that they will need to be disposed of via landfill or incineration. Although both of these disposal routes are not sustainable, the mass of fibre isolated from EOL surfaces is low and significantly reduced compared to the volumes of surface currently disposed of in landfill.

Although the results discussed here suggest the used surface fibres are not suitable for reuse, the data is intrinsically hindered by the small sample sizes and sampling methods used. Further testing into the tensile and cushioning properties of the used fibres is needed before an accurate conclusion on the reusability of the fibres can be made.

4.5 Microplastics

Data presented in Section 4.2.2 revealed how trommel separation of EOL surfaces leads to isolation of microplastics. These secondary microplastics are produced following the breakdown of the large carpet fibres incorporated into surfaces. Owing to their low density, MPs created in surfaces can be transported into other environments by wind. Other MPs remain trapped in the surface and hence contaminate the fractions isolated following mechanical seperation.[115] Currently, there are few regulations regarding the production and disposal of microplastics, however, with growing health and environmental concerns around their production and persistence, it is important that introduction of MPs into the environment be kept to a minimum.[30]

It has been found that the majority of MPs present in surfaces can be isolated using the two-step separation method detailed in Section 4.1, with the MP material isolated in the intermediate sized fraction. Despite this, a small portion of MPs permeate the sieve and contaminate the sands isolated (Figure 52). The impact of these on the properties and the reusability of the isolated sands is hard to determine, however, it is critical that MP contamination is considered at all stages of separation and minimised where possible.

A range of methods are available to aid microplastic removal from environmental media, with major examples including density separation and chemical digestion. However, these have yet to be applied to removal of MPs from contaminated sands, meaning further testing is necessary before an appropriate cost-effective and sustainable microplastic separation technique can be implemented.[116]

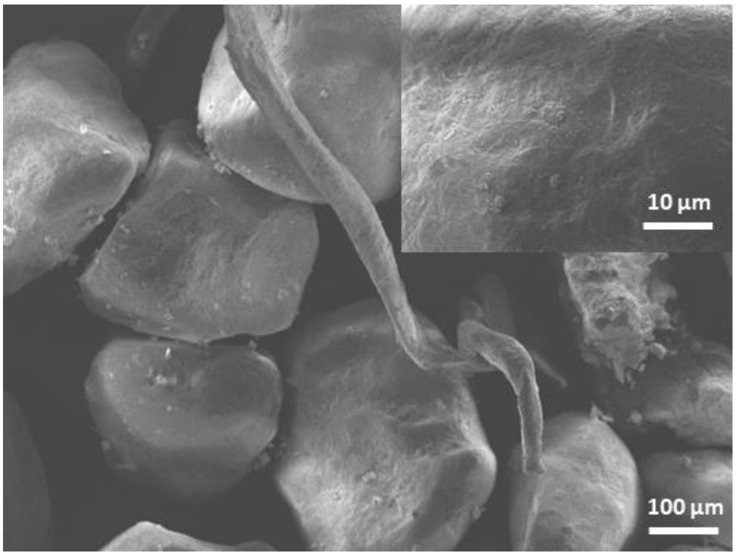


Figure 52. *SEM Image of dewaxed sand isolated from* ***EOL1*** *surface, showing microplastic contamination of the sand following trommel separation.*

Currently, there are limited solutions available for MP disposal, with incineration being the main strategy used in industry. A key example of this includes energy from waste disposal. In this, the contaminated, mixed, or degraded MP residues can be used as feedstocks for waste-to-energy strategies such as pyrolysis and incineration.[31] This process has high emissions and energy costs associated with it, hence it is not a sustainable disposal route.

Research into alternative, more sustainable MP disposal routes has gained traction in recent years, with a major example including the work of Anand and co-workers who explored the application of microbes for the biodegradation of microplastics.[31] Although suitable microbes were identified, these tests are only in initial stages and have so far only been validated under laboratory conditions with reports on their efficiency in field largely lacking. Further research is therefore required before large-scale MP biodegradation can be applied to industry.

4.6 Summary and Conclusions

The research discussed in this chapter has focussed on the ability to separate surfaces using mechanical separation without the need for wax removal. By doing this, it eliminates the high equipment and solvent costs associated with this process, enabling surfaces to be separated in a trivial and sustainable manner.

Trommel separation studies revealed how the mass of sand recovered from surfaces decreases with increasing wax coverage because of the effect the coating has on the sand particulate size and cohesion, meaning surfaces with high remaining wax coverage give low sand recovery (Table 37). This complicates the separation of used surfaces as, although sand can be isolated following trommel separation, the yield of material recovered is reduced for surfaces with higher remaining wax coverage (**EOL4** and **EOL5**, Table 37), meaning alternative separation methods may be needed to optimise the recovery of material. In this instance, trommel modification strategies can be deployed to enhance separation, with re-addition of material to the trommel proving an effective method to boost sand recovery.

Surface Sample	Waxed Sand Recovery % by Mass	Dewaxed Sand Recovery % by Mass
EOL1	93	95
EOL4	70	91
EOL5	68	85
EOL6	81	90

Table 37. *Sand recovery percentages (<0.8 mm) for 1 kg samples of waxed EOL surface, processed in the trommel at 4 mm and then at 0.8 mm, and recovery percentages (<0.5 mm) for small samples of dewaxed EOL surface separated via sieve separation techniques.*

A range of analytical tools have been employed to examine the condition of the sand recovered from the trommel, with SEM-EDX analysis proving useful for establishing the purity and remaining wax coverage of the different samples. Generally, the sand isolated following trommel separation appears pure, with grading tests indicating that the sand is not subject to significant degradation during usage. Furthermore, elemental analysis and EDX data revealed the sand samples to be moderately pure, with any elemental impurities present in insignificant amounts. In light of this, it is concluded that the used sand is suitable for reuse, with the only issue being the minor contamination of the material with microplastic fibres. The presence of such fibres is unlikely to impact the surface manufacturing process especially since, during manufacturing, carpet fibres are shredded in a process which is also likely to generate microplastics. Nevertheless, it is something that needs to be considered when increasing the scale of separation since the effect of this is currently unknown. With this in mind, further research could be carried out to assess how the microplastic content of normal surfaces and surfaces made using recycled sand varies. In summary, the ability to reuse sand isolated from EOL surfaces is a significant step towards developing a circular economy since this material makes up the bulk of all synthetic surfaces and by reusing this it diverts a considerable mass of material from landfill.

As well as sand, trommel separation also leads to the isolation of large fibrous material. SEM tests on samples of fibre isolated from used surfaces revealed the fibres to be highly contaminated with sand and other materials. In addition, preliminary tensile strength tests have suggested a reduction in the tensile strength of these fibres relative to the pre-surface equivalents. With this in mind, it is concluded that the fibres are not suitable for re-incorporation into new surfaces. Instead, alternative routes for reuse need to be considered. This is complicated for fibres isolated from EOL surfaces since these materials also contain significant amounts of wax and sand as well as other impurities. The presence of such materials makes it difficult to repurpose these fibres directly into other streams of use. Instead, it is likely that they will need to be disposed of via landfill or incineration. Although both disposal routes are not sustainable, the mass of fibre isolated from EOL surfaces is low and significantly reduced compared to the volumes of surface currently disposed of in this way.

Similarly, trommel separation of EOL surfaces also leads to isolation of microplastics. Such materials are of concern due to issues surrounding their accumulation and persistence within the environment. Currently, there are limited solutions available for MP disposal, with incineration being the only viable option. Research into alternative, more sustainable MP disposal routes has been highlighted in this thesis, with this likely to continue to increase in the future as concerns around MP waste continue to grow.

The wide range of synthetic surfaces available in the market means the strategy adopted for developing an end-of-life surface solution needs to be broad and flexible. Different EOL surfaces acquired by ES may contain different materials in different relative percentages; hence, separation techniques need to be easily adjustable to account for this. As a simple and modifiable separation tool, trommel separation has repeatedly proved effective for the direct separation of a range of waxed EOL surfaces, with high-purity sand isolated from all surfaces. This therefore provides a sustainable and low-cost method which can be used in industry for the isolation of fibrous material and sand from used equestrian surfaces. The reusability of the material isolated from the trommel is likely to vary between samples, meaning ES will need to develop suitable testing procedures to establish benchmarks against which materials can be compared before reuse can be deemed appropriate.

Chapter 5 – Conclusions and Action Plan

The research presented in this thesis has highlighted various issues with extracting and reusing wax from used equestrian surfaces. The waxes extracted from EOL surfaces using solvent extraction methods appeared as dark brown waxy solids, with the presence of organic and inorganic impurities contributing towards the drastic change in appearance. Analysis of both used and unused surfaces confirmed degradation of the wax over time, with the yield of wax recovered from used surfaces being reduced in all cases. Moreover, analysis of the wax samples revealed changes to the composition of the wax, with IR, GC-MS, and elemental analyses confirming the presence of impurities within all EOL extracts. Because of this, it was concluded that wax purification was necessary for the wax to be suitable for reuse. Although flash column chromatographic purification methods were able to improve the purity of the waxes, the low recovery of material, along with the additional material costs associated with this method mean that this is not a suitable solution for use in industry. This allowed me to conclude that the extraction and removal of wax from surfaces is unlikely to align with the circular economy principals of this research, meaning alternative, greener separation strategies are necessary.

Although large scale extraction of wax is not recommended based on the results of this study, there are potential solutions which could be further explored in the future. Microemulsion extraction proved effective for the removal of wax from surfaces, providing a green extraction technique for industry. The main issue with this surrounds the recovery of wax from the aqueous extraction solution, something that needs to be further investigated for this to be employed in industry. In addition, wax recovery could also be achieved on large scale using fixed bed adsorption techniques. This is typically used in industry as a finishing process to remove colour-inducing contaminants using fixed beds of alumina, silica, or bauxite to adsorb the coloured impurities.[117] Such processes are desirable for commercially scalable processes owing to their simplicity in design and continuous operation. Furthermore, fixed bed packing materials are usually cheap, commercially available and can easily be regenerated by washing with solvents.[117] This is therefore something that ES could explore in the future for recovery of wax from surfaces.

A promising alternative to wax extraction included the separation of surface materials in the waxed form using mechanical separation techniques. Although this method does not involve removal of wax from surfaces, it was found that true EOL surfaces had such low remaining wax contents that the presence of wax does not impact the ability to isolate the remaining surface materials. Trommel separation repeatedly proved effective for isolating sand from EOL surfaces, with a two-step separation process required to isolate clean, fibre-free material.

The presence of wax on the recovered sand complicates sand recycling since each EOL surface acquired by ES will have a different extent of wax coating remaining. Although this does not largely impact the appearance and properties of the sand, the variation in wax content complicates sand reuse as it means the mass of new wax required during surface synthesis is likely to vary for each batch. The relative percentage of each component within a surface has a significant impact on the properties and performance of a surface, meaning this needs to be carefully considered by ES when reincorporating used sand into new surfaces.

For this reason, it may be beneficial for ES to synthesise small samples of surface using recycled sand, new wax, and new fibres in the desired percentages, and then adjust these as required following analysis and inspection of the small sample. The presence of wax on the used sand may enable ES to reduce the relative percentage of new wax added during surface manufacturing. This will reduce help reduce the volume of wax used by ES and hence reduce the costs and emissions associated with wax sourcing and usage.

ES already have a trommel on site, meaning there is no investment costs associated with implementing this separation technique. This project has underlined 4 mm and 0.8 mm sized drums as necessary for efficient surface separation, hence trommel drums of these sizes need to be acquired by ES.

The trommel separation process is not without complications, with some large-scale EOL surface separations requiring repeat cycles due to higher remaining wax contents. This can likely be avoided by utilising trommel modification strategies, with spiral drums and exterior brushes being two major examples. These modifications enhance separation of material and hence should be considered by ES before surface recycling is initiated.

Although trommel separation has proved effective for EOL surface separation, the percentage recovery of sand varies for each EOL surface. Surfaces with low wax coverage give high sand recovery, while surfaces with higher wax coatings give lower yields of sand. This relationship can be exploited, allowing ES to develop a method by which they can classify surfaces as EOL. This can be employed in industry using a combined lab- and field-testing procedure.

In the field-testing procedure, a known mass of surface is passed through the model trommel, with the masses isolated from each separation cycle recorded and used to calculate the mass recovery of each material: fibre (> 4 mm), microplastics (4 mm > x > 0.8 mm), and sand (< 0.8 mm). If the mass recovery of sand is > 90% then this surface can be deemed EOL, and direct addition of material to the trommel is likely to give high yields of reusable sand.

In the lab-testing method, small samples of surface are acquired from customers and extracted with ethyl acetate according to the method described in Section 2.5.2. Ethyl acetate has been selected as the solvent for extraction due to its greener properties compared to the higher-yielding, but more problematic alternatives ($CHCl_3$/toluene).[118] The mass of organic material isolated from the surface is then determined and compared to the theoretical mass of wax expected based on the initial surface make-up. If the yield of organic material is < 50% then this surface can be deemed EOL and direct trommel separation is applicable. If the yield is > 50% then the surface is not fully EOL. In this case, ES may advise the customer that the surface is suitable for further usage. However, if the customer is still wanting to replace the surface, direct addition of the surface to the trommel can be used to isolate reusable sand, however repeat separation cycles may be necessary to maximise the recovery of reusable material.

A summary of the considerations and results used to determine the end-of-life state of a surface is presented as a flow chart in Figure 53. The field and lab testing methods can be used separately to assess the EOL state of surfaces. But, for a more accurate assessment of surfaces, it is advised that the methods are used concurrently.

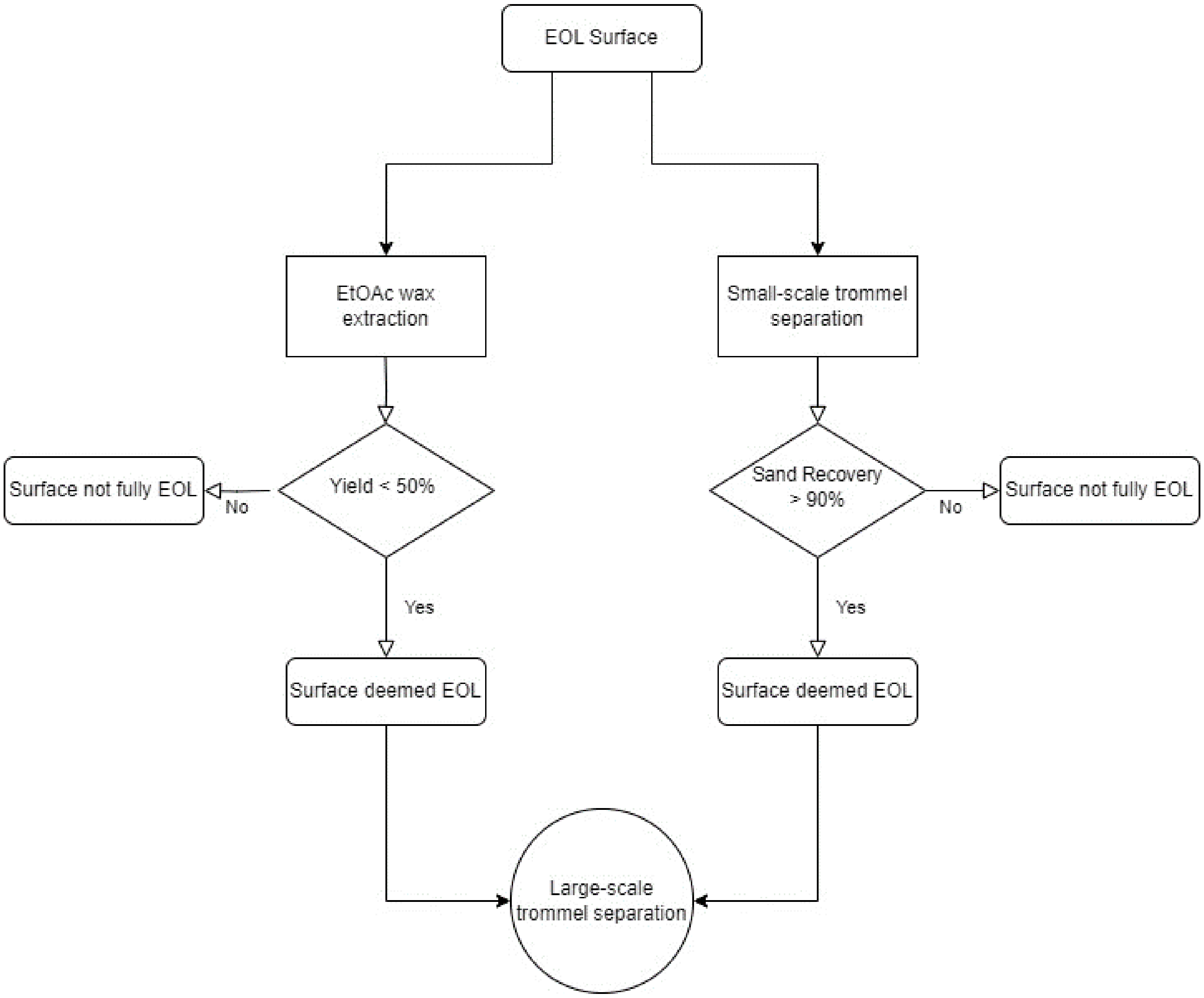


Figure 53. *Flow chart for the classification of surfaces as EOL.*

In summary, this research has explored the reusability of the individual components used within equestrian surfaces, confirming sand as the only current re-usable surface material. SEM-EDX and elemental analysis tests carried out in this project have indicated minimal change to the morphology and purity of sand samples isolated from EOL surfaces; while sieve tests revealed no major changes to the grading of the sand following usage, further validating this material as suitable for reuse.

In contrast, preliminary mechanical strength tests indicated a reduction in the tensile strength of EOL surface fibres relative to pre-surface fibres. This, combined with SEM images of EOL fibres which revealed the samples to be heavily contaminated with sand and other impurities, allowed me to conclude that these fibres are not suitable for reuse. Instead, ES should continue to use the shredded post-industrial and post-consumer waste carpets in their surfaces. Although this does not fully align with the circular economy aims of the project, sand is the principal component of most surfaces, typically making up more than 85% of the surface mass, hence the ability to reuse this material significantly reduces the mass of surface ending up in landfill.

This research has also highlighted the creation and accumulation of microplastics as an area of concern during equine surface usage and disposal. Prolonged surface usage initiates breakdown of fibrous material with the larger fibres breaking down and forming microplastics. With no backing to anchor them after shredding, the microplastic fibres are kicked up during riding – to be breathed in by the horse and rider. As well as being breathed in, the MPs enter waterways through drainage systems, where they can be consumed by aquatic life and later humans. Scientists are still unsure whether consumed microplastics are harmful to human or animal health—and if so, what specific dangers they may pose. Nevertheless, the generation and release of MPs following equestrian surface usage is something that needs to be considered and mitigated as appropriate. This research has shown that microplastics can be isolated from surfaces by utilising two-step size separation techniques, hence this method can be used in industry to monitor the microplastic content of surfaces. ES can employ simple sieve separation techniques to identify the microplastic content of surface samples and use this to infer information about the MP content of surfaces at different stages of life.

Since only the sand recovered from EOL surfaces has been deemed suitable for reuse, alternative disposal routes for the fibres and microplastics isolated following trommel separation also need to be considered. Currently, the equestrian industry contributes to carpet recycling by reusing waste fibres in surfaces, however, these fibres only remain within surfaces for a given period of time, before eventually ending up in landfill when the surface is disposed of. This means the fibres are not properly recycled, and that the equine industry only prolongs their usage lifetime. Other, more-permanent routes for carpet recycling are therefore necessary, with research by CRUK highlighting energy from waste as the most appropriate recycling route for contaminated carpet fibres. As carpet waste has a high calorific value, this unrecyclable waste can be used to produce energy from waste, with the major example being as a fuel replacement for cement kilns.[22] The contaminated nature of the fibres isolated from EOL surfaces means that this is currently the only suitable alternative disposal route available, and hence ES should look to this as a disposal route for EOL surface fibres.

One factor which should be considered when evaluating the results presented in this thesis is sampling. Both the initial surface sampling, and the sampling during testing/extraction are important factors which considerably influence the results recorded. Although repeat tests were carried out for all EOL surfaces, the results discussed in this report are only representative of each individual surface since the condition of the materials in a surface is heavily influenced by external factors including climate and the extent of usage. It is therefore not appropriate to apply these results directly to all used surfaces. Instead, the methods developed in this research to quantify the EOL state of a surface be applied to used surfaces and therefore the conclusions formed relating wax content to sand recovery are likely to be true for all wax-coated surfaces produced by ES.

In conclusion, extensive research has been undertaken to assess the circularity of equine surfaces, with a strong emphasis placed on utilising green techniques to achieve surface separation. It has been found that trommel separation of EOL surfaces is the simplest and most appropriate method for large scale separation of surfaces, enabling the isolation of fibres, microplastics and sand from samples. Of these materials, only the sand has been deemed suitable for reuse, hence the findings of the project do not align fully with the principals of a circular economy. Nevertheless, the research presented in this thesis provides a comprehensive analysis of surface components both in the unused and EOL forms, with a range of analytical techniques employed to quantify the purity and reusability of the different surface components.

Future research should focus on implementing the two-step trommel method in industry and assessing the properties of surfaces made using recycled materials to ensure the surfaces meet company standards. Moreover, waste disposal strategies for the non-recyclable materials need to be explored, with research focussing on green and sustainable disposal routes as alternatives to landfill.

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Chapter 6 - Appendix

6.1 Wax Experimental Data

6.1.1 Supplier Wax

^{1}H NMR (CDCl$_3$, 400 MHz): δ_H 1.28 (-CH$_2$-), 0.92-0.86 (terminal CH$_3$ groups).

