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Article

A Spectroscopic DRIFT-FTIR Study on the Friction-Reducing Properties and Bonding of Railway Leaf Layers

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Abstract

Leaves react with rail steel and form a tribofilm, causing very low friction in the wheel/rail interface. This work uses twin-disc tribological testing with the addition of leaf particulates to simulate the reaction and resulting reduction in the friction coefficient in a laboratory setting. Diffuse Reflectance Fourier-Transform Infrared Spectroscopy was carried out on the organic material and the layers that formed on the twin-disc surface. Dark material, visibly similar to leaf layers formed on tracks during autumn, was used along with a transparent thin film. This “non-visible contamination” has been reported to cause low-adhesion problems on railways, but has not previously been characterised. This article discusses the nature of these layers and builds upon earlier studies to propose a degradation and bonding mechanism for the leaf material. This understanding could be used to improve friction management methods employed to deal with low adhesion due to leaves.

Keywords: low friction; rail; leaf layer bonding; FTIR

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1. Introduction

Deciduous leaf fall in the autumn season can cause very low friction conditions between wheel and rail. Leaves can fall or be blown onto the rail by wind or vehicle air flow, where they react and bond with the railhead, forming a layer that can be difficult to remove (Figure 1). Low friction can result in wheel slides, causing wheel and rail damage, and the inability to brake effectively can result in safety incidents such as signals passed at danger and station overruns, which, in the worst case, could result in a train collision. The build-up of organic material can produce an insulating layer causing track circuit failures. The estimated cost of low friction attributed to autumn leaf fall in the UK is GBP 350 million/year, with GBP 64 million being spent on rail cleaning and methods to improve friction conditions [1].

While it has been investigated extensively, the mechanism of low friction and the nature of bonding between organic material and the rail is still not yet fully understood. A better understanding of these could help develop improved friction management methods, preventing the leaves from bonding to the railhead, removing bonded leaves from the railhead and disrupting the mechanism of low friction.

Previous work has used a range of chemical and tribological techniques to enhance understanding of railhead leaf contamination. For example, Ishizaka [2] reported that a black precipitate formed from sycamore leaves caused low friction, with a carbon-based organic layer surrounding an iron oxide core, and proposed that dissolved iron ions could react with organics species to form an iron carboxylate chelate structure. Watson [3] reported that the black material was composed of iron tannate due to the reaction between tannins in the leaves and the iron in the steel. Zhu et al. proposed a two-layer model, indicating that the leaves had chemically reacted with the bulk material and significantly changed the chemical composition of the outermost surface [4].

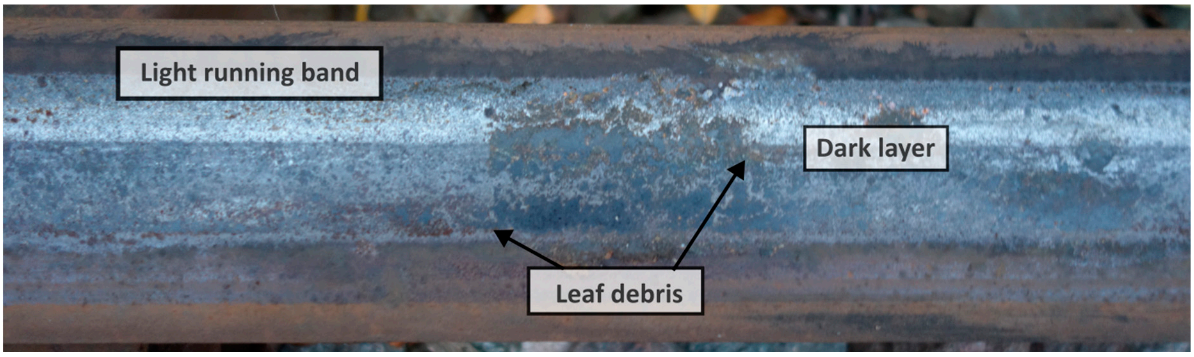

Figure 1. Leaf-contaminated railhead on a railway in the UK experiencing operational low-friction problems, highlighting the leaf degradation.

From this, it has been recognised that chemical reactions are key to leaf layer formation and bonding, but there may be several bonding or low-adhesion mechanisms resulting from different reactions between rail steel and leaf material components.

This paper builds upon previous work to assess the role of leaf layer components in producing low friction in the wheel/rail contact and how they may be broken down in the wheel/rail contact using a combination of tribological and spectroscopic techniques. Leaf layers were formed and their friction tested using twin-disc testing, with the results then compared to full-scale and field data.

A spectroscopic study on the degradation of organic material during twin-disc testing was carried out, which helps elucidate the mechanism of how organic material changes when entering the wheel/rail contact. Fourier-Transform Infrared Spectroscopy (FT-IR) was used to better understand leaf layer composition in this work because it offers rapid insight into the presence of key organic bonds that are known to influence friction, including alcohols and carboxylic acid groups. Furthermore, it is the optimal test for obtaining information on the state of any organic carbon species as thin films [5].