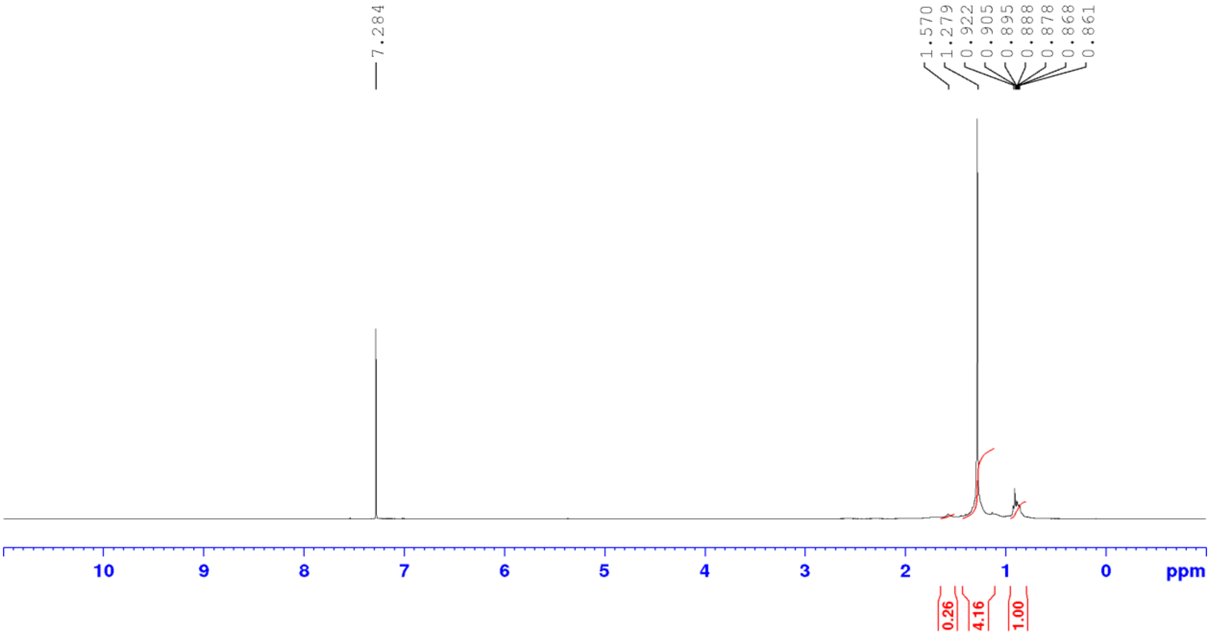


Figure S1. *^{1}H NMR spectrum of GT70 wax.*

^{13}C NMR (CDCl$_3$, 100 MHz): δ_C 31.9 (CH$_3$-CH$_2$-**C**H$_2$-), 29.7 (-(CH$_2$)$_n$-), 22.7 (CH$_3$-**C**H$_2$-), 14.1 (-CH$_3$)

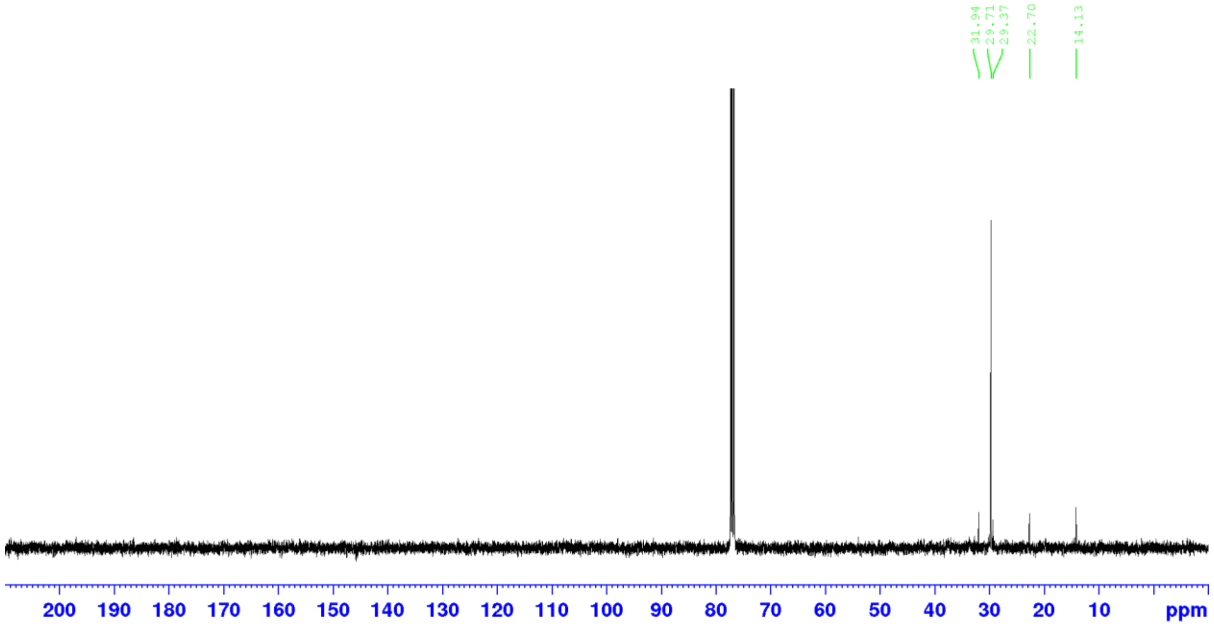


Figure S2. *^{13}C NMR spectrum of GT70 wax.*

IR ν_{max} (neat, cm^{-1}): 2917 (C-H), 2850 (C-H), 1463 (C-H), 1377 (C-H), 719 (C-H).

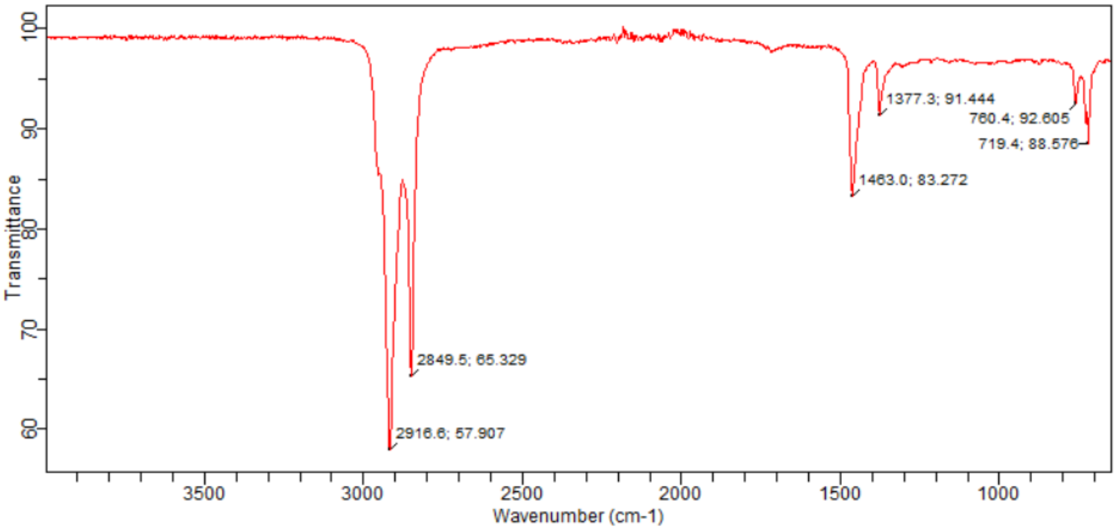


Figure S3. *FTIR spectrum of GT70 wax.*

GC ($CHCl_3$, PTFE filtered)

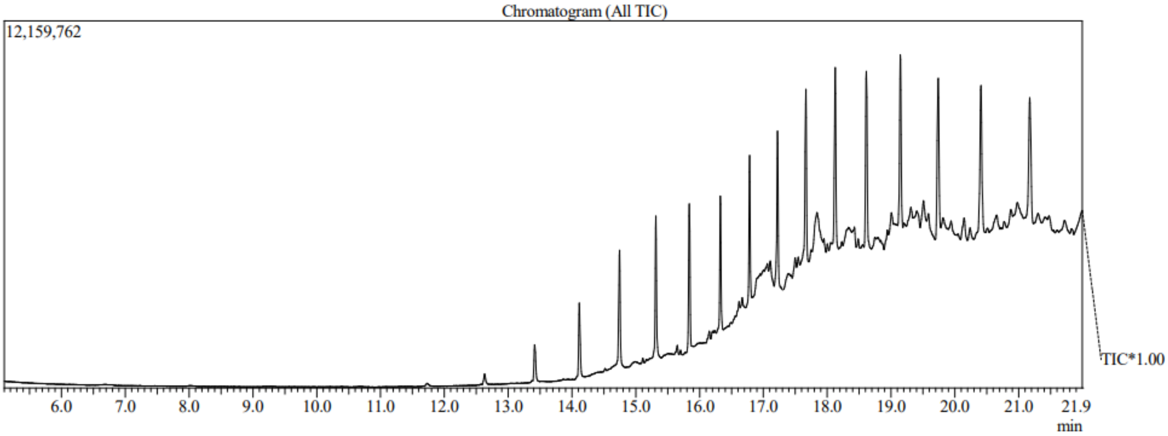


Figure S4. *GC-MS chromatogram of GT70 wax.*

6.1.2 Baseline Surface Wax

^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 1.28 ($-CH_2-$), 0.92-0.86 (terminal CH_3 groups).

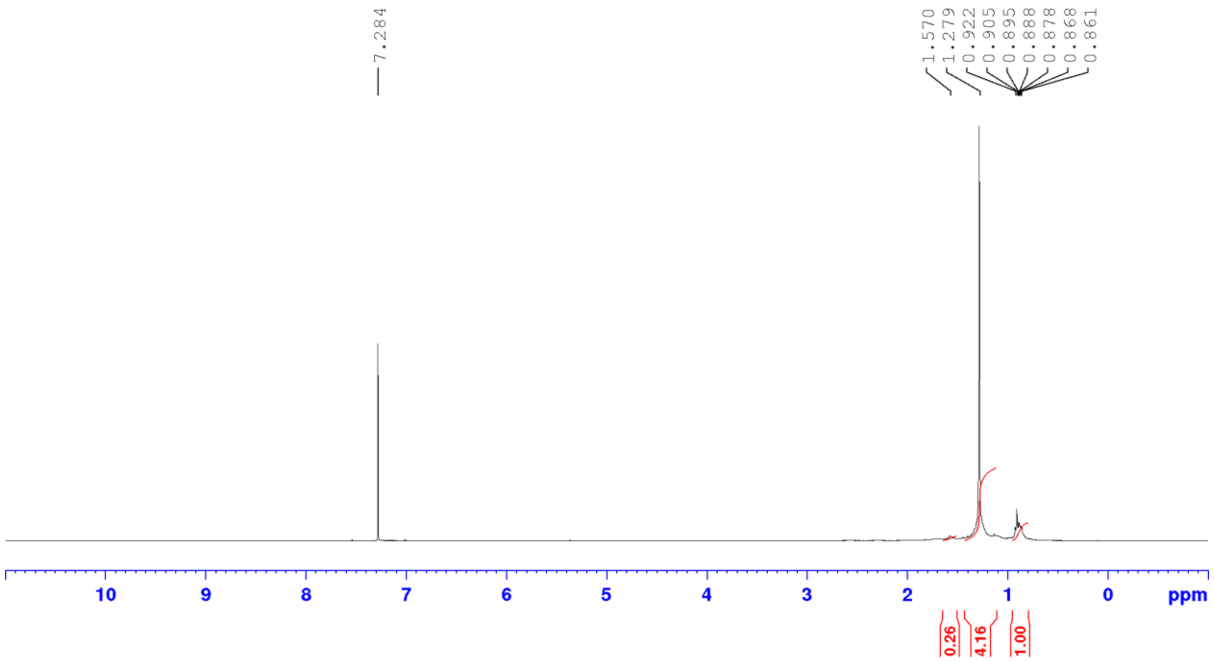


Figure S5. *^{1}H NMR spectrum of wax extracted from the baseline surface.*

^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 31.9 ($CH_3-CH_2-\mathbf{C}H_2-$), 29.7 ($-(CH_2)_n-$), 22.7 ($CH_3-\mathbf{C}H_2-$), 14.1 ($-CH_3$)

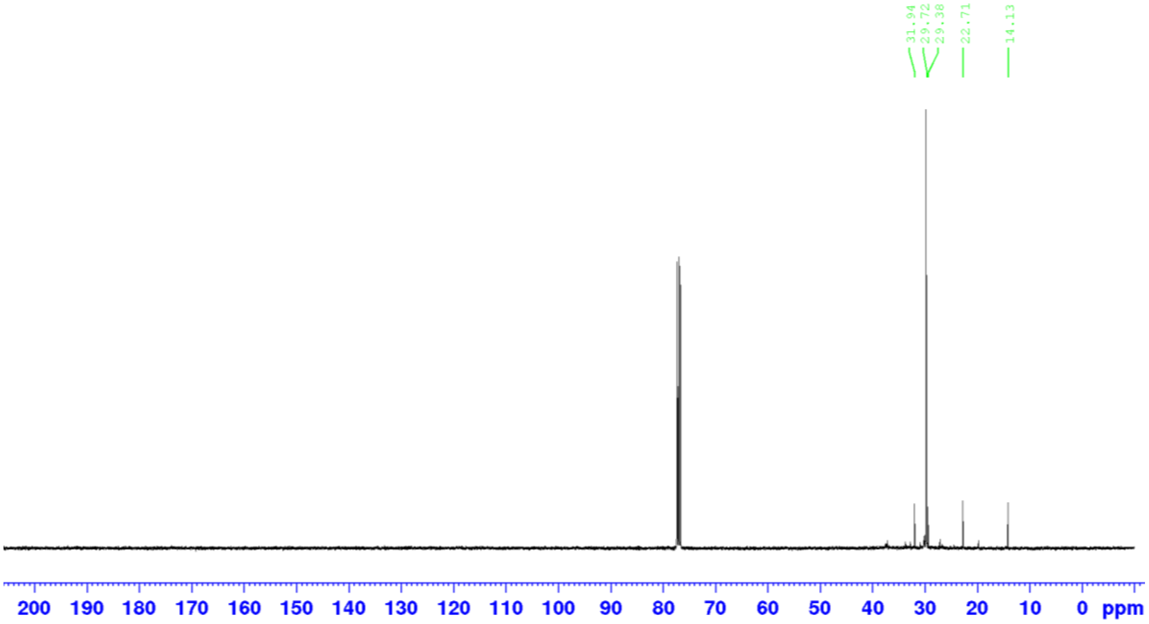


Figure S6. *^{13}C NMR spectrum of wax extracted from the baseline surface.*

IR ν_{max} (neat, cm^{-1}): 2917 (C-H), 2850 (C-H), 1461 (C-H), 1377 (C-H), 719 (C-H).

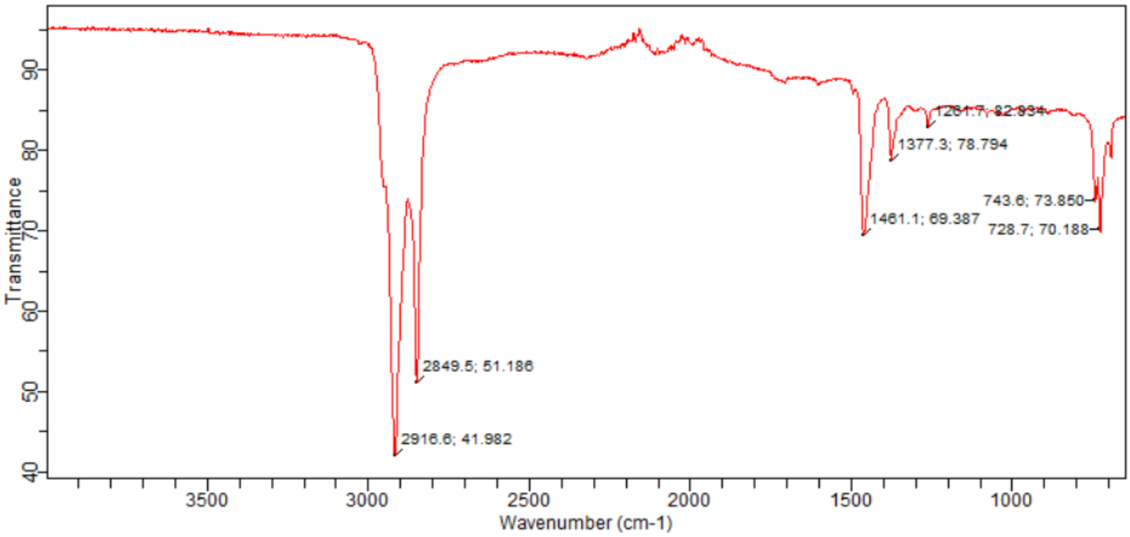


Figure S7. *FTIR spectrum of wax extracted from the baseline surface.*

GC ($CHCl_3$, PTFE filtered)

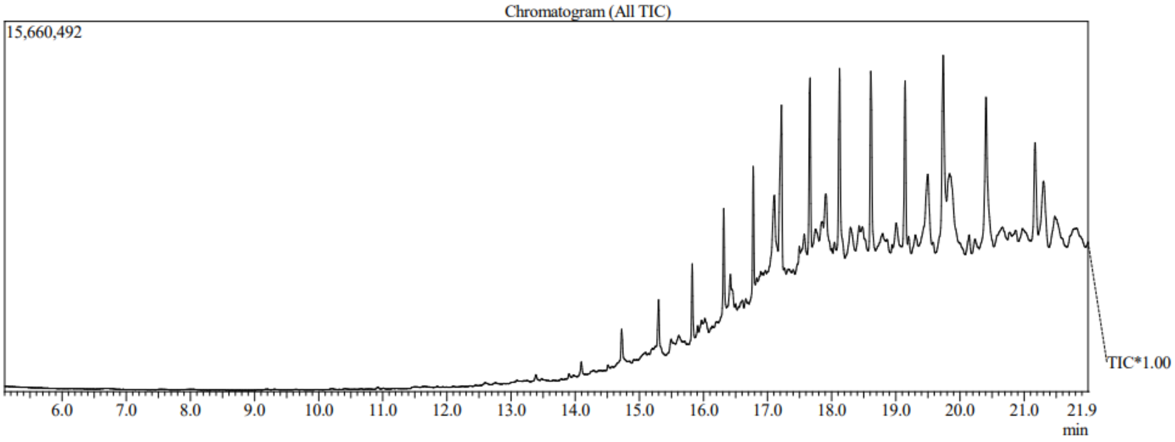


Figure S8. *GC-MS chromatogram of wax extracted from the baseline surface.*

6.1.2.1 Purified Unused Surface Wax

IR ν_{max} (neat, cm^{-1}): 2919 (C-H), 2850 (C-H), 1461 (C-H), 1377 (C-H), 719 (C-H).

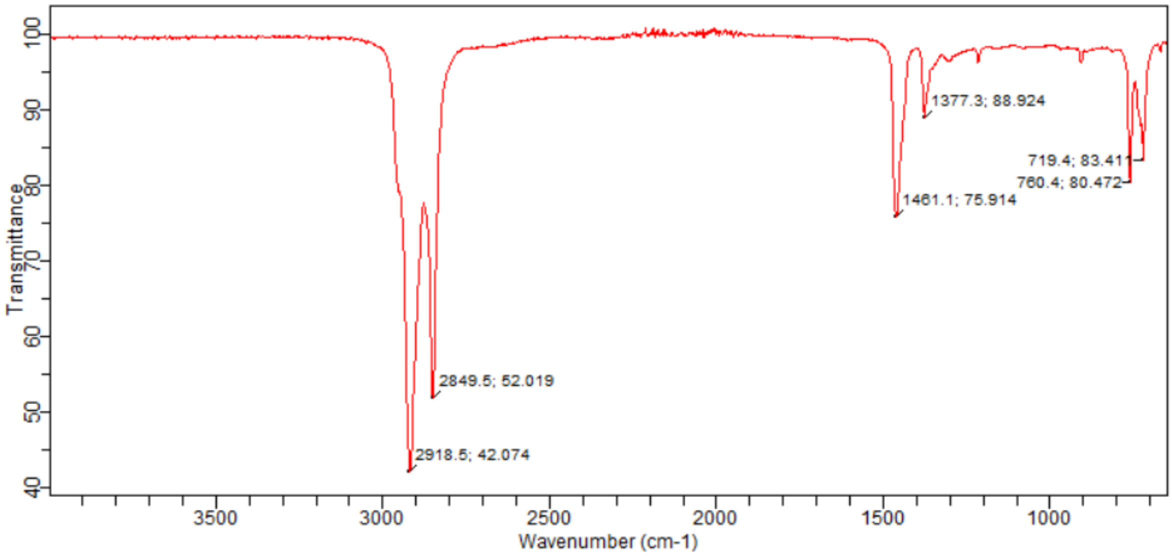


Figure S9. *FTIR spectrum of wax extracted from the baseline surface and purified by column chromatography.*

6.1.3 EOL1 Surface Wax

^{1}H NMR (CDCl$_3$, 400 MHz): δ_H 1.28 (-CH$_2$-), 0.878 (terminal CH$_3$ groups).

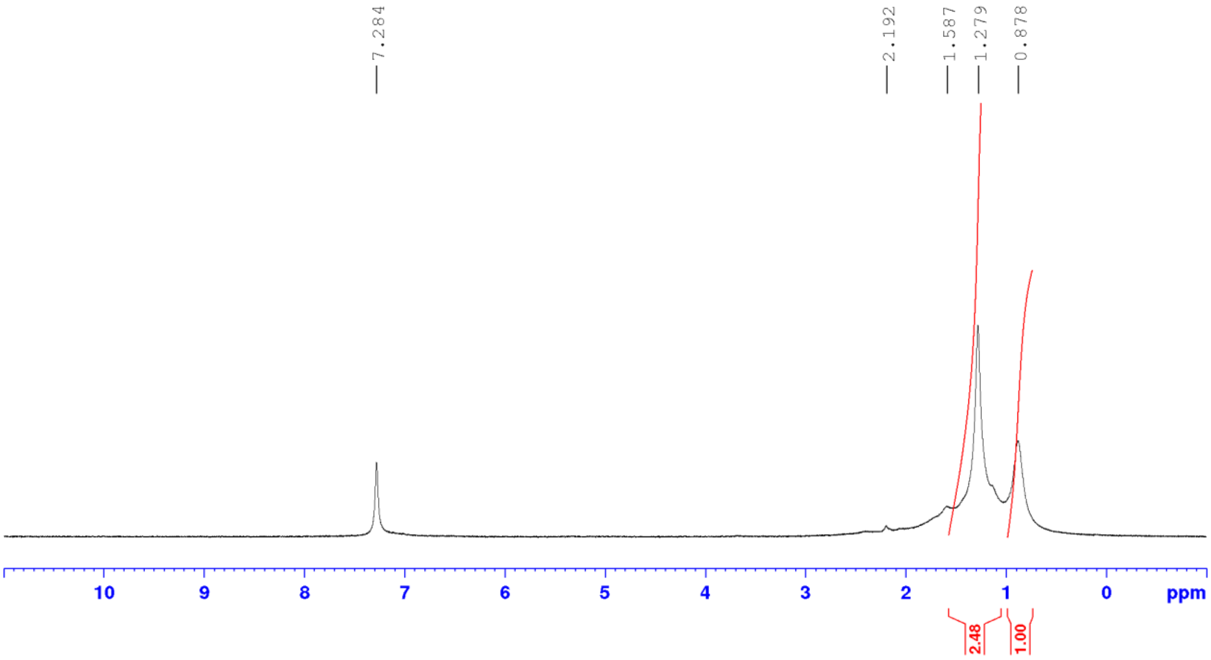


Figure S10. *^{1}H NMR spectrum of wax extracted from **EOL1** surface.*

^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 29.7 (-$(CH_2)_n$-).