Specific focus was paid to the role of metal ions (most abundantly iron ions, which are known to be catalytically active) and their possible catalytic role in the process. There are many examples of iron catalysing biomass, including leaf components (lignin, cellulose, hemicellulose [6–9]).

2. Materials and Methods

2.1. Tribological Twin-Disc Methodology

Tribological tests were carried out to assess whether oak leaf powders could cause low friction, build up a layer representative of that formed in operational use and generate layer material that can be analysed using spectroscopic techniques. Analysing this layer can help us to understand the components that are causing low friction and how to better manage friction in the future.

Oak (Quercus robur) leaves were used to create a layer as they have previously been reported to reduce friction [10,11]. The oak leaves were collected after they had fallen during autumn in Sheffield, UK, and air-dried until brittle. The larger pieces of stem and veins were then removed before the material was blended and sieved to a maximum particle size of 1 mm (see Figure 2).

Location	Description
1	Leaf powder (before application)
2	Material ejected out of contact during the test, stuck to side of disc
3	Dark material on twin disc running band
4	Light material on twin disc running band

Figure 2. Test specimens before (**a**), during (**b**) and after (**c**) organic twin-disc testing.

Laboratory-based twin-disc tribological tests were chosen due to the ease of application of the organic material, controllable conditions and previously published leaf layer formation methodologies [12], which are harder to achieve in full-scale laboratory and field testing; however, layers have been created for these and can be useful when trialling mitigation methods, for example. The advantages and disadvantages of each method for generating a leaf layer are shown in Table 1.

Table 1. Contact conditions and advantages and disadvantages of generating a leaf layer for each tribological test.

Technique	Advantages	Disadvantages
Twin-disc (laboratory)	Easy to remove sample for analysis Realistic contact pressure and real wheel and rail material Standardised leaf layer formation method has been published [12]	Material ejected from contact/curved surface throughout test Typical autumn environmental conditions are difficult to replicate
Full-scale wheel/rail test rig (laboratory)	Real rail and wheel geometry. Length of rail used allows for ‘thermal sink’ similar to the mainline Controllable contact conditions “Pocket” rail can be removed for analysis	Typical autumn environmental conditions are difficult to replicate Cannot remove wheel sample for analysis
Field, using a locomotive to roll over the layer (friction measured using an OnTrak Tribometer)	Can measure field leaf layers under varying and representative environmental conditions	Difficult to remove sample for analysis Often expensive and time consuming to conduct field trials

The rolling/sliding line contact of twin-disc testing [13], as opposed to a purely sliding point contacts used on universal tribometers, more closely represents the wheel rail contact and provides more-representative entrainment of the organic third-body material. The material remains in the contact for multiple cycles (rather than being pushed aside), representing multiple train wheel passes. These repeated extreme contact conditions cause layer formation, and physical and chemical changes. Previous testing has successfully formed low-friction leaf layers using twin-disc test facilities [12].

The SUROS twin-disc test rig uses two counter-rotating steel discs, made of R260 rail and ER8 wheel steel. These can be rotated at independent speeds to apply creep to the contact. A methodology to create leaf layers was developed in previous work [14]. The tests were run at 900 MPa, 3% creepage (creepage appears to aid black leaf layer formation) and 400 rpm. The test parameters were chosen to represent a typical wheel tread/railhead contact stress and saturated creepage. Four repeats were taken for each rail condition. The test conditions have also been used for previous studies using leaf layers [3] to enable comparison with previous research [3].

Oak leaf powder was mixed with water in a glass beaker to a weight percentage of 20% organic matter. This produced a viscous slurry that could be fed through a wide-nosed syringe and tubing into the twin-disc contact. The discs were brought into contact and, once a dry traction coefficient of above 0.4 had been reached (with the running in procedure also generating a third-body layer containing iron oxide and wear particles), the organic slurry was applied to the contact. Oak leaf paste was then applied at 2 mL/minute for 2000 cycles (5 min), which built up a visible layer on the disc surface (Figure 2).

The twin-disc specimen surface had two dissimilar materials during and after the test: dark banding that appeared to be accumulations of loosely bonded powder and a light, transparent material that was well adhered to the steel specimen. The layer thickness of the dark material was approximately 2–5 µm, measured with an Alicona InfiniteFocus SL 3D non-contact profilometer. Due to the very thin, transparent film, the light layer could not be measured with available techniques for this study. Some material had also been ejected from the contact during testing and stuck to the side of the twin-disc specimen; this was analysed as an intermediate.

2.2. DRIFT-FTIR Spectroscopy Methodology

After tribological testing, the steel samples were wrapped in aluminium foil to prevent cross contamination when transported for spectroscopic analysis. Abrasive sticks were used to sample material from locations 1–4, as labelled in Figure 2.

Diffuse Reflectance Fourier-Transform Infrared (DRIFT-FTIR) Spectroscopy using a Perkin Elmer Frontier FTIR/NIR spectrometer with a DRIFT accessory was carried out by LPD Lab Services Ltd. on the leaf material for each location described in Figure 2, on the wheel disc, to determine which functional groups were present for each sample and assess material degradation. DRIFT-FTIR was developed for the analysis of non-homogenous materials such as powders; thus, it is ideally suited to this application, where there is likely a change in material composition during formation and degradation.

The spectrometer measures the amount of light that is eventually directed back to the detector of the spectrometer via a process of transmission, refraction and reflectance, which depends on the bulk properties of the sampled material. The whole process is described by the term "diffuse reflectance". There are losses of intensity associated with both the absorption and transmission processes, and the spectrum obtained is a combination of the spectra generated by the sample medium (including the sample holder; this is accounted for by recording a background spectrum which is subtracted by the software).

3. Results

3.1. Tribological Twin-Disc Results

The twin-disc testing showed a visual change when the organic material was exposed to the steel, alongside a large reduction in the friction coefficient, as shown in Figure 3. The dry baseline test had a median friction coefficient of 0.52, depending on test rig, within previously reported thresholds for dry values [15]. Twin-disc testing often produces a high dry friction coefficient, explained by previous work due to the thicker natural third-body layer (made up of wear debris/oxides) in comparison to steel substrate roughness, creating a higher shear viscosity [16].

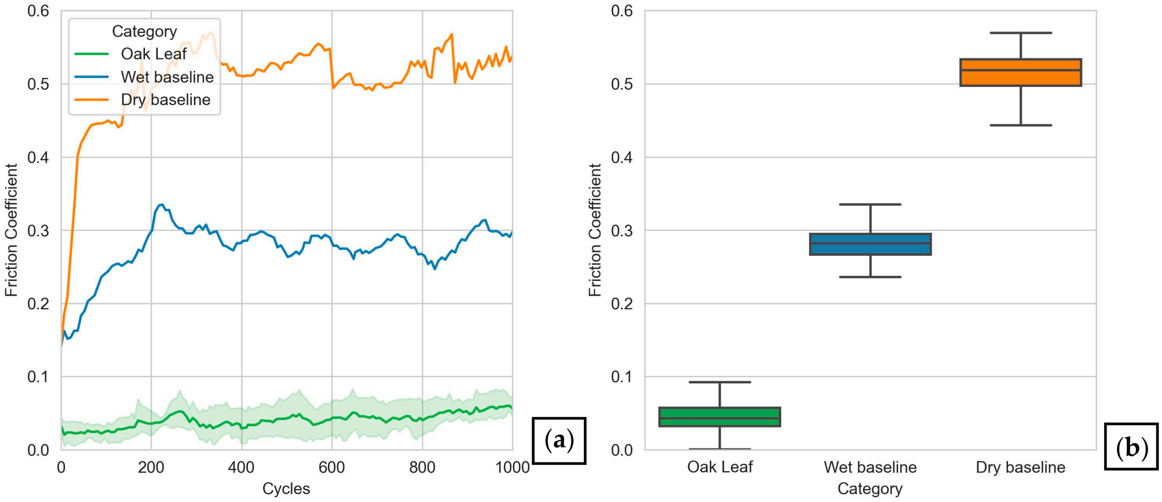

Figure 3. Twin-disc test friction results: (**a**) the first 1000 test cycles (the shaded area of "Oak Leaf" results show the 95% percentile and the solid line the mean, over 4 repeats); (**b**) a box plot of twin-disc results for each test category. The central line represents the median, the box representing the upper and lower quartile and the whiskers the minimum and maximum.

The organic material visibly reacted to form black material when added to the twin-disc contact, also observed on an operational railway when a vehicle runs over leaf material (Figure 1). During twin-disc testing, this loosely bound black material accumulated and some was ejected from the contact; this was visible from the residue that surrounded the disc holders after the test. There were darker areas of the contact band that resembled a loosely bonded powder. The lighter central band of the test specimens formed during the test, which had no loose powder and resembled a polished metallic surface. Spectroscopic analysis was carried out to assess the chemical changes that happened to the material in the subsequent section.

3.2. DRIFT-FTIR Spectroscopy Results

3.2.1. Raw Powdered Material (Sample 1)

The spectra are shown as "%R", i.e., percentage reflectance, which is analogous to the commonly encountered transmission spectra: the more intense the peak, the "deeper" the trough observed. The wavenumber associated with this trough can be used to assess which functional group—and therefore the likely leaf component—is present.

The DRIFT-FTIR results showed that the oak leaf powder was composed of water, lignin, cellulose, hemicellulose and tannins, which correlates to previous work [17,18]. The spectrum of the raw dry powdered material is shown in Figure 4, and peak assignment information, showing the wavenumbers of peaks in the spectra and likely organic component attributions, is shown in Table 2.