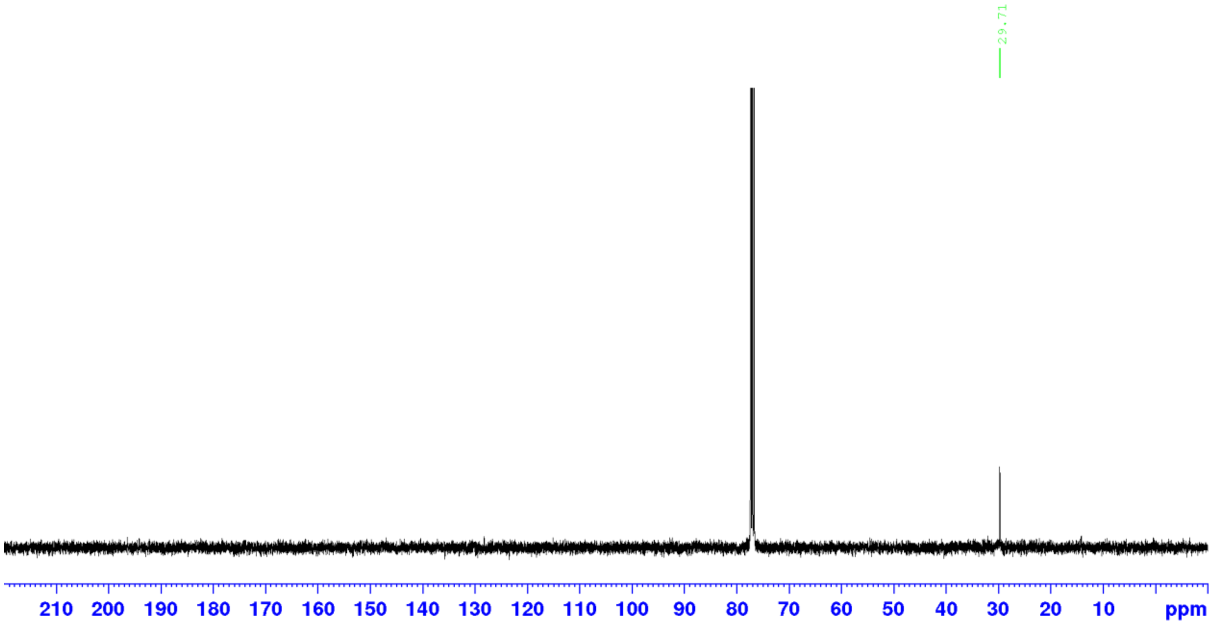


Figure S11. *^{13}C NMR spectrum of wax extracted from **EOL1** surface.*

IR ν_{max} (neat, cm^{-1}): 2917 (C-H), 2850 (C-H), 1707 (C=O), 1461 (C-H), 1377 (C-H), 719 (C-H).

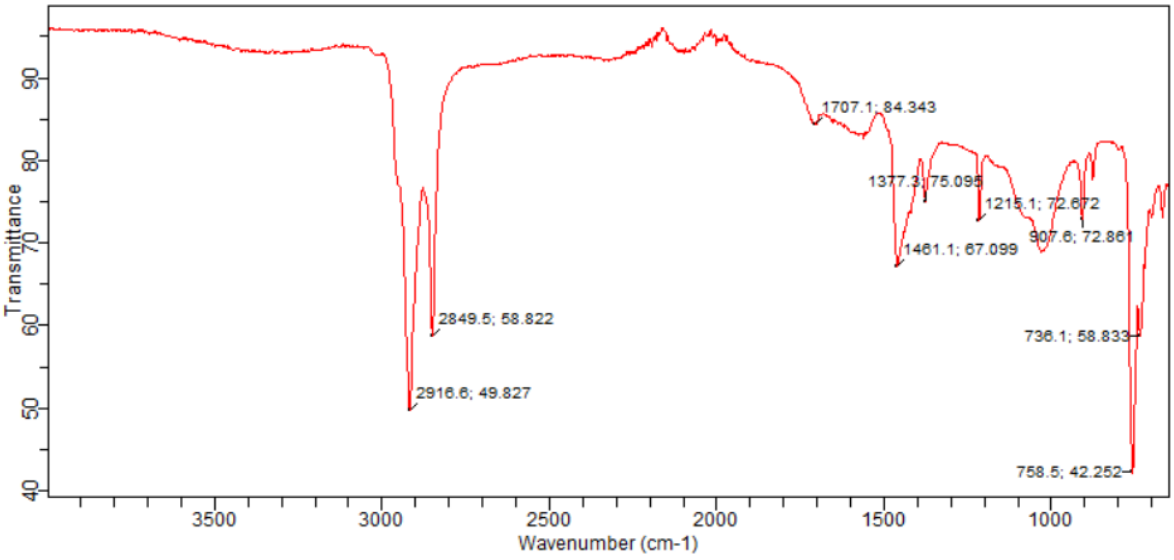


Figure S12. *FTIR spectrum of wax extracted from **EOL1** surface.*

GC ($CHCl_3$, PTFE filtered)

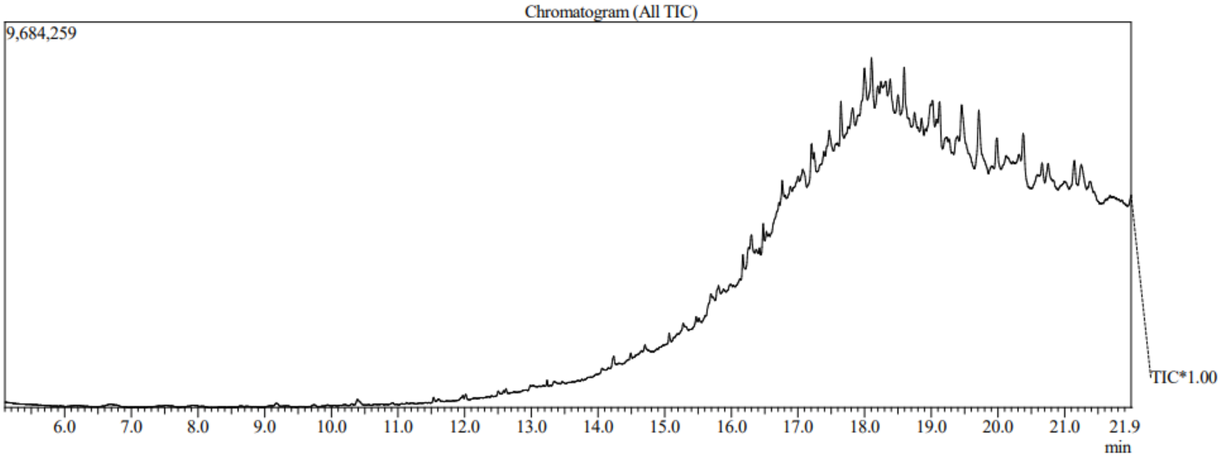


Figure S13. *GC-MS chromatogram of wax extracted from* ***EOL1*** *surface.*

6.1.3.1 Purified EOL1 Wax

IR ν_{max} (neat, cm^{-1}): 2920 (C-H), 2853 (C-H), 1457 (C-H), 1377 (C-H), 721 (C-H).

Appears pure – with only 5 environments present which are all identical to GT70 wax and correspond to simple paraffin wax.

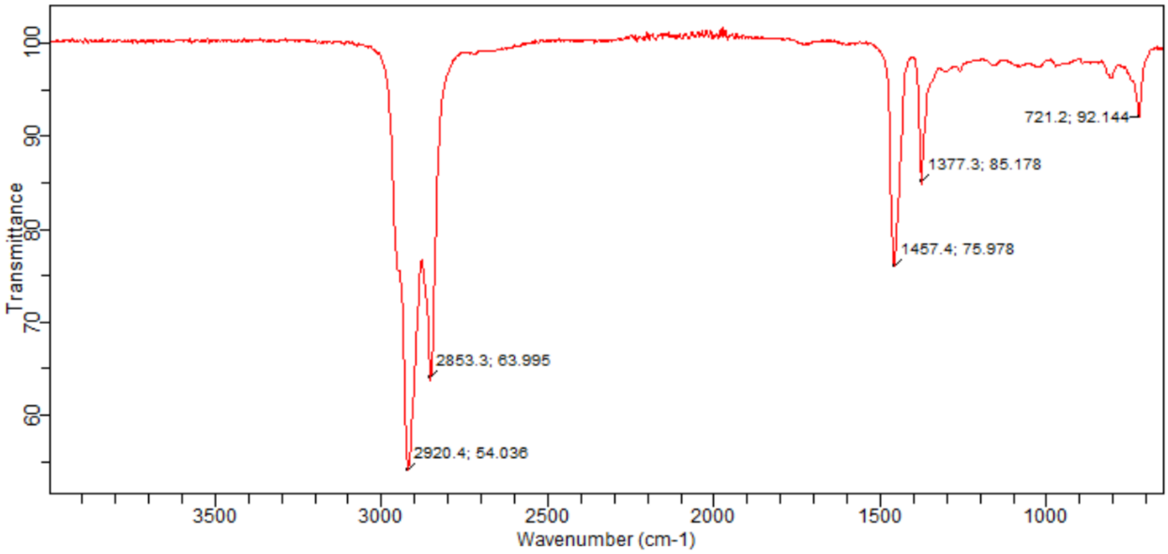


Figure S14. *FTIR spectrum of wax extracted from* ***EOL1*** *surface purified by column chromatography.*

6.1.4 EOL4 Surface Wax

^{1}H NMR (CDCl$_3$, 400 MHz): δ_H 1.28 (-CH$_2$-), 0.90 (terminal CH$_3$ groups).

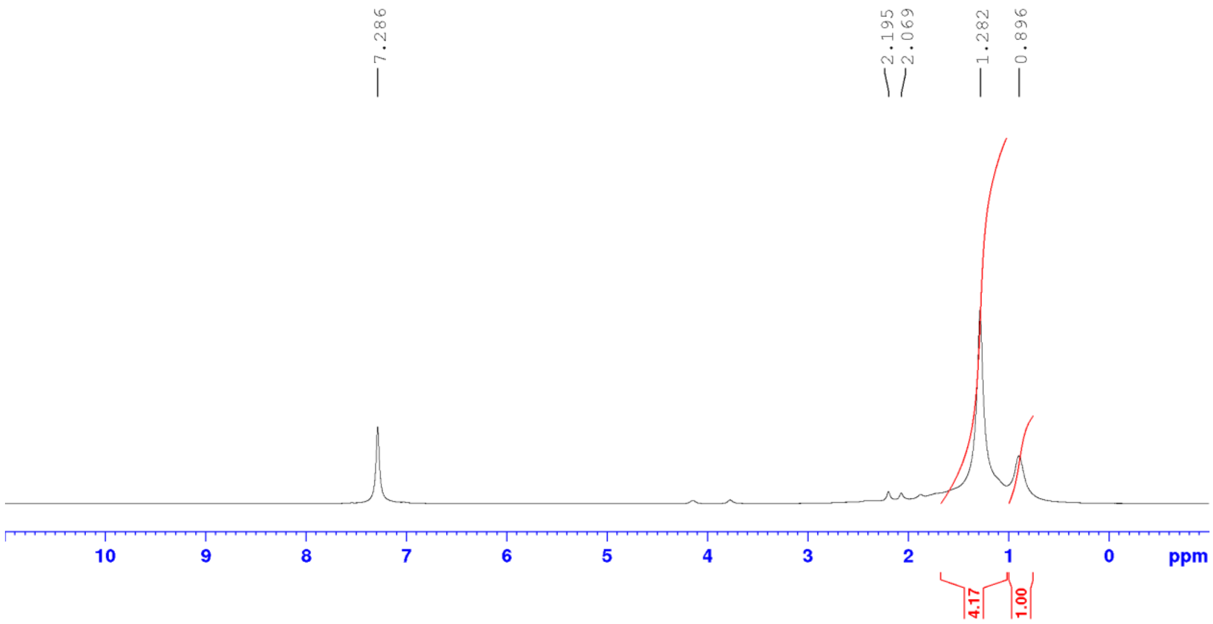


Figure S15. *^{1}H NMR spectrum of wax extracted from* ***EOL4*** *surface.*

^{13}C NMR (CDCl$_3$, 100 MHz): δ_C 29.7 (-(CH$_2$)$_n$-).

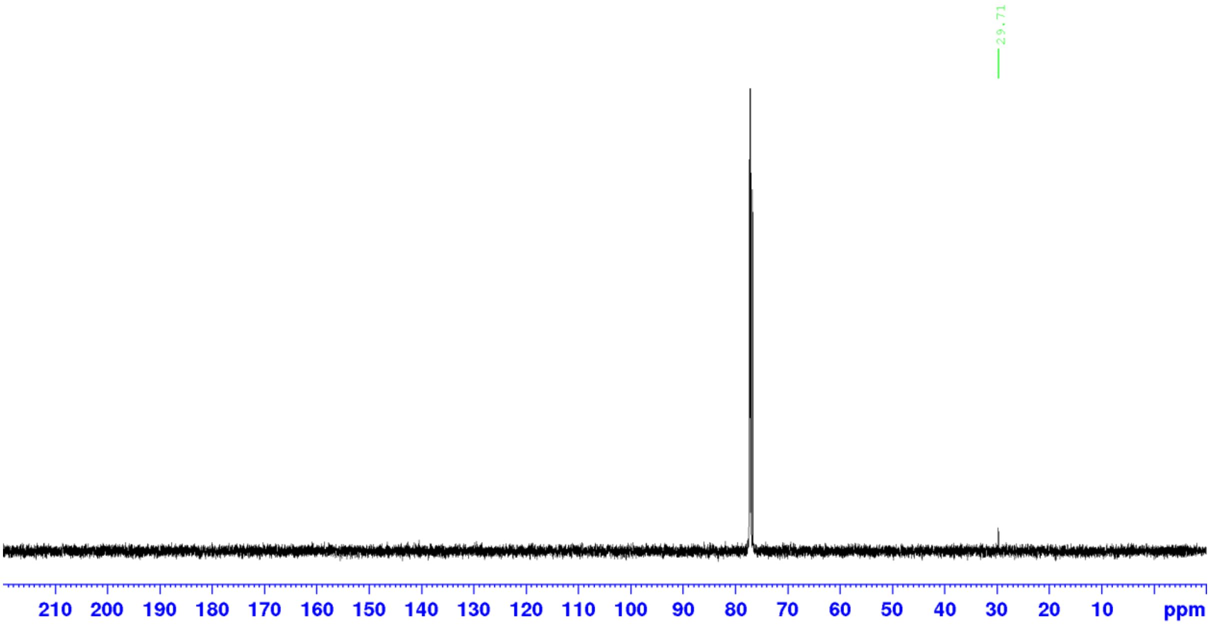


Figure S16. *^{13}C NMR spectrum of wax extracted from* ***EOL4*** *surface.*

IR ν_{max} (neat, cm^{-1}): 2917 (C-H), 2850 (C-H), 1684 (C=O), 1461 (C-H), 1377 (C-H), 719 (C-H).

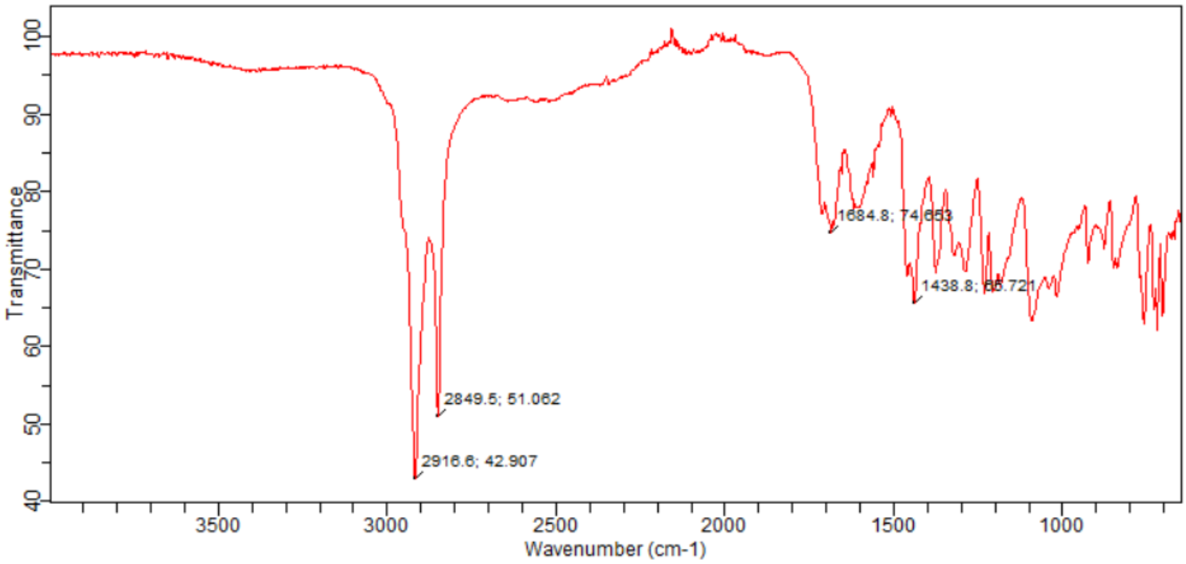


Figure S17. *FTIR spectrum of wax extracted from **EOL4** surface.*

GC ($CHCl_3$, PTFE filtered)

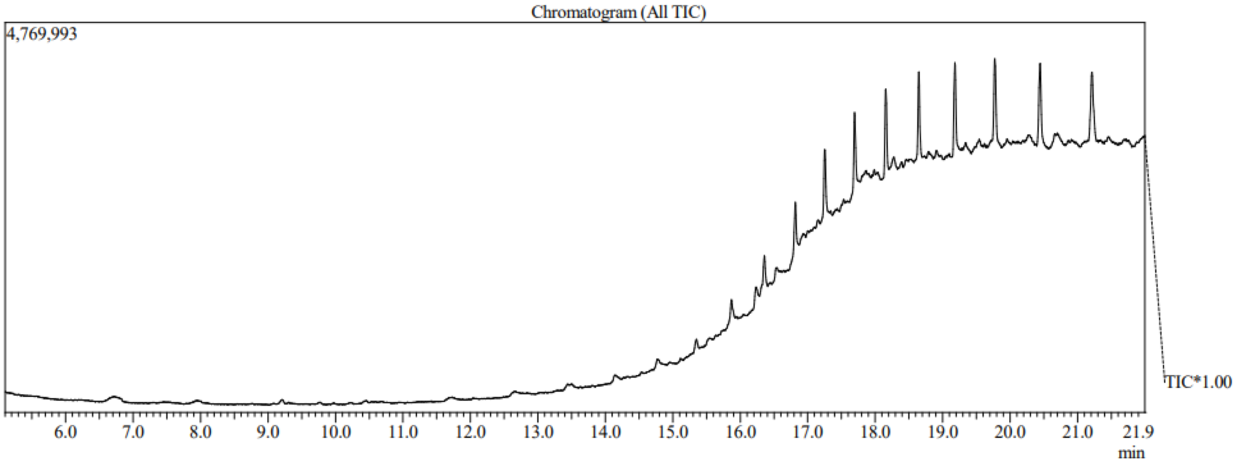


Figure S18. *GC-MS chromatogram of wax extracted from **EOL4** surface.*

6.1.4.1 Purified EOL4 Wax

IR ν_{max} (neat, cm^{-1}): 2917 (C-H), 2850 (C-H), 1716 (C=O), 1463 (C-H), 1377 (C-H), 719 (C-H).

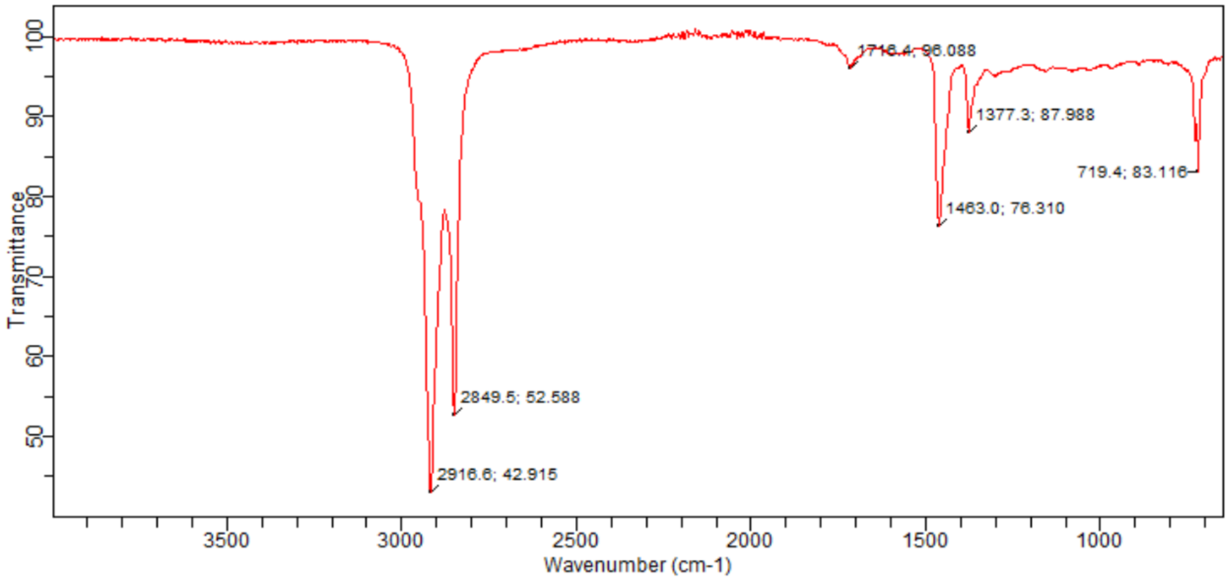


Figure S19. *FTIR spectrum of wax extracted from **EOL4** surface purified by column chromatography.*

6.1.5 EOL5 Surface Wax .

^{1}H NMR (CDCl$_3$, 400 MHz): δ_H 1.28 (-CH$_2$-), 0.88 (terminal CH$_3$ groups).

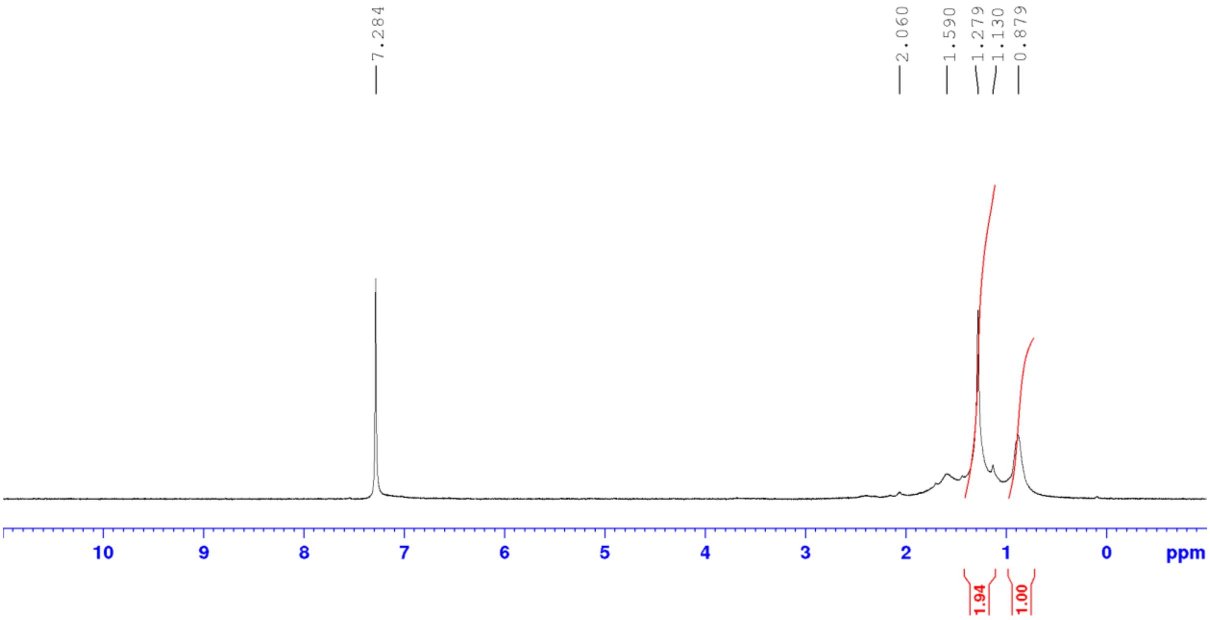


Figure S20. *^{1}H NMR spectrum of wax extracted from **EOL5** surface.*

^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 29.7 (-$(CH_2)_n$-).