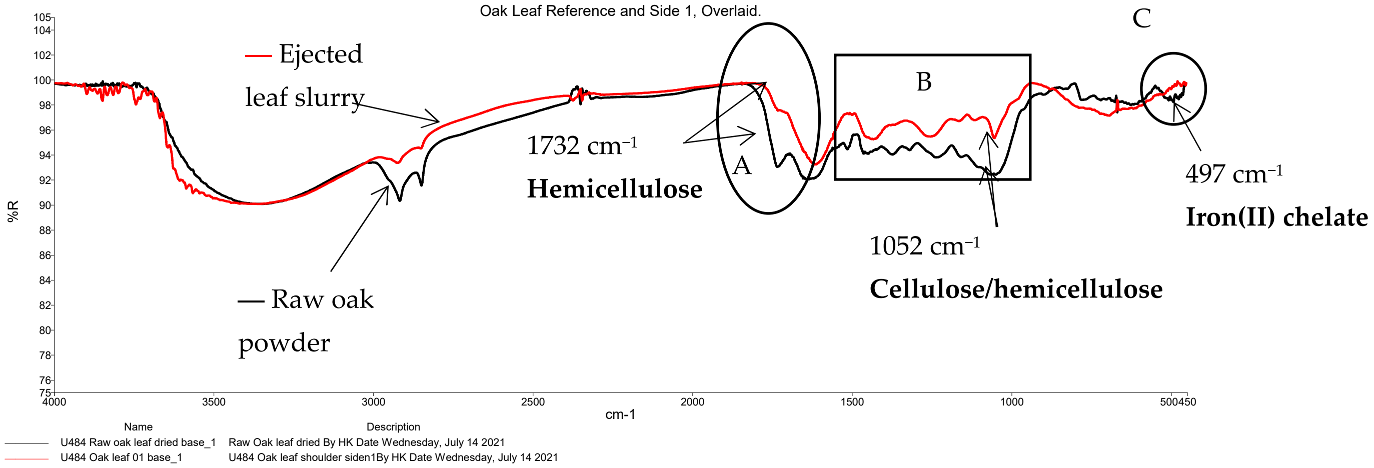

Figure 4. DRIFT-FTIR spectra of oak leaf reference (black line) and "ejected" leaf slurry material from twin-disc test (red line) (A: Hemicellulose; B: Cellulose/hemicellulose; C: Iron(II) chelate).

Table 2. Peak assignment spectra for the dry leaf powder.

Oak Leaves	**Assignment and Comments**	**Attributed to...**
Wavenumber/ cm^{-1}		
1635	Aromatic skeletal C=O stretch	Lignin
1514	C=C stretching of aromatic skeletal vibration	Lignin
1448	C=C and C-H bond. O-H in plane deformation	Lignin and hemicellulose (C-C)
1373	C-H deformation vibration	Cellulose
1318	C-H deformation vibration	Cellulose
1235	Indicates the syringyl ring of synaptyl alcohol (also present in the lignin structure), also C-O stretch)	Lignin and xylan (a hemi-cellulose).
1157	C-O-C symmetric stretching	Cellulose and Hemicellulose
1049	C-O stretch	Cellulose and hemicellulose.
836	Aromatic C-H, out-of-plane deformation	Lignin and tannins.

3.2.2. Ejected Material Found on Side of Test Specimen (Sample 2)

Two samples were taken for the ejected material (both sides of the twin-disc specimen) to assess the consistency of material ejected from the twin-disc contact; there was very little difference in DRIFT-FTIR spectra between them, so only one set of results is presented here.

The spectra from one sample and peak assignments are shown in Figure 4 and Table 3 and compared to the oak leaf powder before testing. Compared to the raw powdered material, free water was lost and there is a reduction in the peak at 1732 cm^{-1} for the ejected material. This peak is assigned to carbonyl (C=O) bonding of the hemicellulose, suggesting that the carbonyl group is being lost from the samples. This contrasts with the peak at 1618 cm^{-1}, which arises from the carbonyl of the lignin content, which is only a little reduced.

Table 3. Peak assignment data for oak leaf powder and "ejected" leaf slurry material from the twin-disc test.

Material from Flat Side 1		**Material from Flat Side 2**		**Assignment and Comments**	**Attributed to...**
Peak No.	**Wavenumber cm^{-1}**	**Peak No.**	**Wavenumber cm^{-1}**		
1–20	3950–3500	1–9	3950–3500	This type of "noise" indicates that free water is present in the sample which was analysed as received. Side 1 appears to be wetter than side 2.	Water
21	3359	10	3406	Broad group indicating the presence of H-bonded OH groups. The breadth of the peak suggests a multiplicity of chemical environments.	Lignin, cellulose, polysaccharides, and tannins
22	2926	11	2926	CH_3 group (typically terminates an organic molecule or a branch of one).	Lignin
23	2853	Present		CH_2 group (typically occurs in the backbone of an organic molecule).	
24–26	2375–2250	12–14	2375–2250	Carbon dioxide	
28	1732	Present, but indistinct		C=O stretch of acetyl and carbonyl groups	Hemicellulose
29	1618	15	1621	Aromatic skeletal and C=O stretch vibration	Lignin
30	1432	16	1428	C=C and C-H bond. O-H in plane deformation	Lignin and Hemicellulose
31	1252	17	1263	G-ring plus C=O stretch	G-Lignin
32	1164	18	1160	C-O-C symmetric stretching	Cellulose and Hemicellulose
33	1115	19	1110	Ring asymmetric valence vibration	Polysaccharides
34	1053	20	1050	C-O stretch	Cellulose and Hemicellulose
39	497	27	502	Likely Fe(II)-O bond in a chelate	Iron(II) chelate