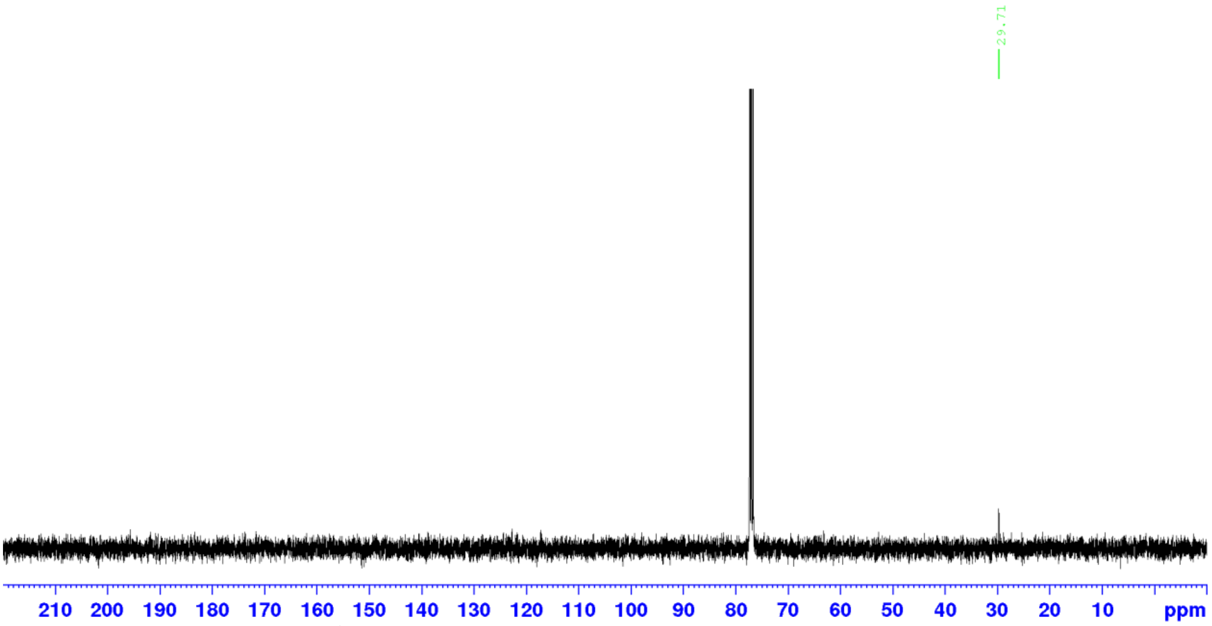


Figure S21. *^{13}C NMR spectrum of wax extracted from* ***EOL5*** *surface.*

IR ν_{max} (neat, cm^{-1}): 2917 (C-H), 2850 (C-H), 1720 (C=O), 1463 (C-H), 1377 (C-H), 1030 (Si-O), 719 (C-H).

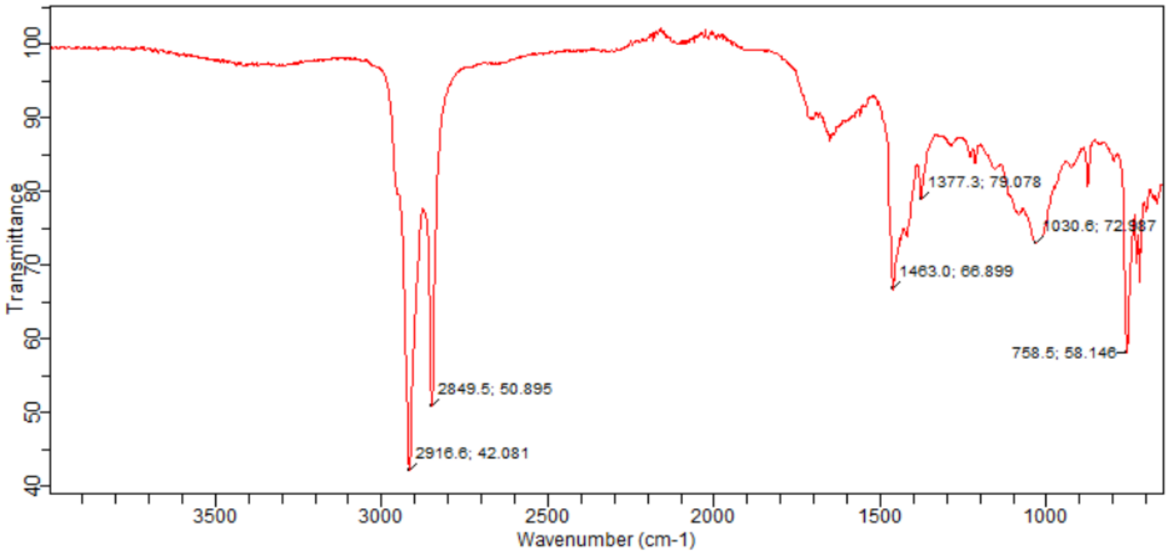


Figure S22. *FTIR spectrum of wax extracted from* ***EOL5*** *surface.*

GC ($CHCl_3$, PTFE filtered)

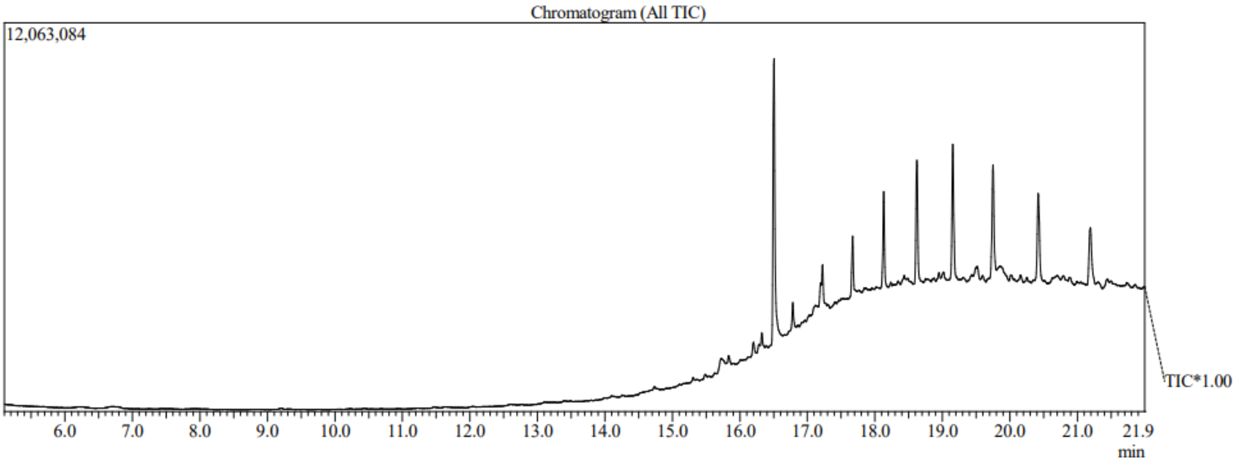


Figure S23. *GC-MS chromatogram of wax extracted from **EOL5** surface.*

6.1.5.1 Purified EOL5 Wax

IR ν_{max} (neat, cm^{-1}): 2917 (C-H), 2850 (C-H), 1716 (C=O), 1463 (C-H), 1377 (C-H), 719 (C-H).

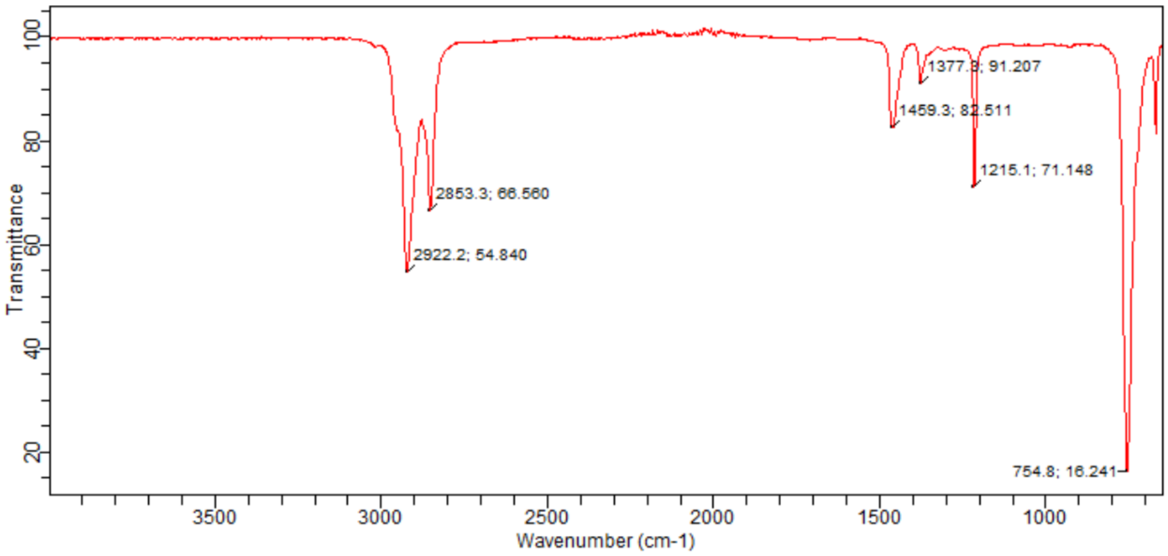


Figure S24. *FTIR spectrum of wax extracted from **EOL5** surface purified by column chromatography.*

6.1.6 EOL6 Surface Wax

^{1}H NMR (CDCl$_3$, 400 MHz): δ_H 1.28 (-CH$_2$-), 0.90 (terminal CH$_3$ groups).

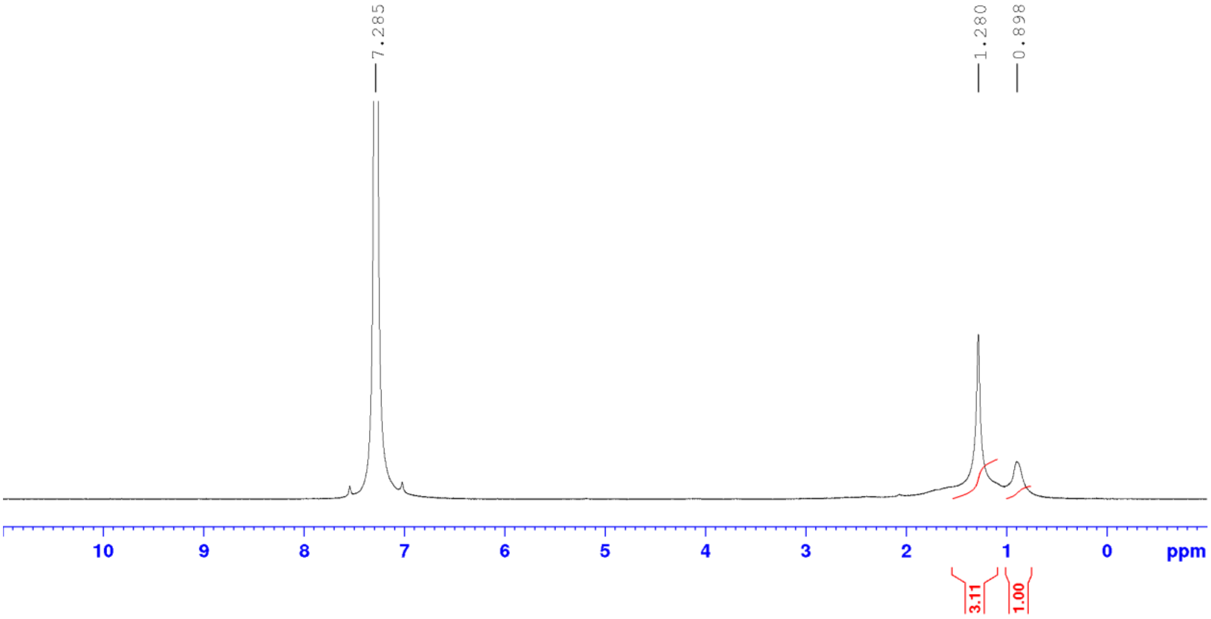


Figure S25. *^{1}H NMR spectrum of wax extracted from* ***EOL6*** *surface.*

^{13}C NMR (CDCl$_3$, 100 MHz): δ_C 29.7 (-(CH$_2$)$_n$-).

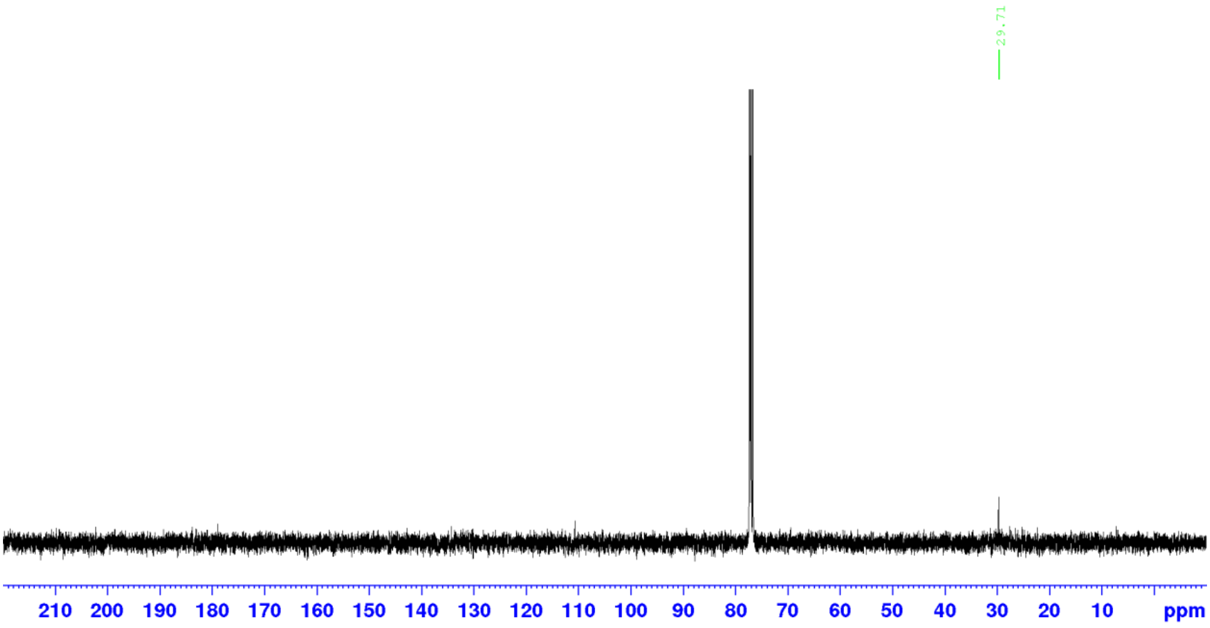


Figure S26. *^{13}C NMR spectrum of wax extracted from* ***EOL6*** *surface.*

IR ν_{max} (neat, cm^{-1}): 2917 (C-H), 2850 (C-H), 1707 (C=O), 1437 (C-H), 1377 (C-H), 1027 (Si-O), 719 (C-H).

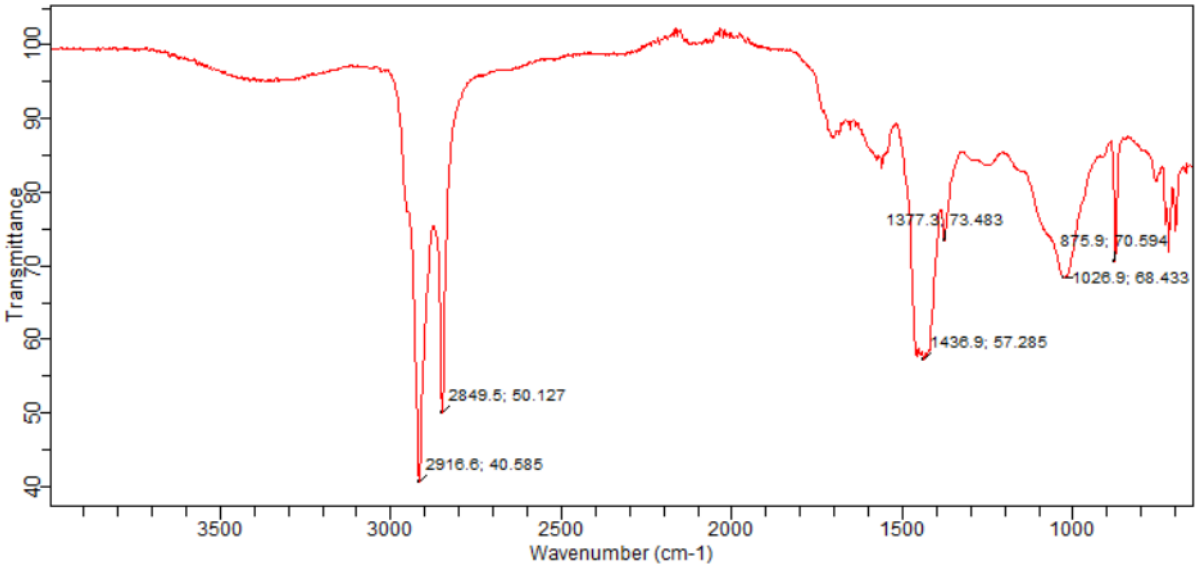


Figure S27. *FTIR spectrum of wax extracted from* ***EOL6*** *surface.*

GC (CHCl$_3$, PTFE filtered)

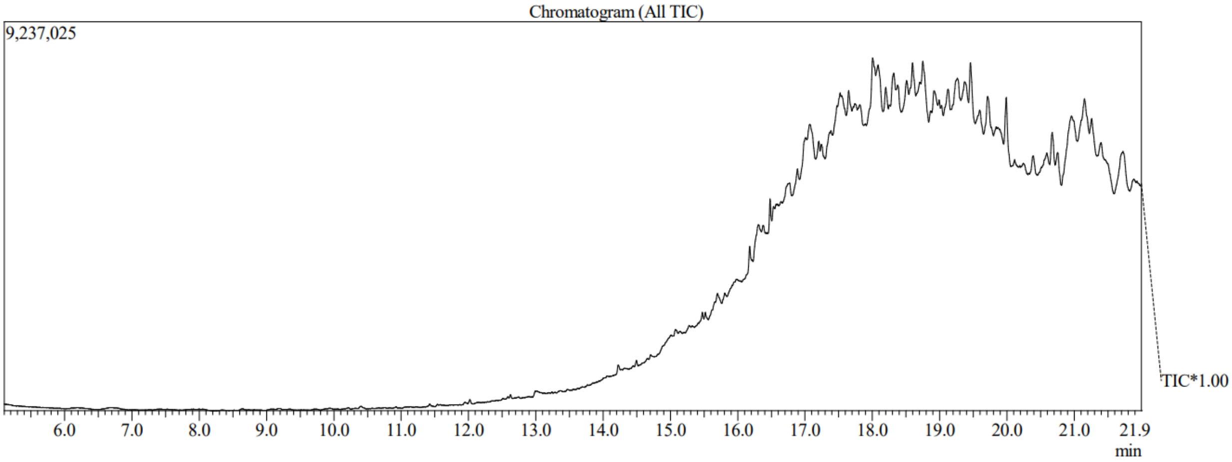


Figure S28. GC-MS chromatogram *of wax extracted from* ***EOL6*** *surface.*

6.1.6.1 Purified EOL6 Wax

IR ν_{max} (neat, cm^{-1}): 2920 (C-H), 2851 (C-H), 1707 (C=O), 1459 (C-H), 1377 (C-H), 719 (C-H).

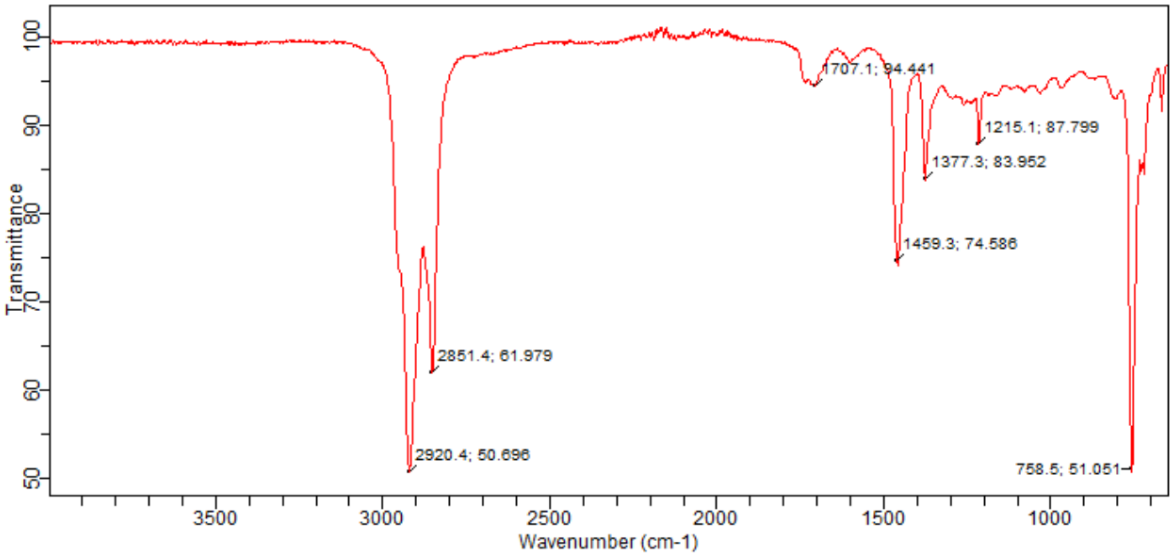


Figure S29. *FTIR spectrum of wax extracted from* ***EOL6*** *surface purified by column chromatography.*

6.2 Sand Experimental Data

6.2.1 FTIR Analysis

FTIR spectra recorded according to the procedure described in Section 2.6.1. **BS** and **EOL1** sands are in the waxed form.

6.2.1.1 Supplier Sand

IR v_{max} (neat, cm^{-1}): 3353 (O-H), 1651 (O-H), 1060 (Si-O), 772 (Si-O), 691 (Si-O).

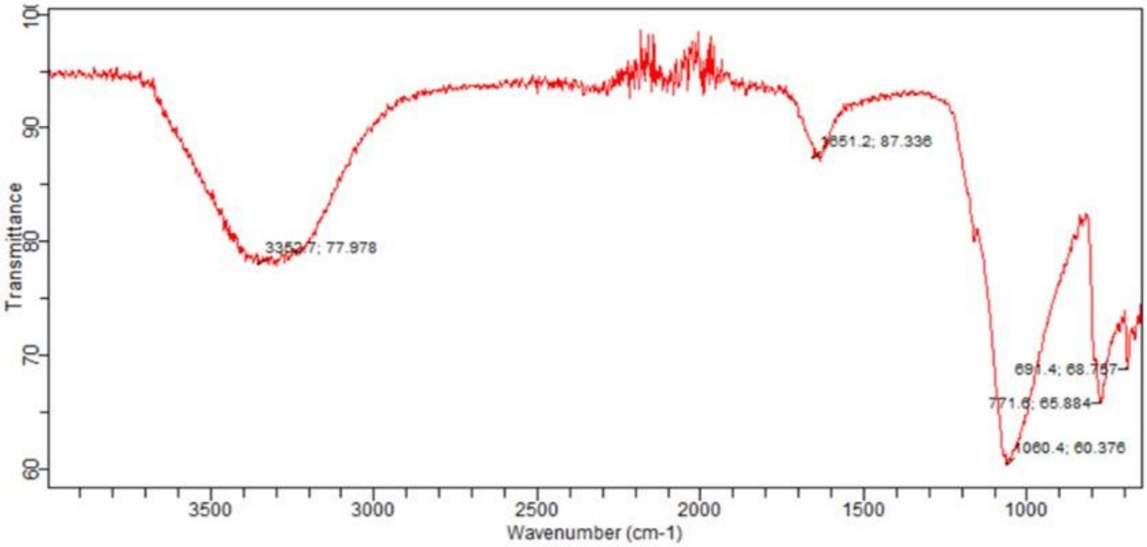


Figure S30. *FTIR spectrum of supplier MOIST60 sand.*

6.2.1.2 Baseline Surface Sand

IR v_{max} (neat, cm^{-1}): 2917 (C-H), 2850 (C-H), 1463 (C-H), 1075 (Si-O), 795 (C-H), 777 (Si-O), 693 (Si-O).

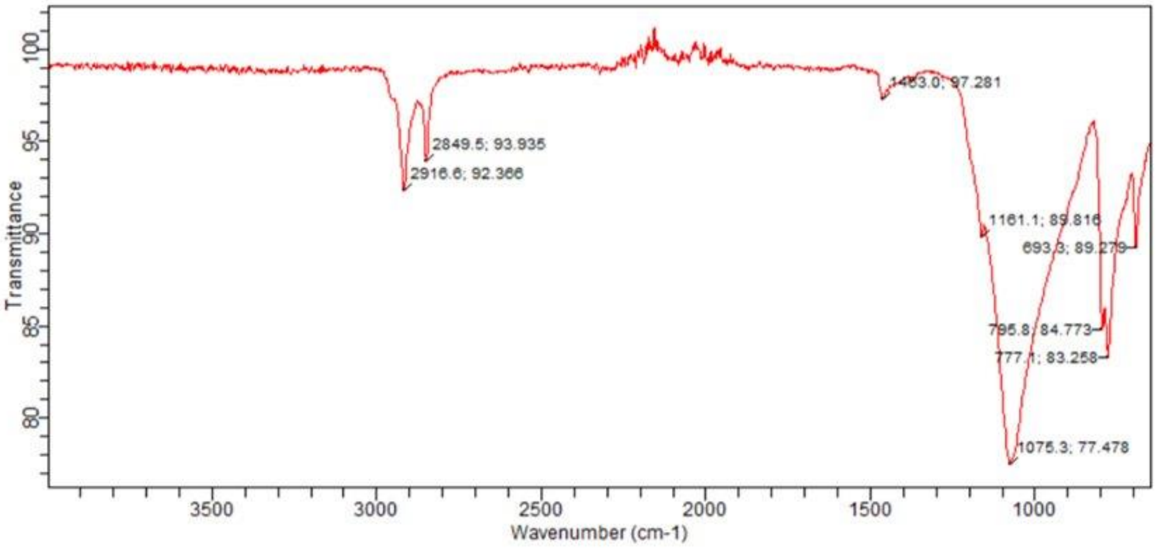


Figure S31. *FTIR spectrum of sand isolated from the* ***BS****.*

6.2.1.3 EOL1 Surface Sand

IR ν_{max} (neat, cm^{-1}): 2922 (C-H), 1422 (C-H), 1080 (Si-O), 798 (C-H), 779 (Si-O), 695 (Si-O).

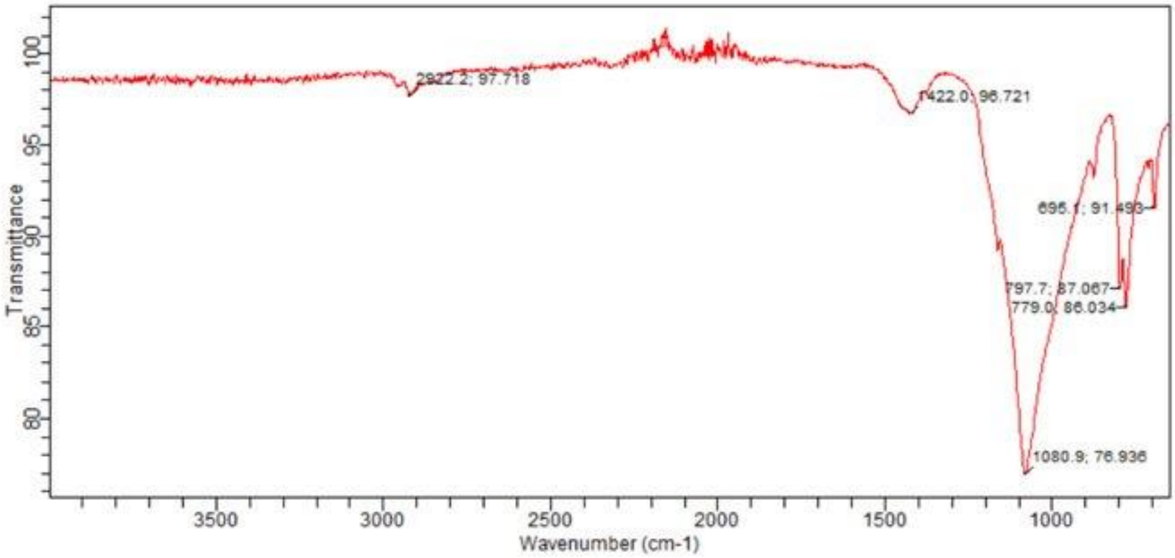


Figure S32. *FTIR spectrum of sand isolated from the* ***EOL1*** *surface.*

6.3.1 EDX Analysis

EDX analysis was performed according to the procedures described in Section 2.6.7. All images shown in this section are for sands in the original form (all surfaces are in the waxed state).

6.3.1.1 Supplier Sand

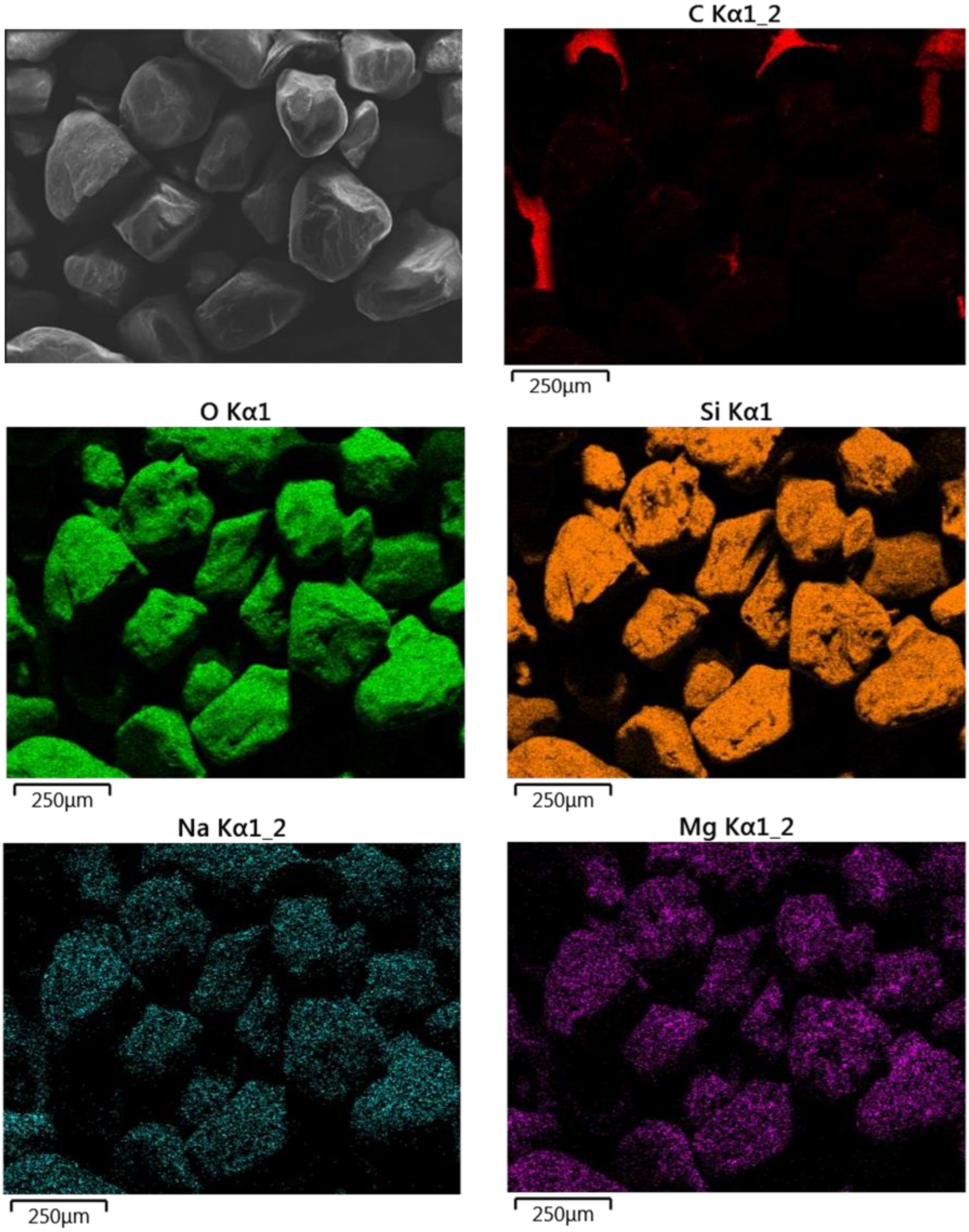


Figure S33. *EDX surface maps showing the elemental distribution for a sample of supplier sand. X100 magnification.*

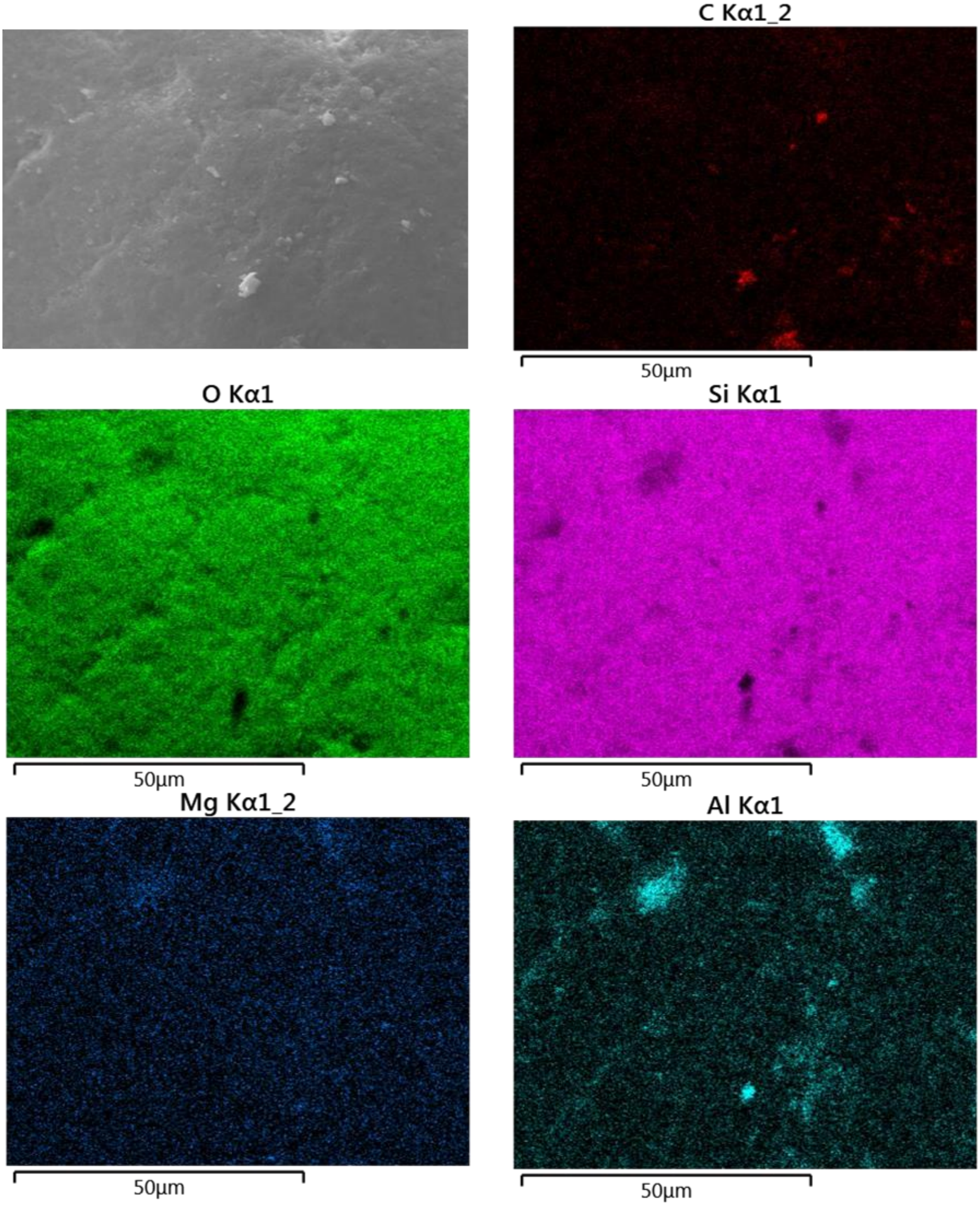


Figure S34. *EDX surface maps showing the elemental distribution for a sample of supplier sand. X1000 magnification.*

6.3.1.2 Baseline Surface Sand

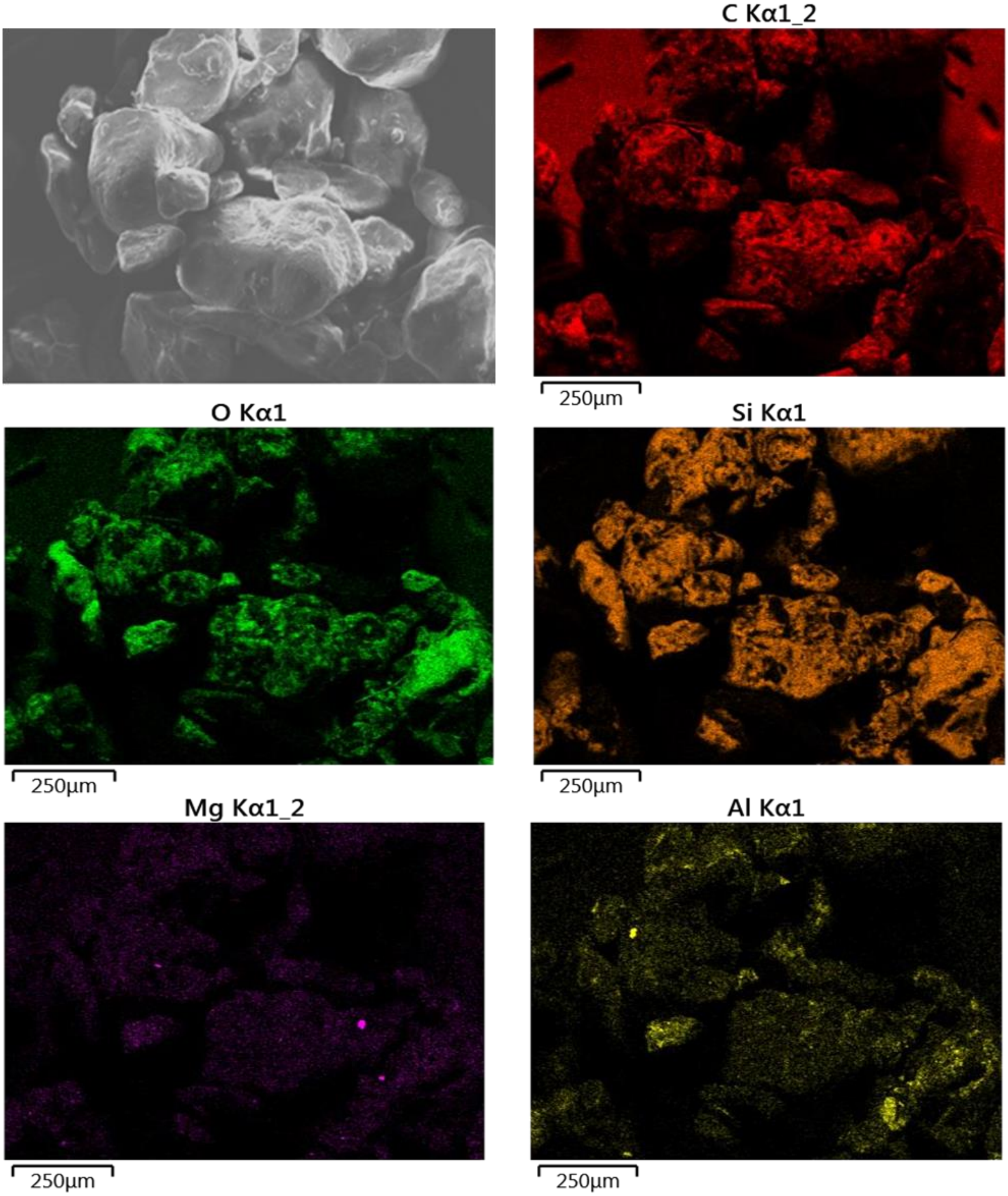


Figure S35. *EDX surface maps showing the elemental distribution for a sample of* ***BS*** *sand. X100 magnification.*

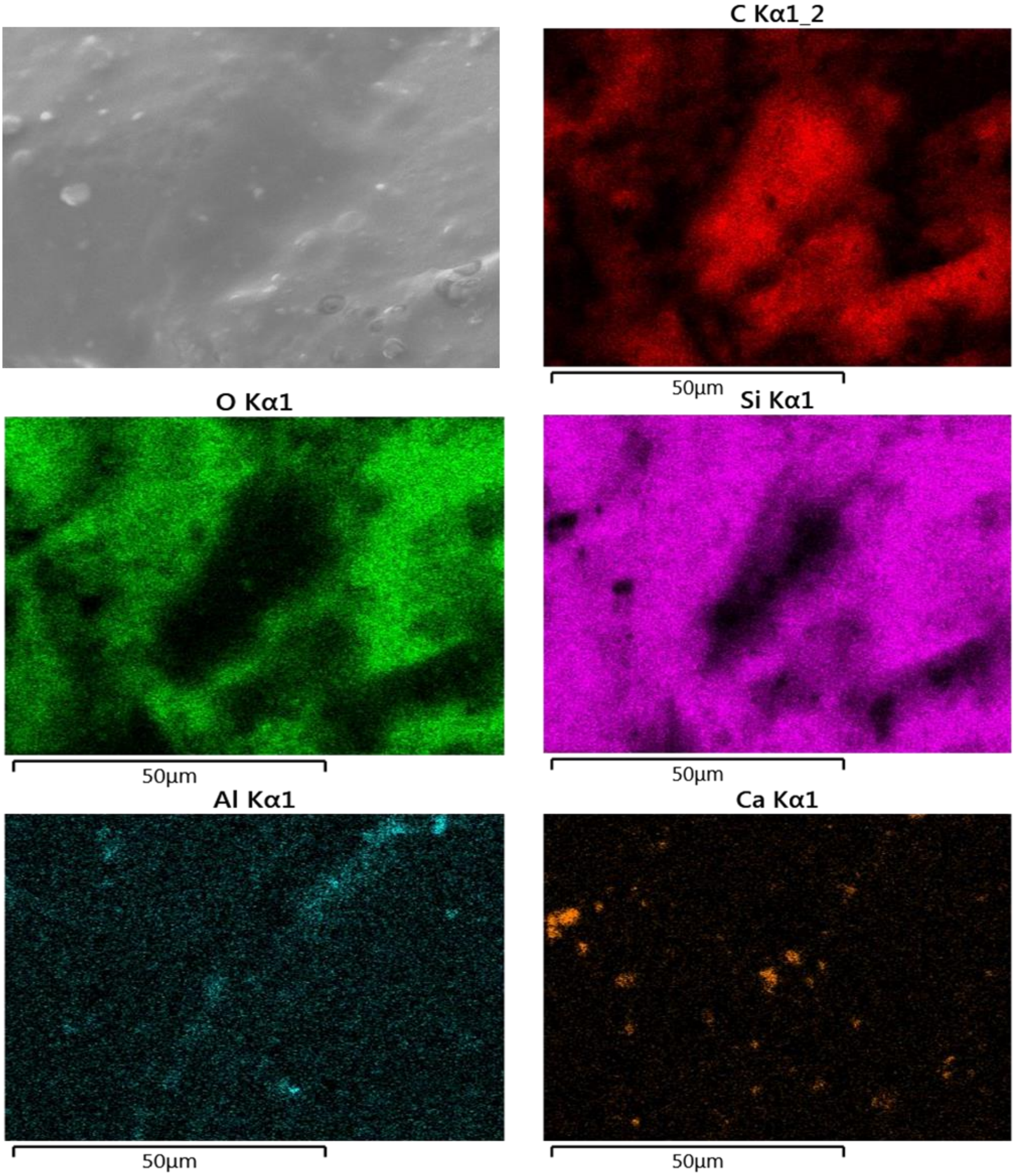


Figure S36. *EDX surface maps showing the elemental distribution for a sample of* ***BS*** *sand. X1000 magnification.*

6.3.1.3 EOL1 Sand

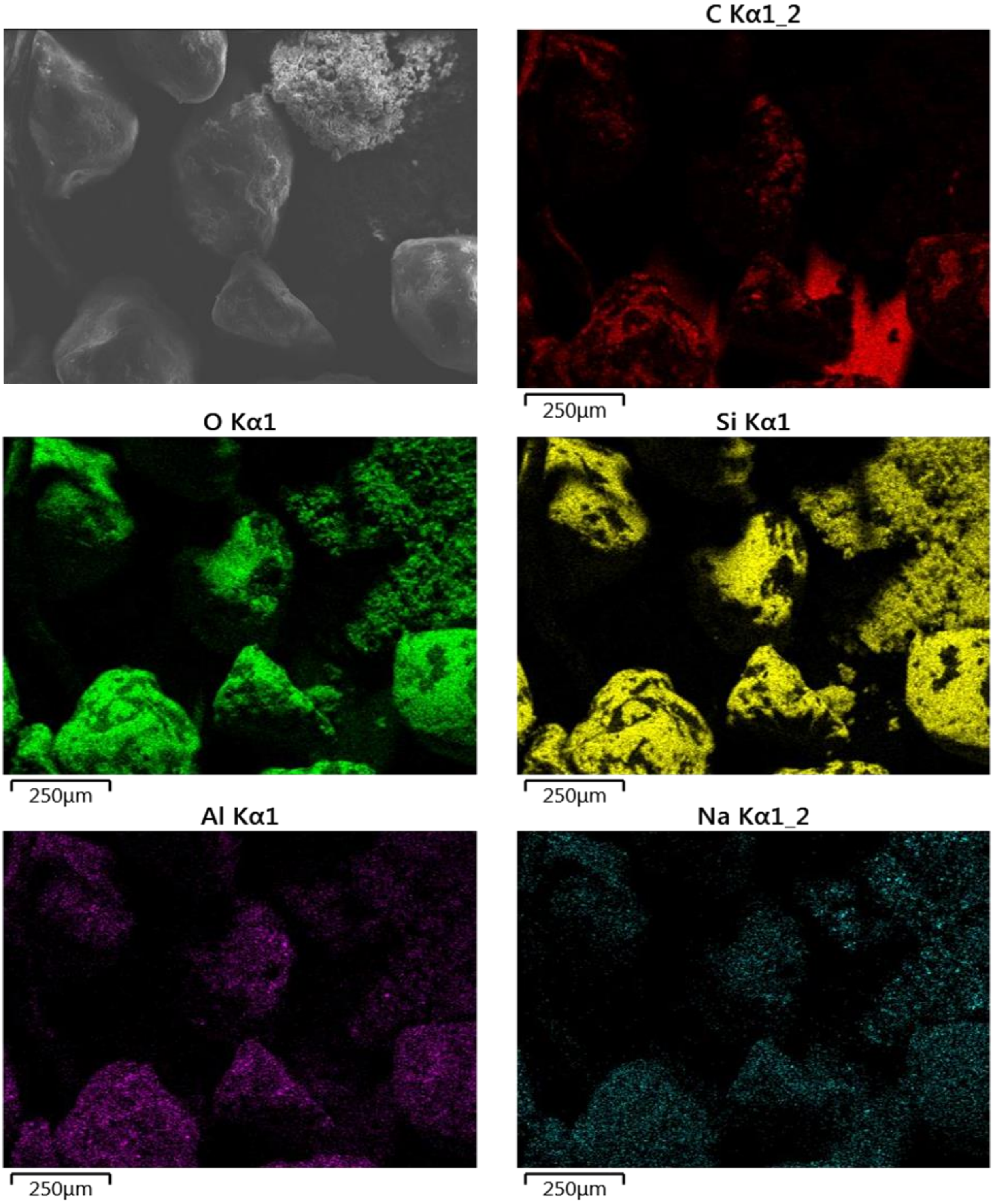


Figure S37. *EDX surface maps showing the elemental distribution for a sample of* ***EOL1*** *surface sand. X100 magnification.*