Between 3000 and 3700 cm^{-1}, there is a broad peak which arises from hydroxyl (OH) groups of the polysaccharide (hemicellulose and cellulose) components of the oak leaf. Disappearance of this peak would indicate either the disappearance of those compounds or their oxidation. Hydroxyl groups are usually oxidised by the formation of aldehydes, ketones or carboxylic acids, all of which contain the carbonyl groups (C=O) in their structure. Although this group, shown by the band at 1732 cm^{-1}, appears to be present in the oak leaf, probably arising from the hemicellulose, it is smaller in the samples from the ejected material. This suggests that rather than oxidation of the hydroxyl groups, the component with this carbonyl group, identified as hemicellulose, has been lost from the samples after being broken down.

The region marked "B" in Figure 4 evidences a number of shifts in wavenumber, which may suggest changes in chemical environment, in particular, the sharpening of the peak at 1052 cm^{-1}, which may imply that the chemical environment here has simplified, with changes causing a more uniform orientation of the bond giving rise to this peak.

There is a small peak attributed to a Fe-O bond in an iron(II) chelate. This was identified by comparing against the spectra in previous analysis of iron(II) and iron(III) oxalates [19], which gave a peak arising from this bond at 493 cm^{-1} and 'ferric oak tannate' at approximately 500 cm^{-1} [18]. Iron may be chelated by tannins due to the hydroxyl groups on the aryl ring of tannins, which was previously reported during previous testing of leaf material friction effects [3].

3.2.3. Dark Material (Sample 3)

The spectra for the dark contact band sample and the ejected material, along with peak assignments, are shown in Figure 5 and Table 4. Cellulose and possibly hemicellulose were found in the dark areas of the contact band, along with polysaccharides, lignin and tannins. Compared to the raw powdered oak leaf, there is a reduction in the peak at 1734 cm^{-1}, which corresponds to the C=O stretch in the hemicellulose.

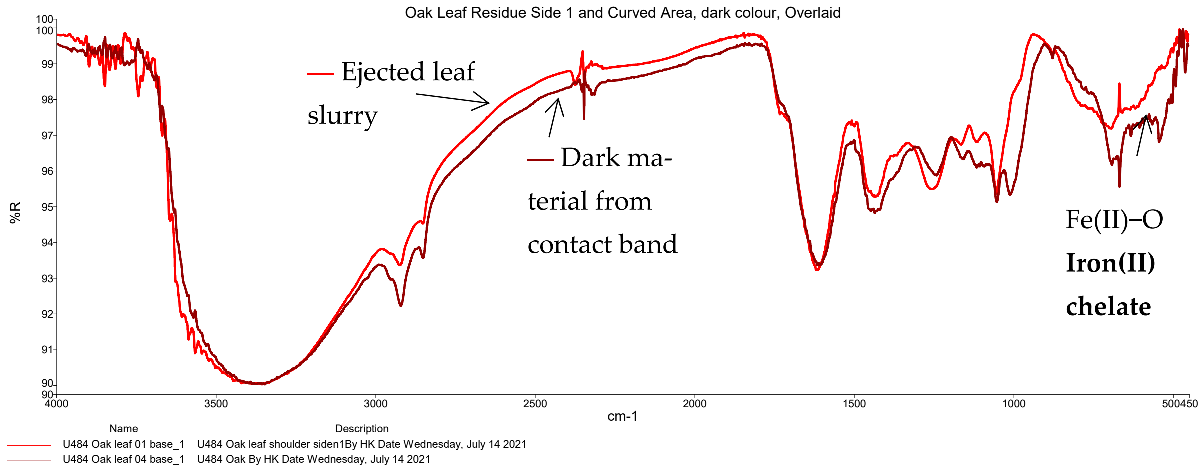

Figure 5. DRIFT-FTIR spectra of the sample of oak leaf residue taken from the dark area of the curved surface (brown line) compared to "ejected" leaf slurry material from the twin-disc test.

Table 4. Peak assignment data for the oak leaf residue sample taken from the dark area of the curved surface and "ejected" leaf slurry material from the twin-disc test.

Peak Number	**Wavenumber/ cm^{-1}**	**Assignment and Comments**	**Attributed to...**
1–19	3960–3550	Presence of free water	Water
20	3350	Broad group indicating the presence of H-bonded OH groups.	Lignin, cellulose and poly saccharides, tannins
21	2923	CH_3 group (typically terminates an organic molecule or a branch of one).	Many organic compounds, Lignin
22	2852	CH_2 group (typically occurs in the backbone of an organic molecule).	