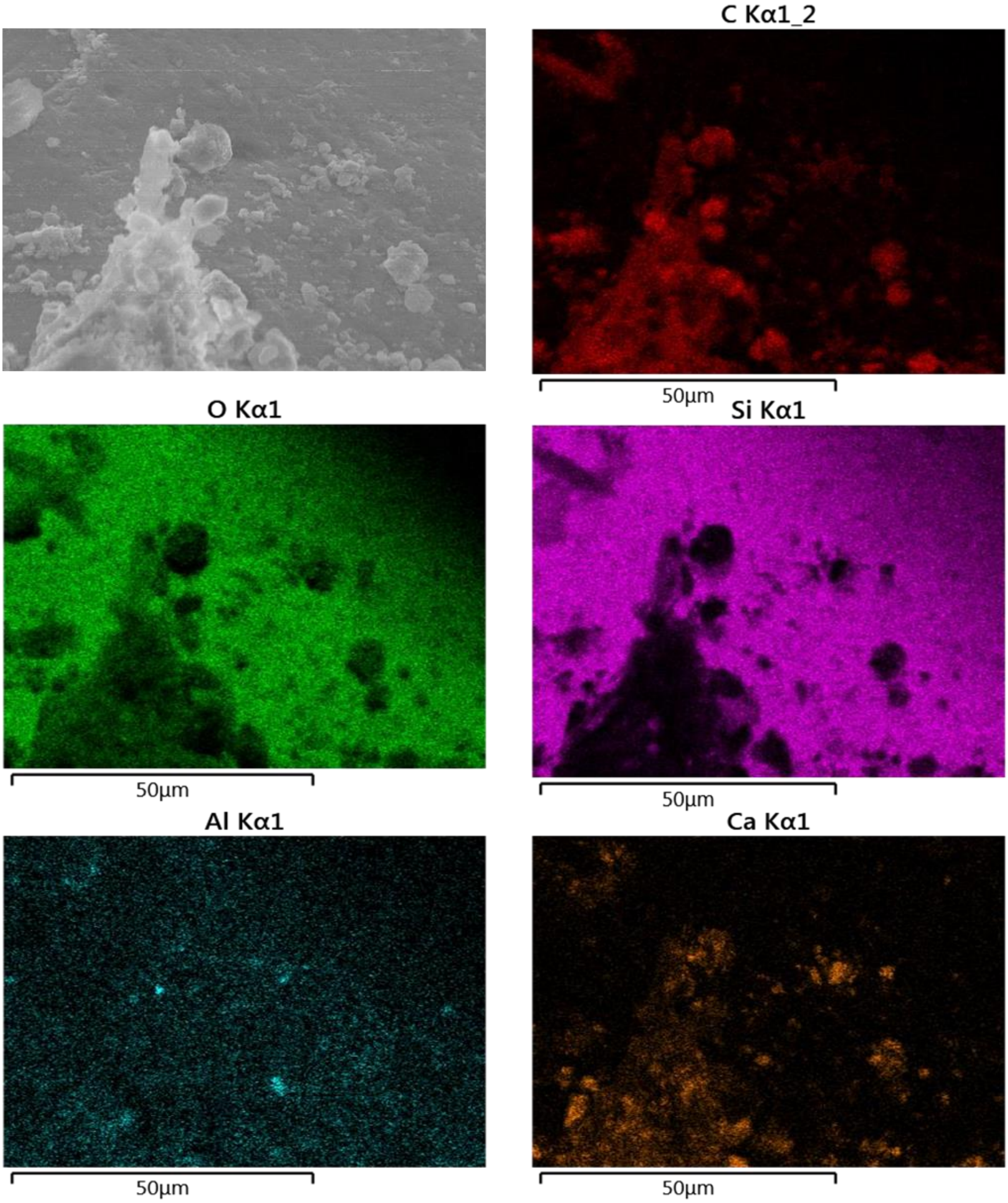


Figure S38. *EDX surface maps showing the elemental distribution for a sample of* ***EOL1*** *surface sand. X600 magnification.*

6.3.1.4 EOL4 Sand

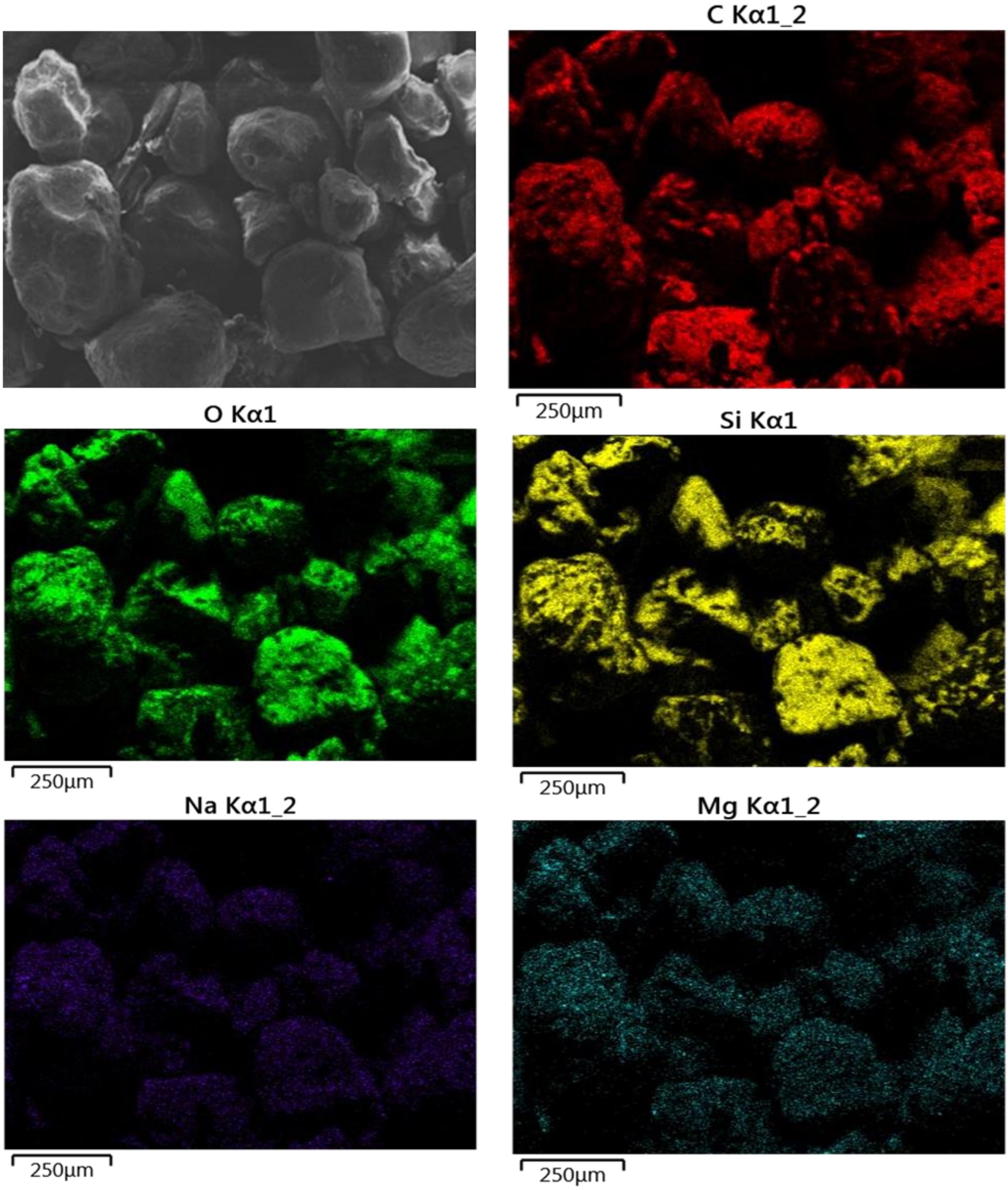


Figure S39. *EDX surface maps showing the elemental distribution for a sample of* ***EOL4*** *surface sand. X100 magnification.*

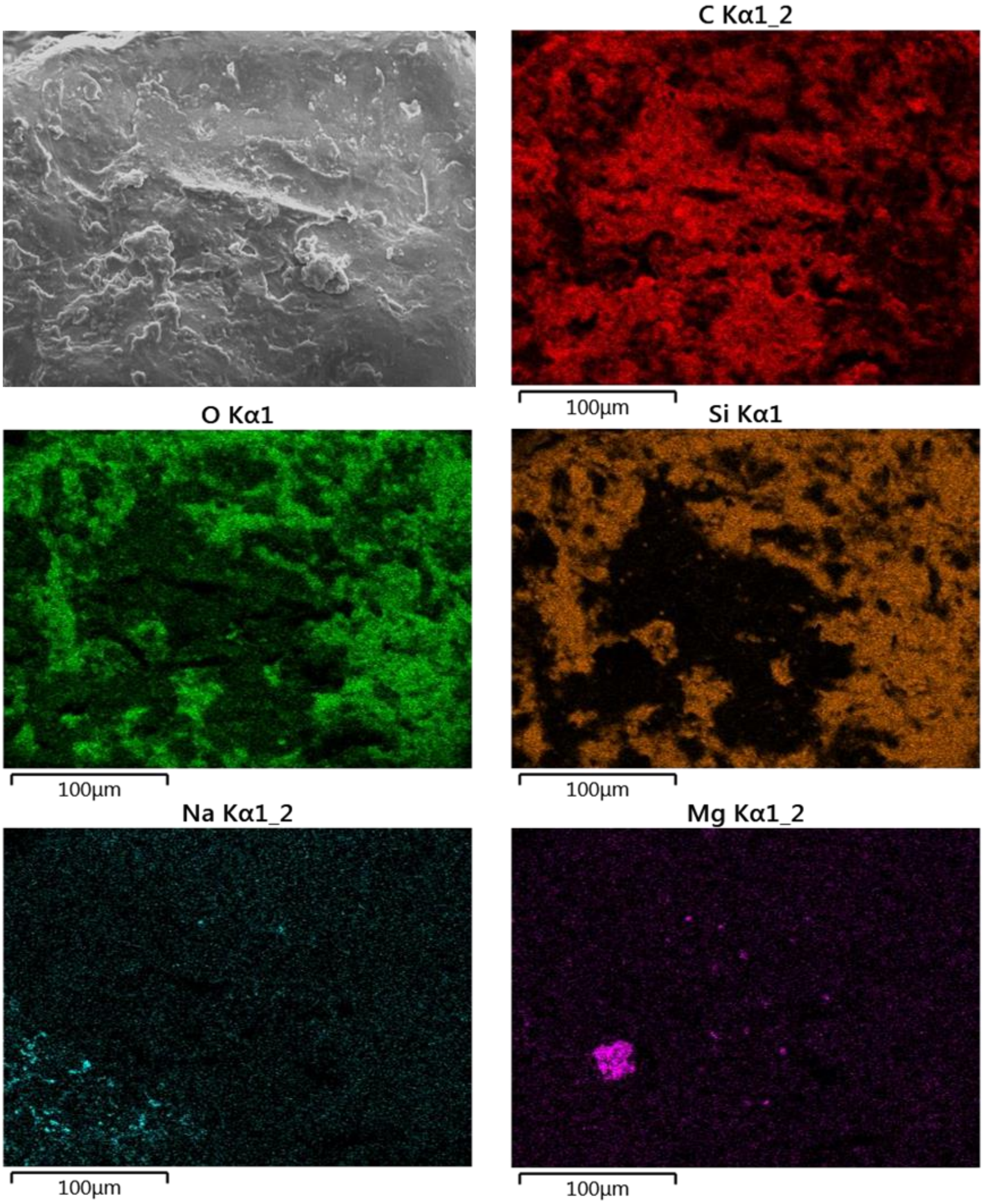


Figure S40. *EDX surface maps showing the elemental distribution for a sample of* ***EOL4*** *surface sand. X600 magnification.*

6.3.1.5 EOL5 Sand

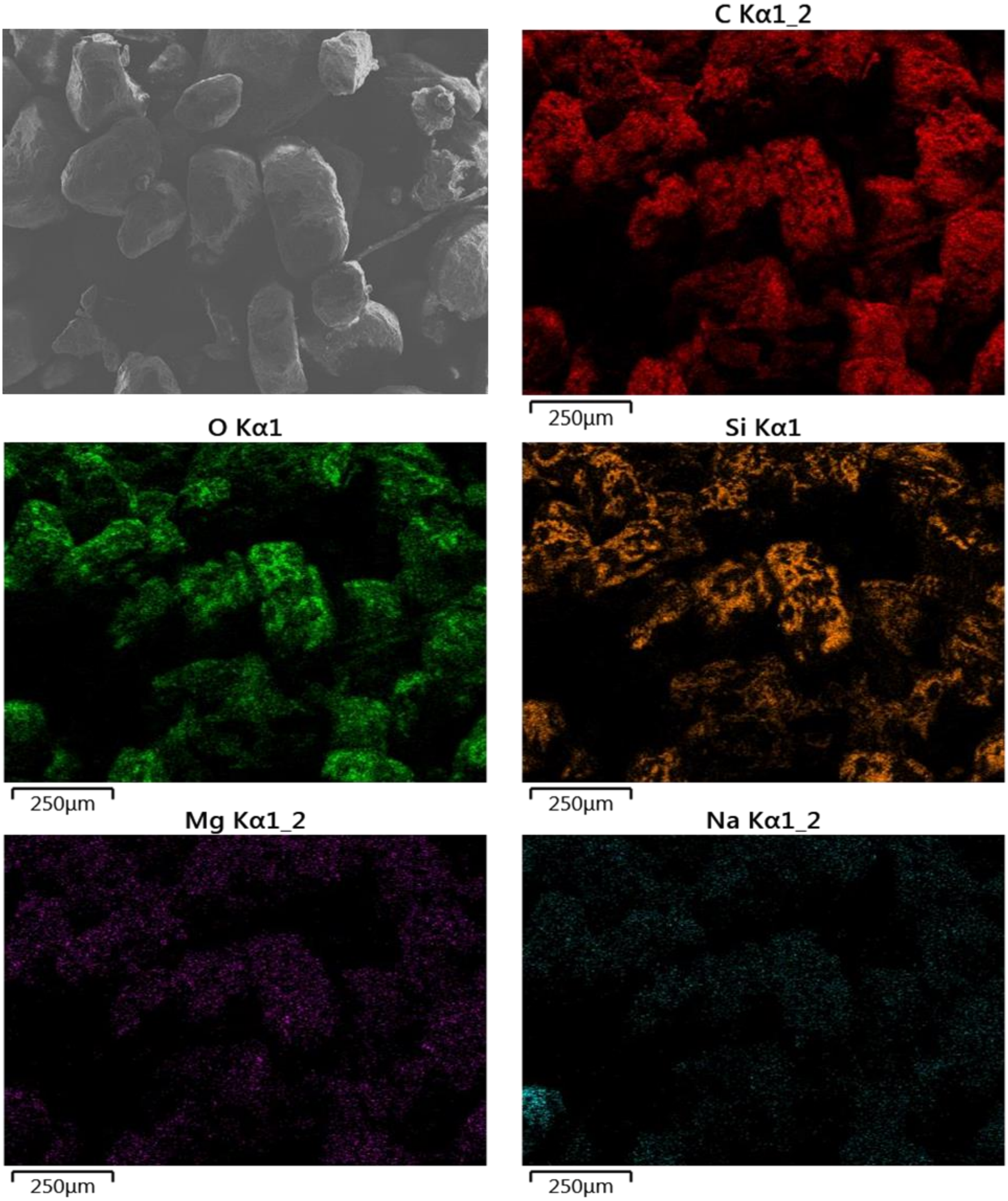


Figure S41. *EDX surface maps showing the elemental distribution for a sample of* ***EOL5*** *surface sand. X100 magnification.*

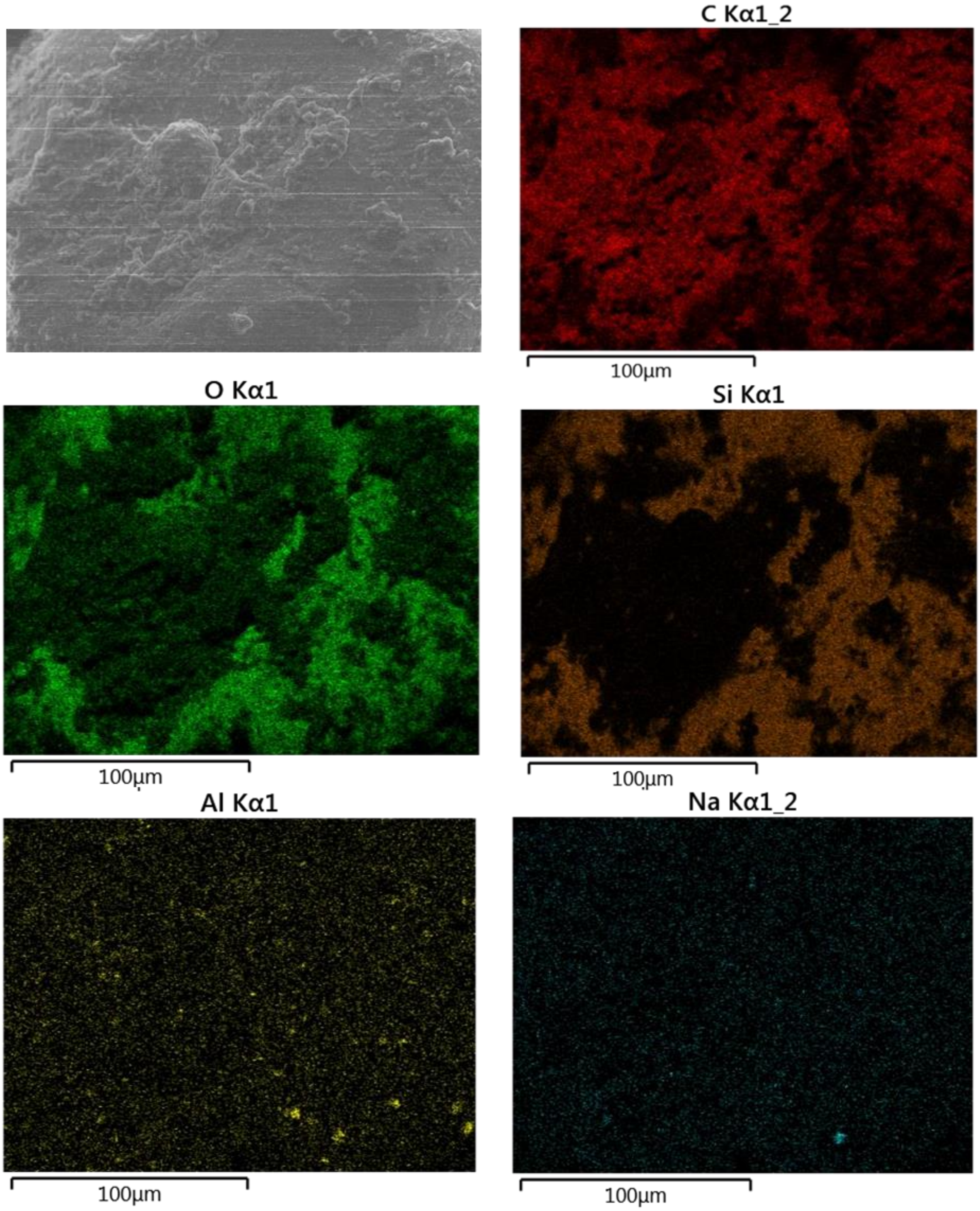


Figure S42. *EDX surface maps showing the elemental distribution for a sample of* ***EOL5*** *surface sand. X600 magnification.*

6.3.1.6 EOL6 Sand

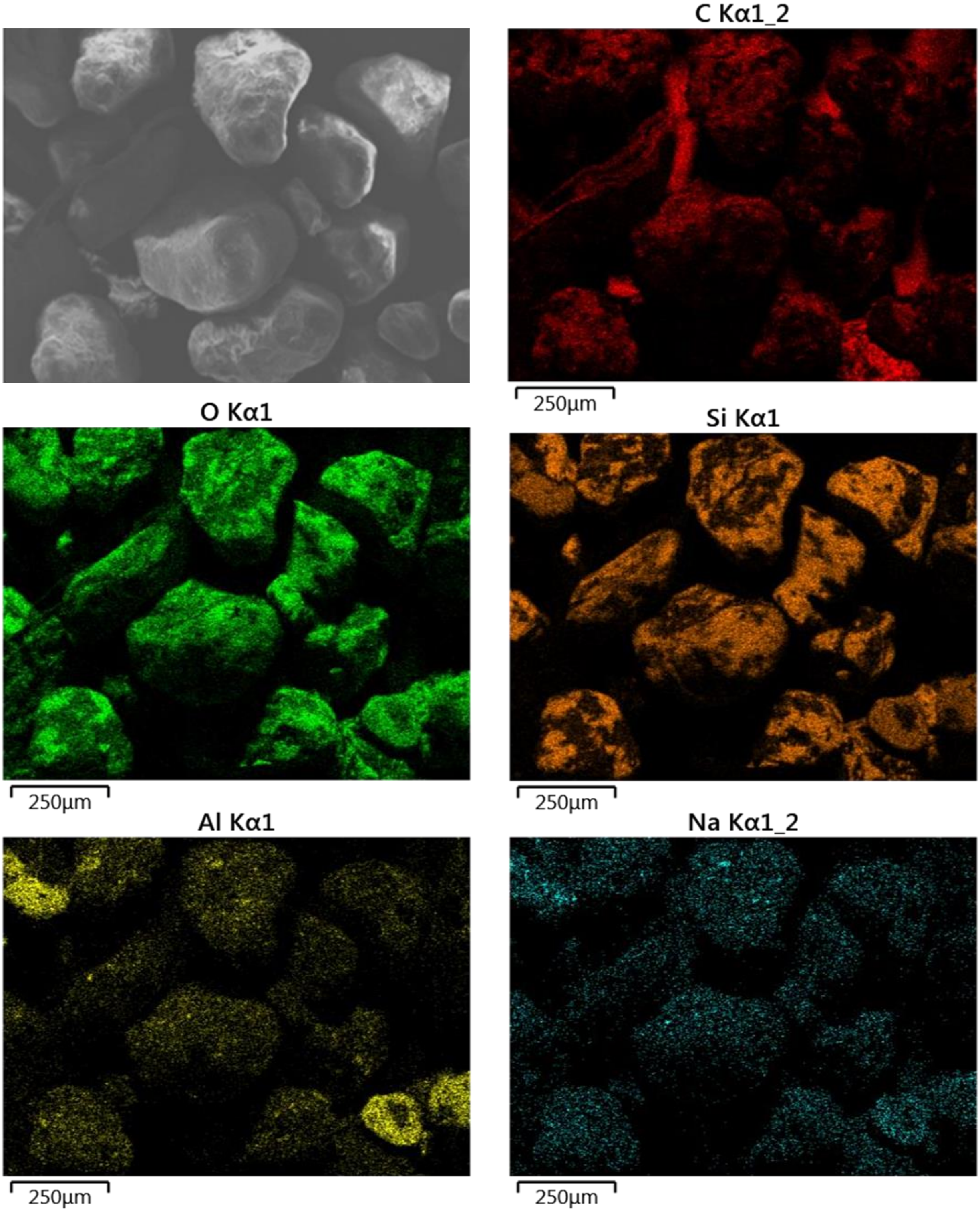


Figure S43. *EDX surface maps showing the elemental distribution for a sample of* ***EOL6*** *surface sand. X100 magnification.*