Table 4. *Cont.*

Peak Number	Wavenumber/ cm^{-1}	Assignment and Comments	Attributed to…
23–25	2350–2320	Carbon dioxide	
26	1614	Aromatic skeletal C=O stretch	Lignin
27	1435	C=C, C-H bonds/OH deformation. (C-C), C=C (aryl) in lignin and tannins	Lignin, hemicellulose and tannins
28	1240	Indicates the syringyl ring of synaptyl alcohol (present in the lignin structure), also C-O stretch)	Lignin and xylan (a hemi-cellulose).
29	1157	C-O-C symmetric stretching	Cellulose and Hemicellulose
30	1114	Not assigned	
31	1091	Ring asymmetric valence vibration	Polysaccharides
33	1010	C-O stretch	Cellulose and Hemicellulose
34	876	Aromatic C-H out-of-plane deformation	Cellulose, hemicellulose, and pectin
43	508	Ring deformation	
44	500	Likely Fe(II)-O bond in a chelate	Iron(II) chelate

There appears to be a higher concentration of iron chelate, observed as an Fe(II)-O bond at 500 cm^{-1} [18], compared to the ejected material found on the side of the test specimen.

3.2.4. Light Material (Sample 4)

The spectra for the light and dark areas of the contact band and peak assignments are shown in Figure 6 and Table 5. The spectrum is less intense for the light-coloured areas compared to the darker areas, showing that there is less light material than dark. So, while organic film was detected, the light-coloured material is likely much thinner than the dark material.

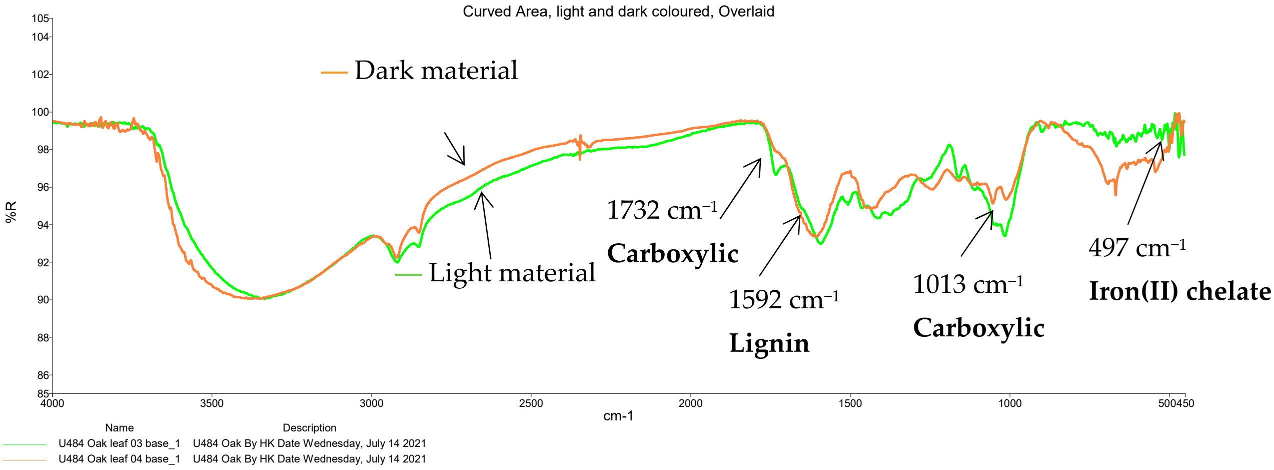

Figure 6. Overlaid spectra of light (green line) and dark (orange line) areas of the layers on the twin-disc specimen from the oak leaf experiment.

Table 5. Peak assignment data for light and dark areas of the layers on the twin-disc specimen from the oak leaf experiment.

Peak Number	Wavenumber/cm^{-1}	Assignment and Comments	Attributed to...
1	3338	Broad group indicating the presence of H-bonded OH groups. Nearly absent in the oak bark sample.	
2	2920	CH_3 group (typically terminates an organic molecule or a branch of one).	Many organic compounds, lignin
3	2857	CH_2 group (typically occurs in the backbone of an organic molecule).	
4	1732	C=O stretch from acetyl or carbonyl group	Carboxylic acid
5	1592	Aromatic skeletal C=O stretch	Lignin
8	1158	C-O-C symmetric stretching	Cellulose and hemicellulose
		Not assigned	
9	1013	C-O stretch	Carboxylic acid
10	898	Aromatic C-H, out-of-plane deformation	Lignin and tannins
	520	Ring deformation	
	497	Possible Fe(II)-O bond in a chelate	Iron(II) chelate

At 1158 cm^{-1}, there is a peak indicating the presence of cellulose or hemicellulose. The peak at 1592 cm^{-1} representing lignin is persistent and indicates that the lignin remains present. The iron chelate was still present. The presence of carbonyl groups in the light-coloured material suggests the presence of carboxylic acids, which would imply that oxidation has taken place.

It is suggested that the loss of colour may be due to the destruction, or loss by other means, of the tannins, resulting in a colourless residue. In a railway situation, this leads to the suggestion that organic low adhesion could take place where no organic contamination is visible to the naked eye.

4. Discussion

Normal service brake application in the UK typically requires a friction coefficient of at least 0.09 [15]. The oak leaf layer reduced friction to a median average of 0.04, which would be classed as an "ultra-low" friction level on an operational railway, impeding traction and braking. This ultra-low-friction coefficient after leaf application has also been measured using full-scale wheel/rail test facilities [20,21].

The dark band on the running surface is visibly similar to that observed in the field. The dark colouration has been hypothesised to be produced by iron tannate [3], and the current work reinforces this. There is an increased concentration of iron(II) chelate and a decreased concentration of hemicellulose and polysaccharides compared to the ejected material, which is in agreement with findings from [22]. The light/transparent material in the central contact band was well bonded to the steel substrate and may represent a final degradation product. It contained lignin with an iron-chelated material, with the lighter colour due to the destruction of tannins under the temperatures and pressures of the twin-disc contact. Lignin is a highly cross-linked polymer which may render it more stable under these extreme conditions. The light-coloured material also contains carbonyl groups suggesting the presence of carboxylic acids, which were previously hypothesised to form iron carboxylates [2].

It is proposed that the ejected material from the twin-disc testing represents an intermediate degradation material. Compared to the raw material, there is a loss of free water, reduction in hemicellulose and a small amount of iron(II) chelate formed.

In the operational railway, low friction was reported due to "non-visible contamination" and "when the visible leaf layer is removed from the rail the wet rails still remain extremely slippery. It is not clear why this is so." [23]. In the current work, the black layer appeared more loosely bonded and visibly obvious than the transparent thin film, which reflects these field observations.

The peaks found in this sample are as expected for the raw leaf material. Attention is brought to the presence of 'aromatic' carbon species (planar molecules rich in pi-electrons, similar to graphite in structure) [24,25]. While these were expected, it should be noted that other pi-electron-rich carbon compounds like graphite and graphene are known for their low-friction behaviour [26,27]. In addition, alcohol or O-H bonds are noted in the sample. These functional groups are able to form hydrogen bonds, another mechanism by which low friction on steel is often achieved [28,29]. These may oxidise during the process of leaf degradation to form carboxylic acids, which were found in the light material in the tribological contact.

The formation of iron tannate is noted in the literature. In one study, tannic acid reacted with metallic iron to precipitate ferric tannates. Mono-complexes were formed at first, followed by the bis-type complex [30]. The precipitated tannates formed a corrosion-inhibiting protective layer.

Other research concluded that plant extracts in aqueous solution on steel substate inhibited the formation of corrosion products such as lepidocrocite and goethite, which have been previously identified as forming on rail steel, in situ, using a portable X-ray diffractometer [31]. Instead, insoluble chelating iron compounds were obtained, with a mixture of mono- and bis-type complexes.

Some research has focused on using this effect in steel protection, rust-converting products and pigment for ink. Characteristic dark-coloured complexes formed after reactions between iron salts (Fe(III)) and polyphenols with hydroxyl (OH) groups in ortho positions [32]. These reactions also occurred between iron, corrosion products and polyphenols.

A stepwise formation of an iron tannate via two types of chelation is viable with the organic species present in leaves. It is notable that the film generated is described as 'protective' and being able to inhibit corrosion. This would be in line with the leaf-derived layers found on rail, which exhibit problematic anti-wear abilities (requiring high pressure water to remove or chemical solvation).

The presence of chelates in the sample, such as iron carboxylate formed from these carboxylic acids, helps elucidate a potential bonding hypothesis between the organic film and the metal beneath. Typically bonding between metal surfaces and carbonaceous films/layers is achieved using an intermediate layer when being produced in industry. This is because the surface of steel is quite polar and usually does not favour interactions with covalently bonded carbon. In the production of diamond-like carbon, a carbide interlayer is employed by manufacturers to ensure good bonding between the metal being coated and the carbon film [33].

The presence of chelating species here sheds light on how favourable bonds are formed between carbon compounds and a steel surface. Organic species appear to latch onto the electron-deficient iron species through oxygen's lone pairs. This helps to explain why the film is so strongly adhered when encountered on rail. It also indicates that the layer may be inherently wear-resistant as metal chelates are able to resist corrosion to a certain extent [34].

Scanning electron microscopy (SEM) images of the shoulder residue in separate unpublished testing using oak leaf bark powder, a readily available off-the-shelf alternative for simulating wheel/rail low friction, suggested that this residue is an agglomerate of fine particles of the bark with discreet calcium-rich crystals embedded in the matrix. EDX analysis showed that the agglomerate was mainly carbon and oxygen, with some calcium and iron. Small amounts of iron were observed in the EDX analysis, but no discreet iron particles were observed. This suggests that the iron may be part of the organic matrix.

Previous work has highlighted the formation of iron chelates on steel under a ball-on-flat tribological contact, and their ability to enhance chemisorption between steel substrate and organic molecules to create a low-friction layer. The removal of oxide layers in a sliding steel on steel contact provided defects which enhanced the chemisorption of iron carboxylate. The formation of this iron carboxylate was accelerated at high pressures and by local temperature increase due to friction [35]. During field trials involving leaf material, this layer has been formed by a single train pass [36], highlighting the rapid layer formation under the extreme contact conditions which are common between wheel and rail.