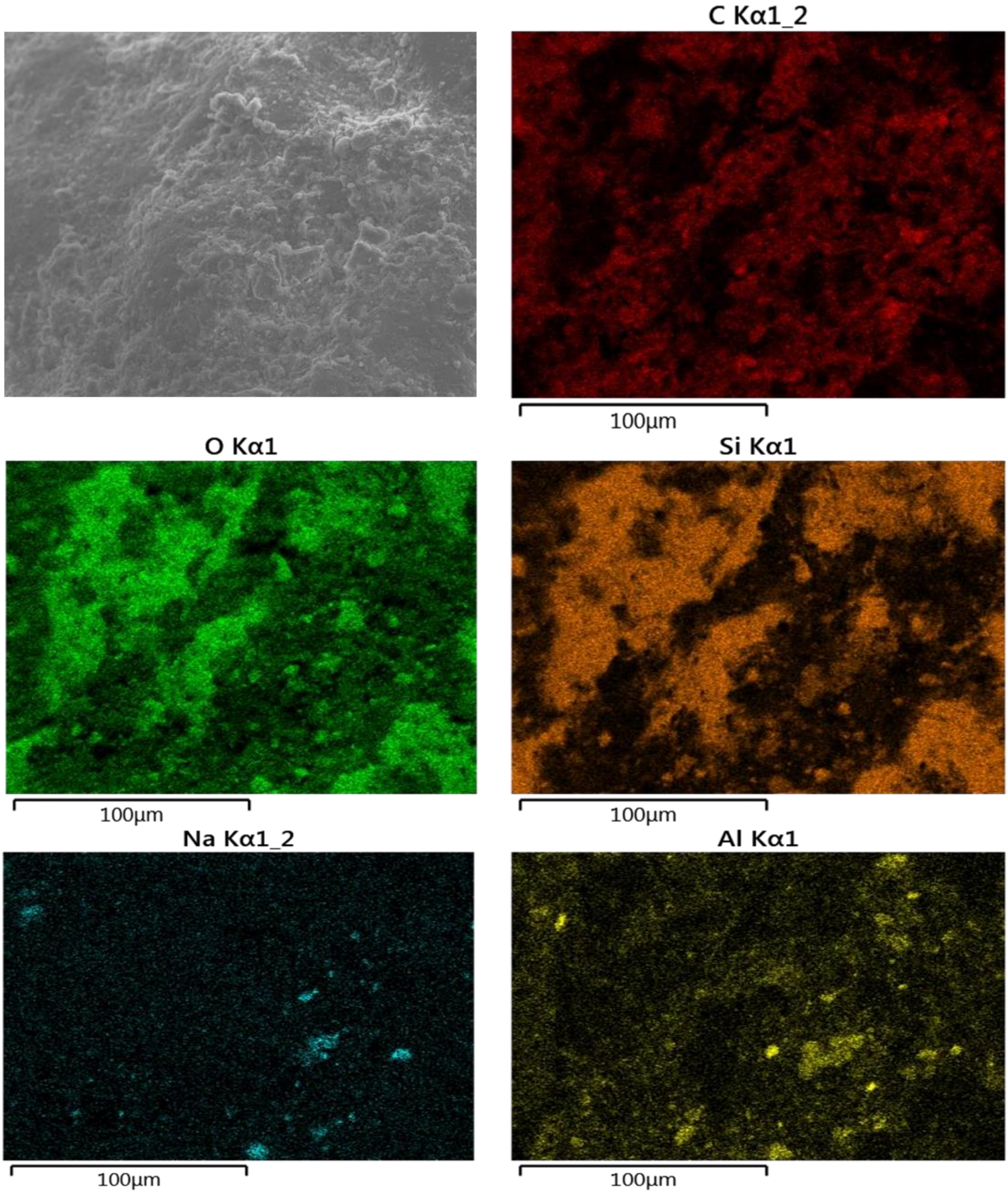


Figure S44. *EDX surface maps showing the elemental distribution for a sample of* ***EOL6*** *surface sand. X600 magnification.*

6.4 Carpet Fibre Experimental Data

6.4.1. Organic Extracts Characterisation

6.4.1.1 Post-industrial fibres

Following solvent extraction with chloroform, post-industrial fibres (9.0 g) gave 228 mg of green waxy solid (2.4% mass recovery)

IR ν_{max} (neat, cm^{-1}): 3409 (O-H), 2952 (C-H), 2917 (C-H), 2850 (C-H), 1731 (C=O), 1451 (C-H), 1375 (C-H), 698 (C-H).

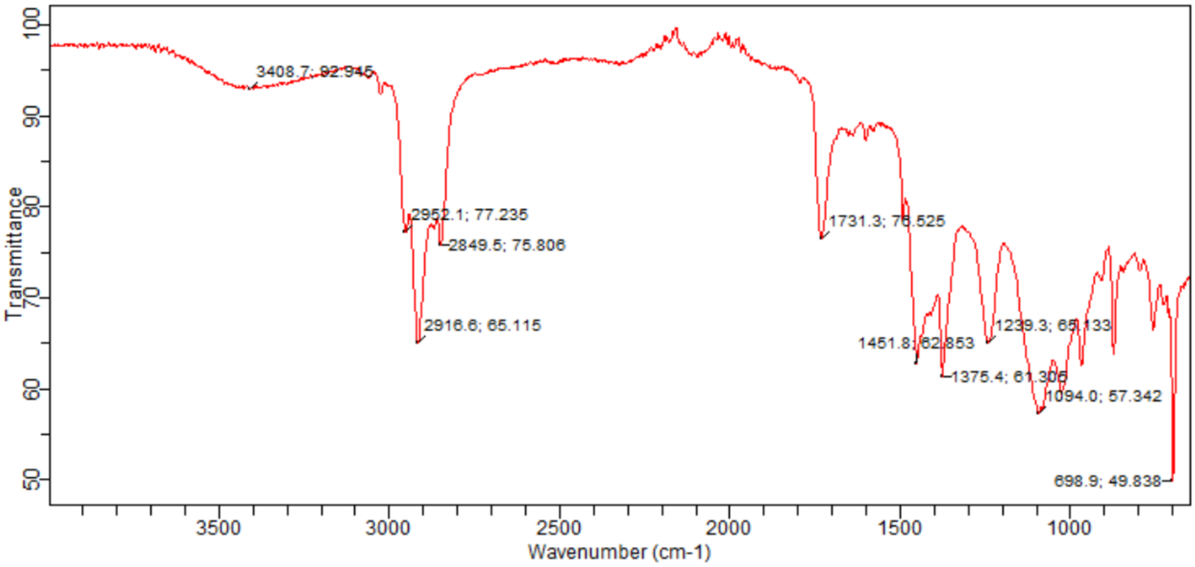


Figure S45. *FTIR spectrum of organic material extracted from shredded post-industrial carpet fibres with chloroform.*

GC ($CHCl_3$, PTFE filtered)

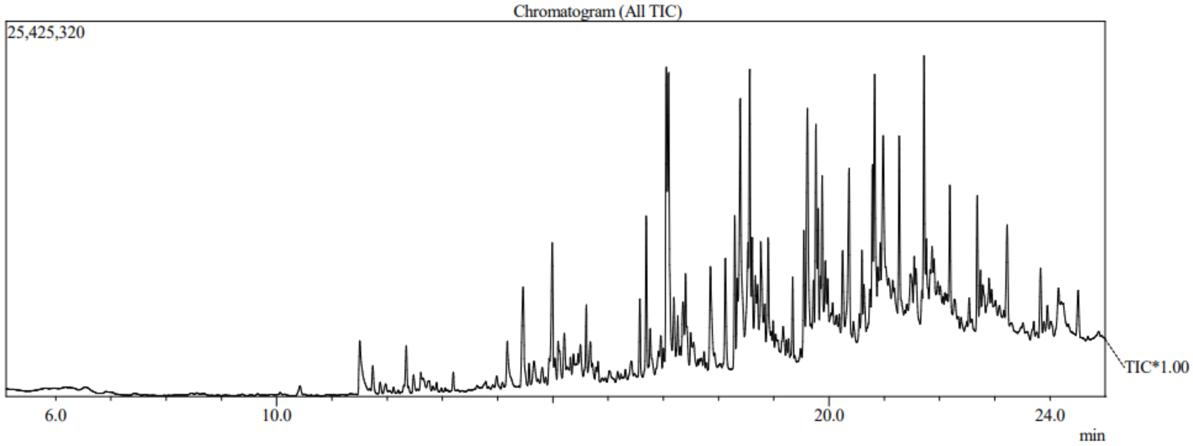


Figure S46. *GC-MS chromatogram of organic material extracted from shredded post-industrial carpet fibres with chloroform.*

6.4.1.2 Post-consumer fibres

Following solvent extraction with chloroform, post-consumer fibres (9.0 g) gave 228 mg of dark grey waxy solid (2.5% mass recovery)

IR ν_{max} (neat, cm^{-1}): 2919 (C-H), 2850 (C-H), 1730 (C=O), 1452 (C-H), 1375 (C-H), 755 (C-Cl), 699 (C-H).

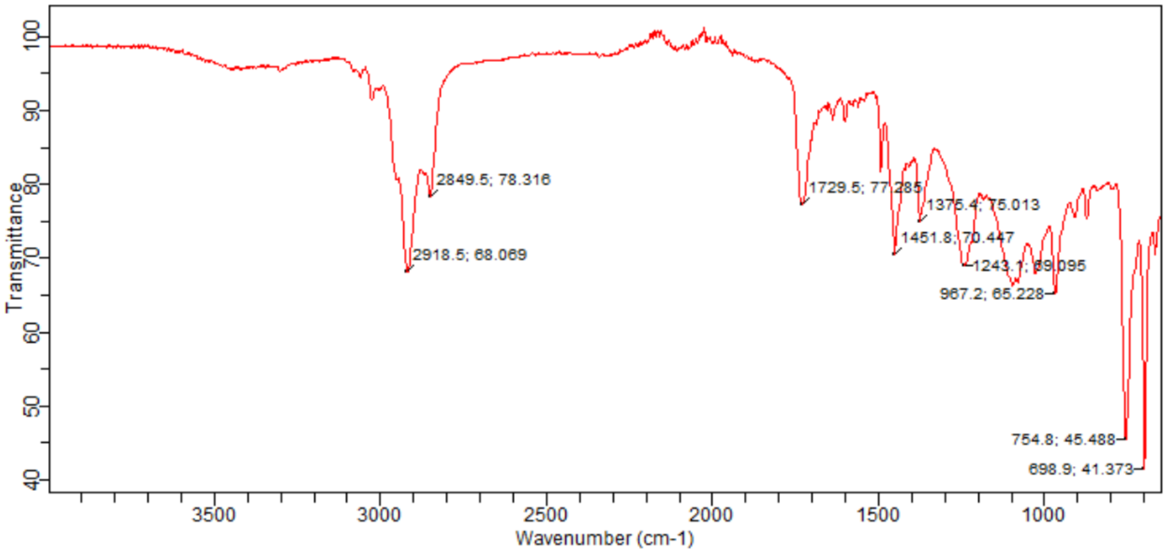


Figure S47. *FTIR spectrum of organic material extracted from shredded post-consumer carpet fibres with chloroform.*

GC ($CHCl_3$, PTFE filtered)

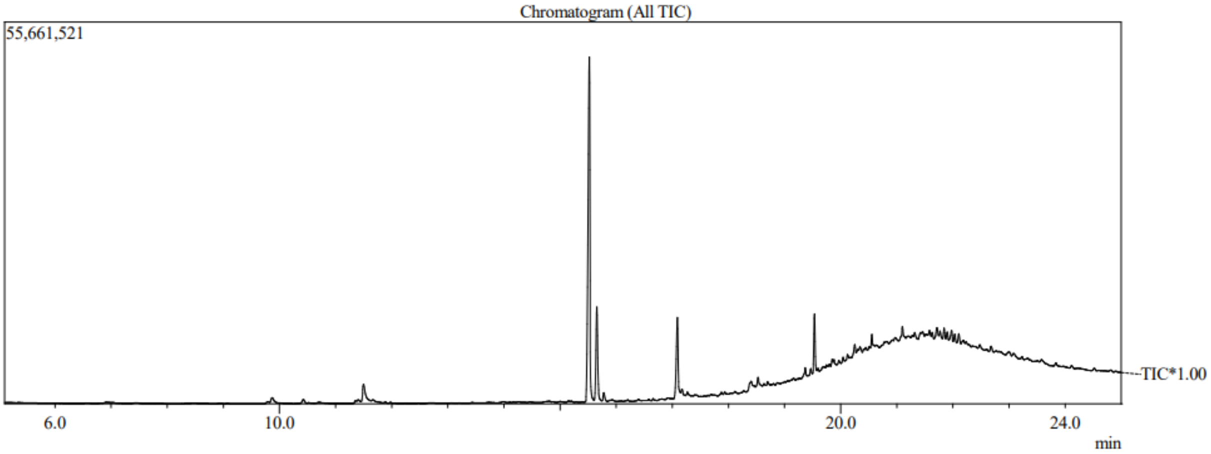


Figure S48. *GC-MS chromatogram of organic material extracted from shredded post-consumer carpet fibres with chloroform.*

6.4.1.3 Underlay

Following solvent extraction with chloroform, underlay (5.0 g) gave 540 mg of dark orange oil (11% mass recovery)

IR ν_{max} (neat, cm^{-1}): 2922 (C-H), 2853 (C-H), 1724 (C=O), 1457 (C-H), 1377 (C-H), 755 (C-Cl).

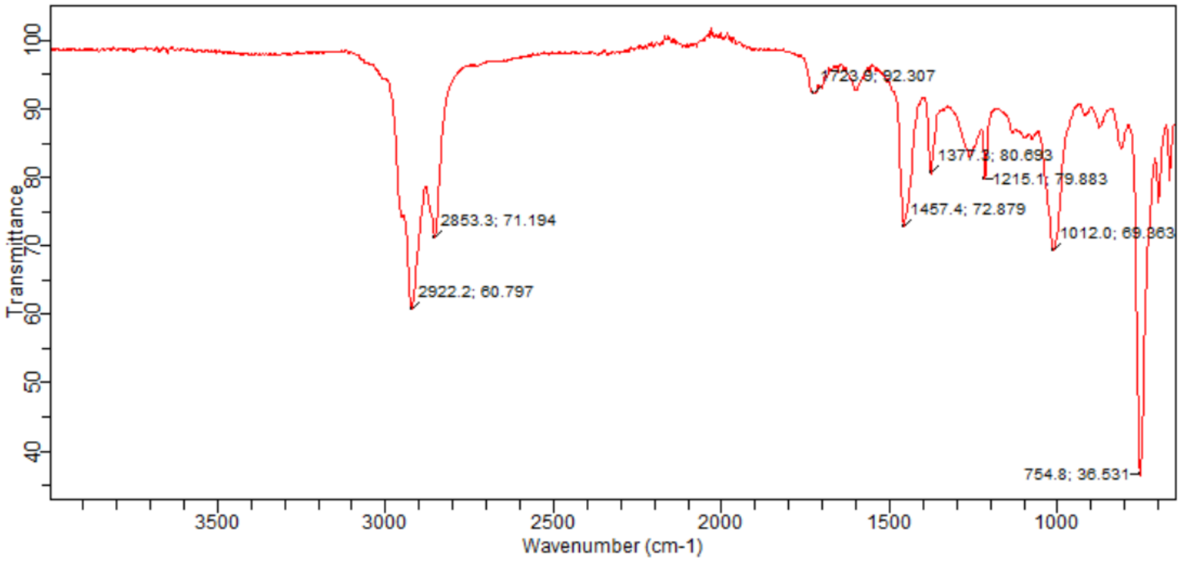


Figure S49. *FTIR spectrum of organic material extracted from shredded underlay with chloroform.*

GC ($CHCl_3$, PTFE filtered)

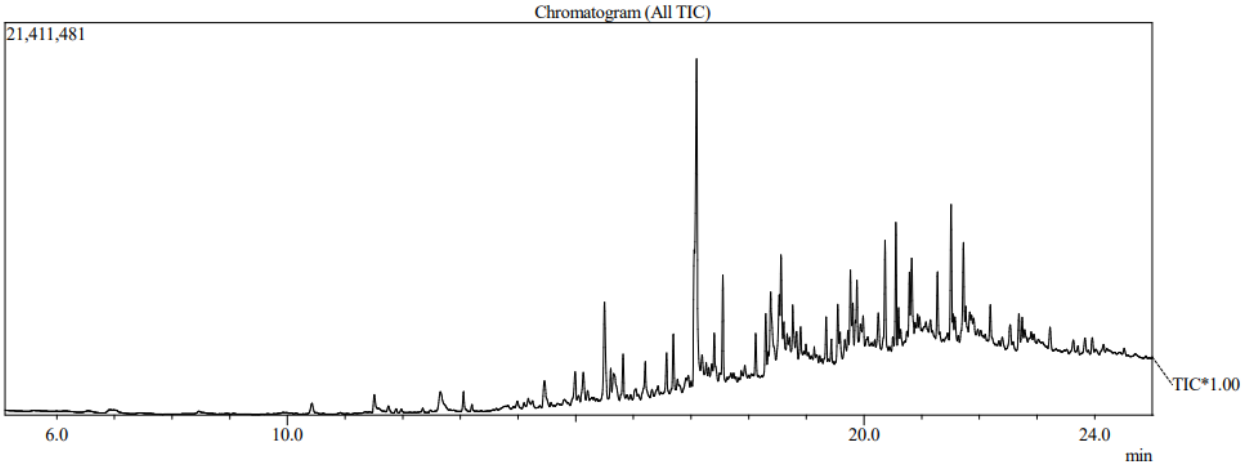


Figure S50. *GC-MS chromatogram of organic material extracted from shredded underlay with chloroform.*

6.4.2 EDX Analysis

Samples of unused and used fibres were analysed via SEM-EDX to assess the purity before and after incorporation into a surface. Here, unused fibre refers to post-consumer and post-industrial fibres which have not yet been used in equestrian surfaces.

EDX analysis was performed according to the procedures described in Section 2.6.7. All data for **EOL1** fibres shown here are for dewaxed fibres, i.e. those isolated following extraction of the **EOL1** surface with chloroform.

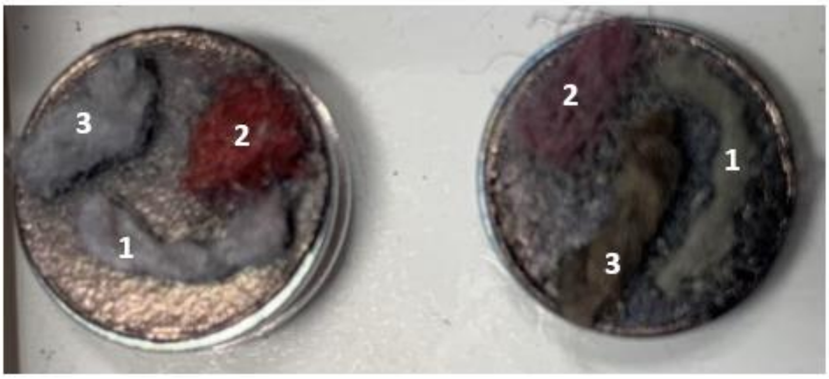
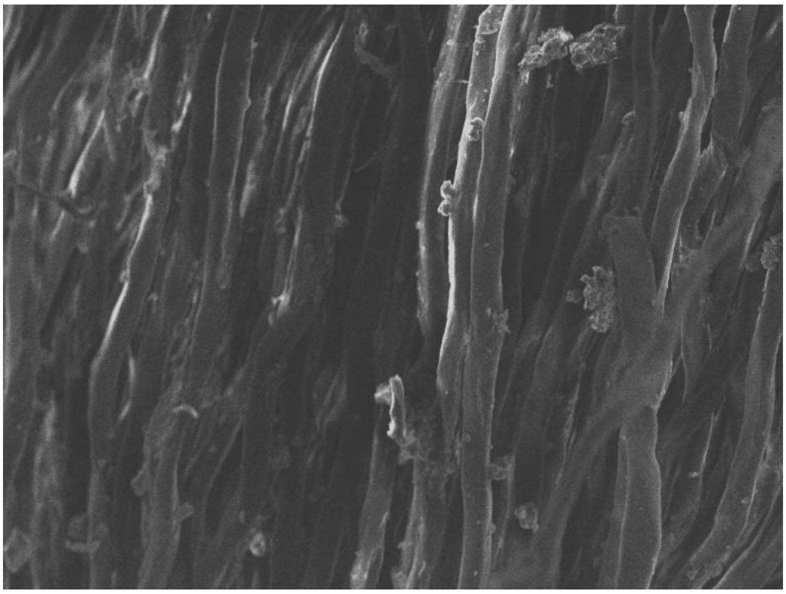


Figure S51. *SEM samples before analysis showing (a) post-industrial/post-consumer fibres, and (b) dewaxed fibres isolated from* ***EOL1*** *surface.*

6.4.2.1 Post-industrial & Post-consumer Fibres



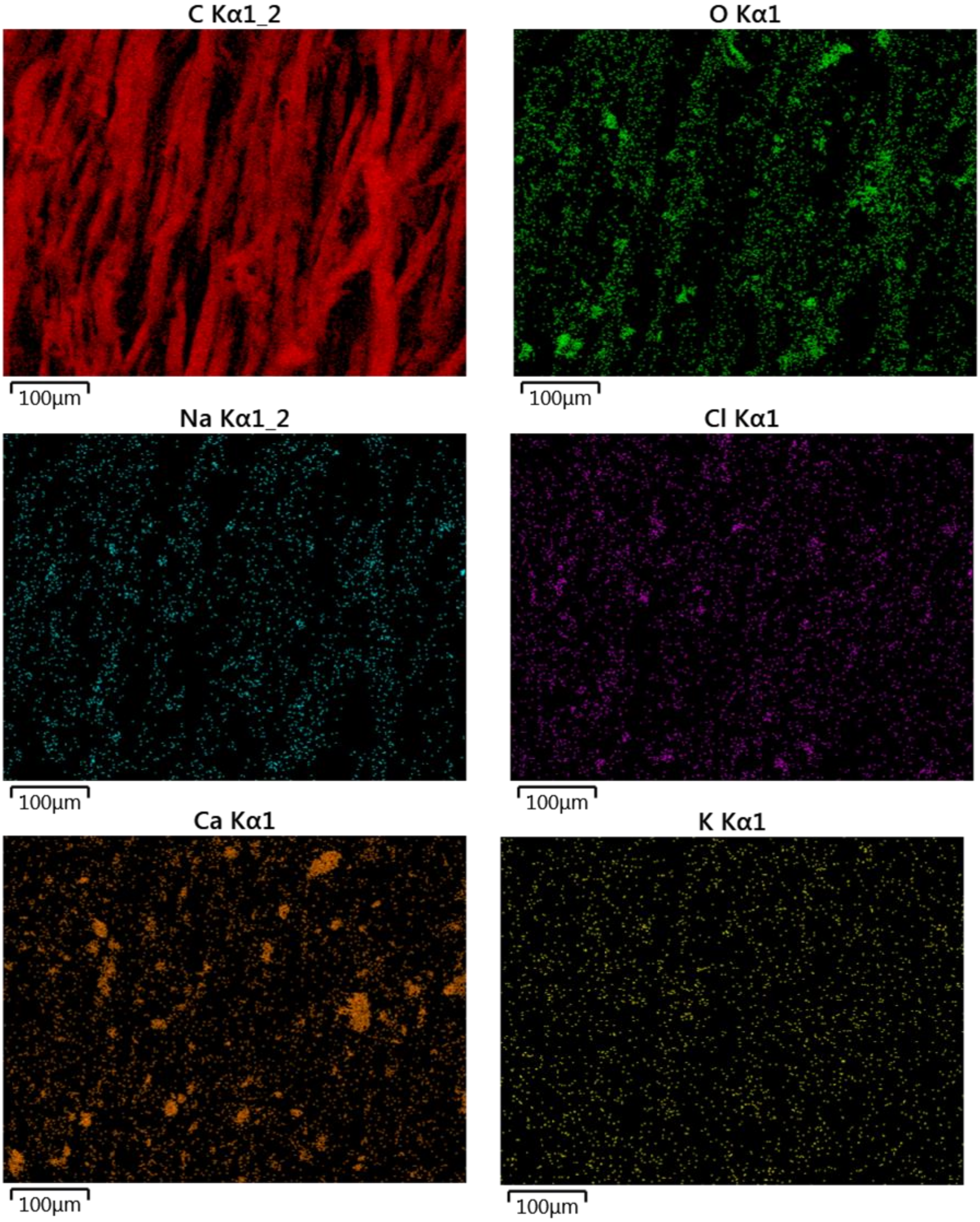


Figure S52. *EDX surface maps showing the elemental distribution of fibre 1 from the post-industrial/post—consumer fibres. X100 magnification*

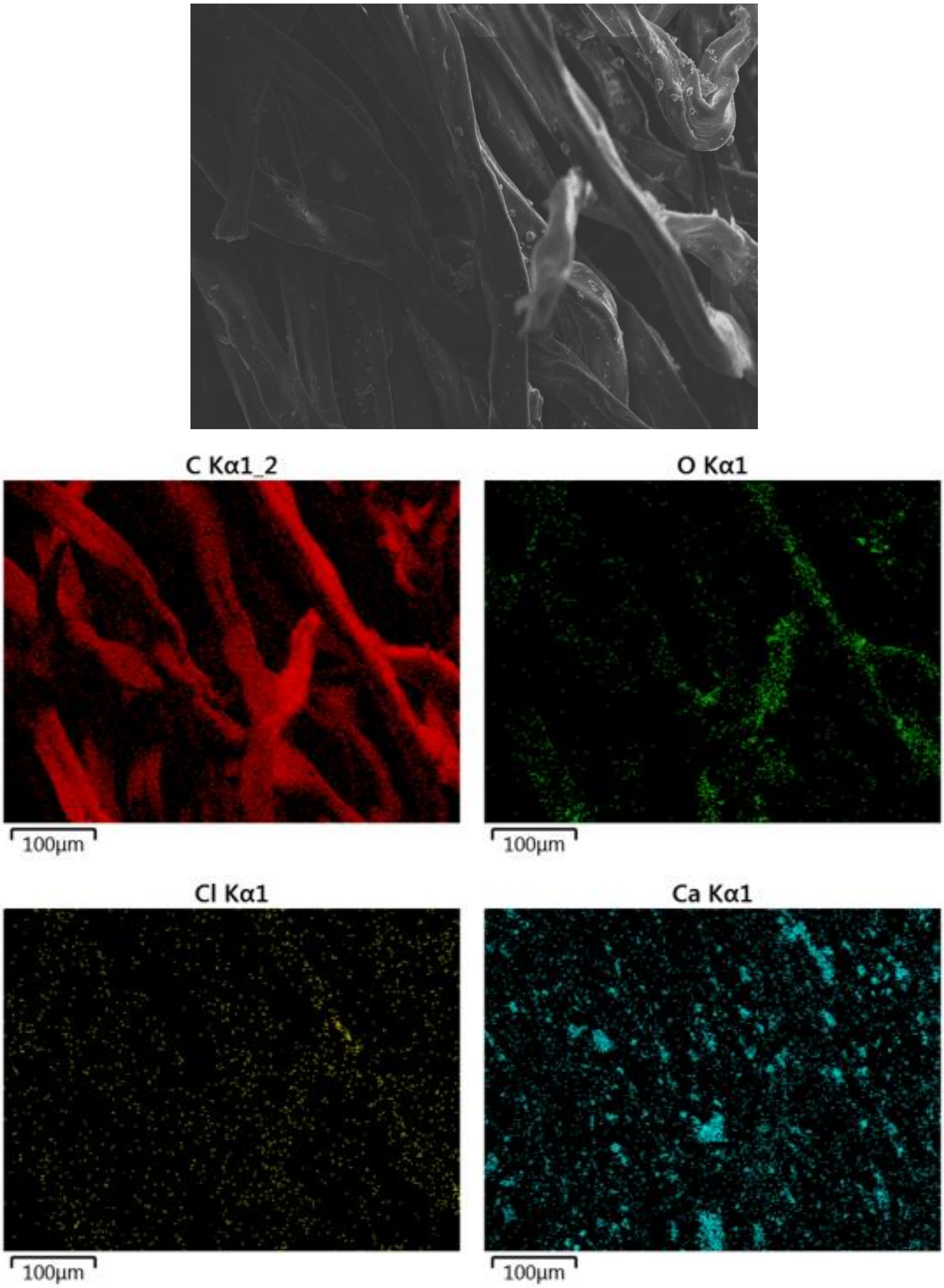


Figure S53. *EDX surface maps showing the elemental distribution of fibre 2 from the post-industrial/post—consumer fibres. X100 magnification*.

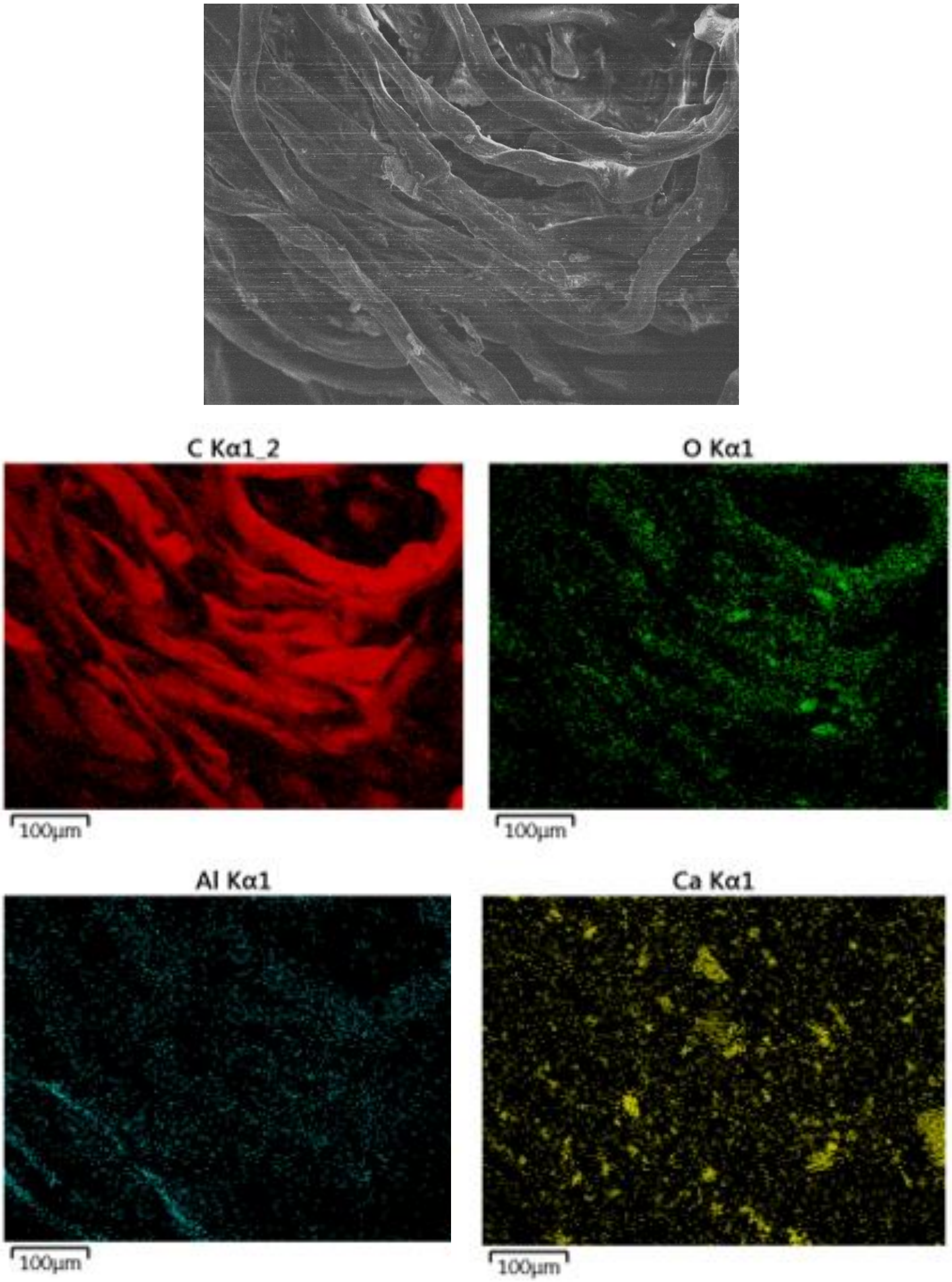
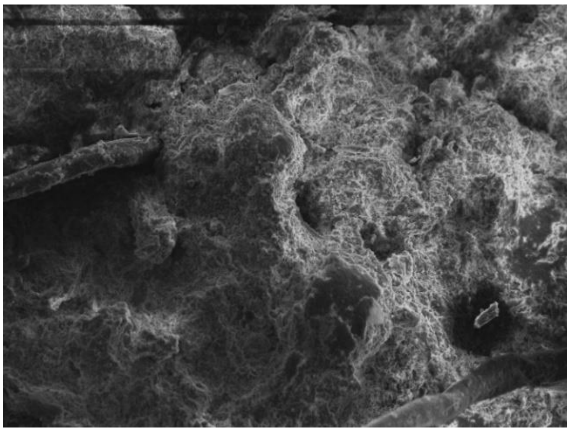


Figure S54. *EDX surface maps showing the elemental distribution of fibre 3 from the post-industrial/post—consumer fibres. X100 magnification*.

6.4.2.2 EOL1 Surface Dewaxed Fibre



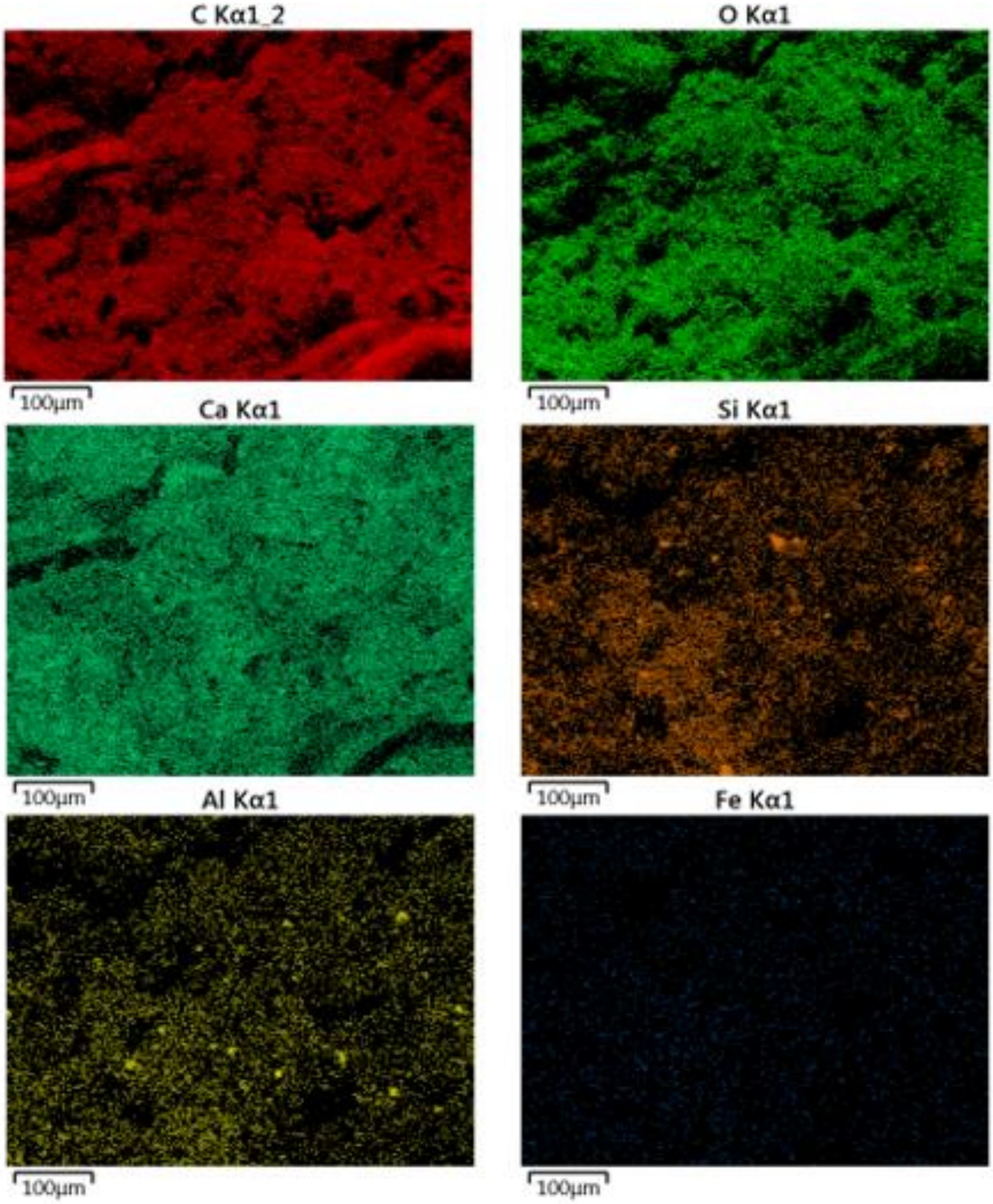


Figure S55. *EDX surface maps showing the elemental distribution of fibre 1 from the **EOL1** surface dewaxed fibres. X100 magnification*.

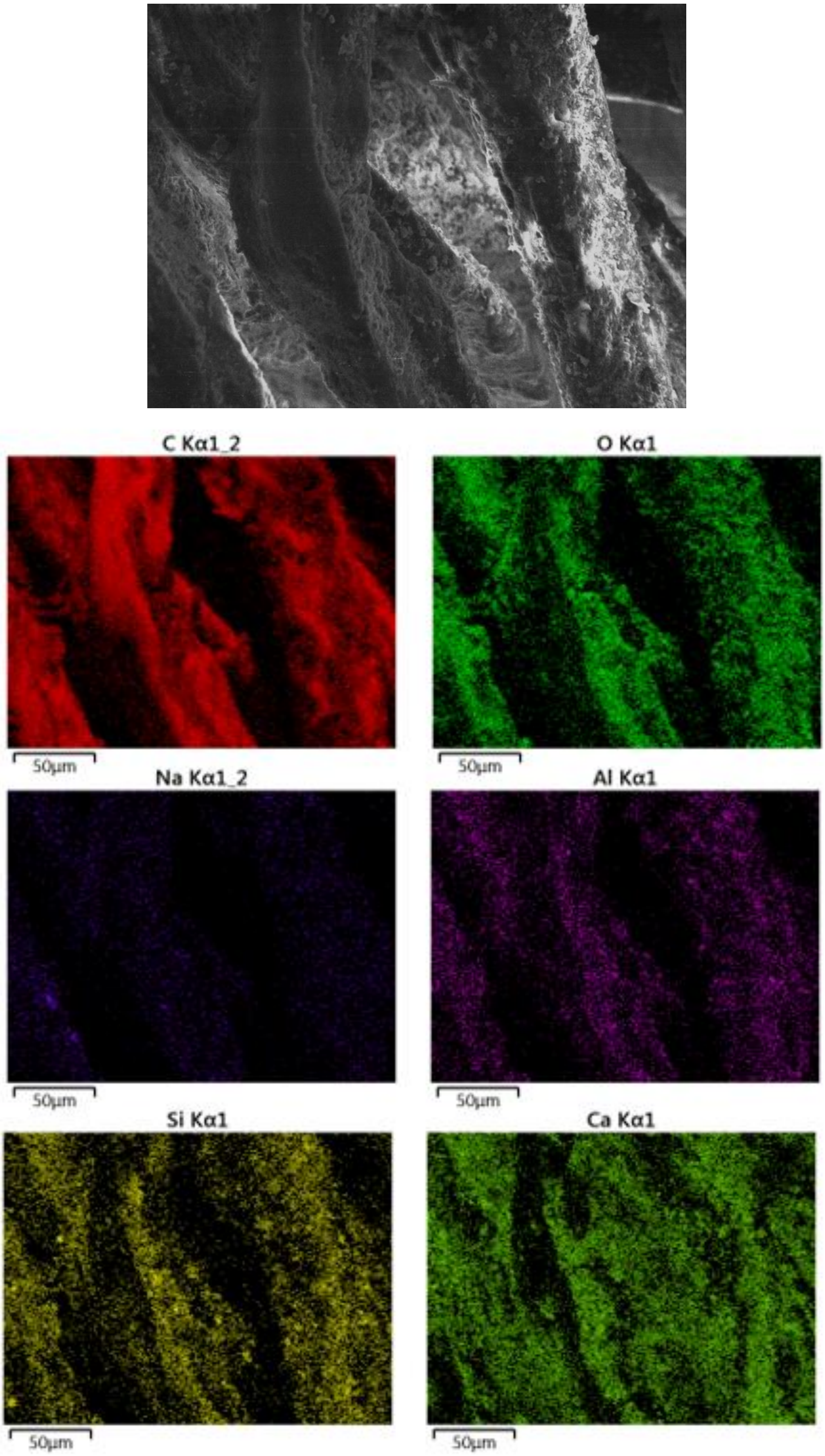


Figure S56. *EDX surface maps showing the elemental distribution of fibre 2 from the* ***EOL1*** *surface dewaxed fibres. X100 magnification*.

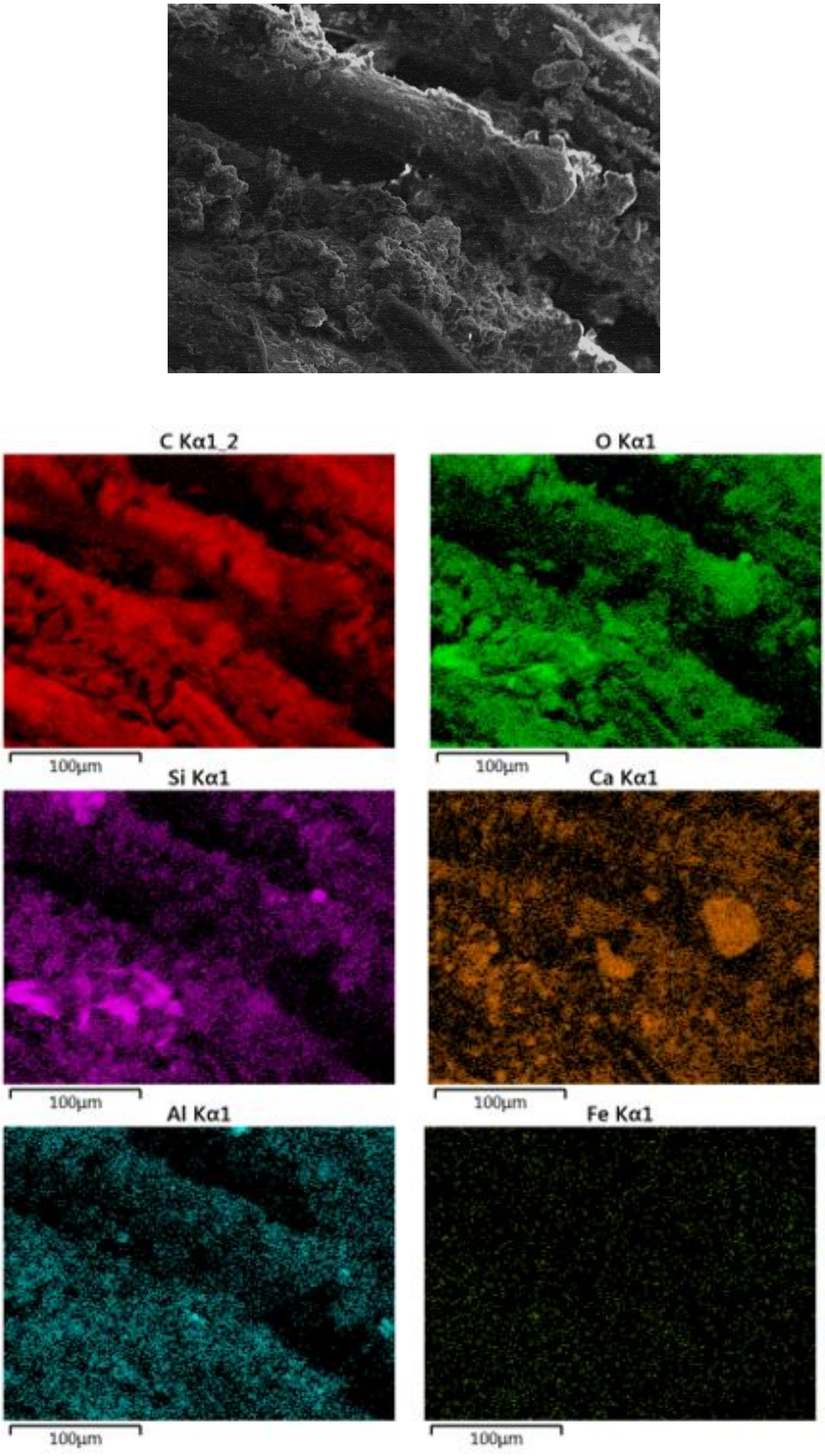


Figure S57. *EDX surface maps showing the elemental distribution of fibre 3 from the* ***EOL1*** *surface dewaxed fibres. X100 magnification.*