A schematic showing a proposed bonding mechanism is shown in Figure 7. A layer rich in iron chelates bonds to the freshly exposed rail steel, protecting it from corrosion and allowing further organic bonding, such as the easily sheared aromatic species or hydroxyl/alcohol-rich species identified during this work.

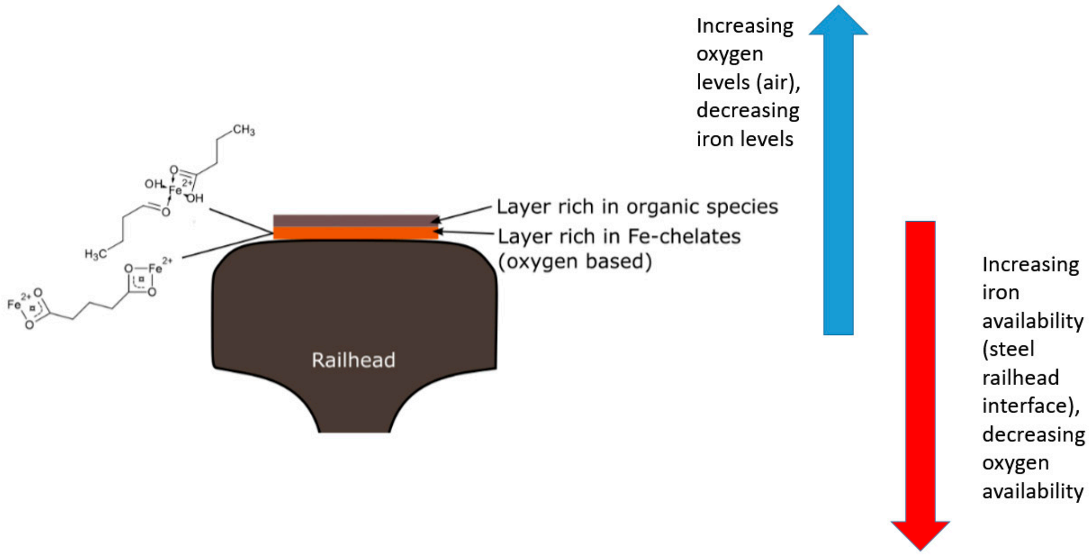

Figure 7. A proposed bonding mechanism involving mono- and bis-type insoluble chelating iron compounds.

Steel surfaces are polar in nature and tend toward reactions with sources of oxygen (such as rust formation). Chelation with an oxygen-containing species to the iron in the railhead is a potential mechanism by which temporary bonds are formed between the alloy's surface and the chelate. A larger number of oxygen groups in a chelate maximise these interactions to form stronger bonds.

As organic components are rich in oxygen-containing species that bind metals, these are able to react with the railhead as iron is revealed from the alloy (either from cleaning or wearing processes). The build-up of chelates upon the railhead should alter the surface energy when compared to the non-contaminated steel alloy. This change in surface energy is likely to accelerate further film formation.

Further work involving depth analysis of this layer, such as time-of-flight secondary ion mass spectrometry and X-Ray Photoelectron Spectroscopy, could be used for depth-profiling of these leaf layers at different points in their formation during tribological testing to investigate the proposed mechanism.

5. Conclusions

The autumn "leaves on the line" problem, specifically the formation of a black layer and accompanying reduction in friction coefficient when the leaf material reacts with rail and wheel steel, was simulated using a twin-disc test rig. The twin-disc tribological test rig was chosen due to representative wheel/rail contact conditions and the entrainment of third-body material, which allows representative layer formation.

Over 1000 cycles, two visibly dissimilar materials formed: a black and loosely bonded layer, as well as a transparent thin film that was well bonded to the steel substrate. Intermediate material had been ejected and stuck to the side of the twin-disc sample.

Diffuse Reflectance Fourier-Transform Infrared Spectroscopic analysis was carried out on four different twin-disc test samples to assess changing material composition during the tribological test.

The lighter areas of the twin-disc contact band, with no visible layer, were found to have a thin and transparent organic film. This layer may the cause of low friction due to non-visible contamination, as has been reported by the rail industry since the 1980s.

Iron(II) chelate was not present in leaf material before testing, but appeared in every sample that had entered the twin-disc contact. This concentration of chelate increased in materials believed to have remained in the contact for longer, likely due to the temperatures and pressures of the wheel/rail contact. This chelate enhances chemisorption between the steel substrate and organic molecules to form a low-friction layer.

A range of potentially friction-reducing species was detected in the organic layer, aligning with the findings from previous work and highlighting that low adhesion may not be caused by a single component.

A bonding mechanism has been proposed in this work, which would allow these species to adhere to and build up on the railhead, which may remain consistent amongst different organic species. A better understanding of this bonding mechanism and how to prevent it will allow for the development of improved low-friction mitigation methods.

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