KTH Architecture and
the Built Environment

Fish Oil in Icelandic Road Constructions

A case study of bituminous binder mixtures modified with bio-oil

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Master of Science Thesis
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KTH Architecture and the Built Environment

Master of Science Thesis MMK 2014:XX MDA XXX

Fish Oil in Icelandic Road Constructions

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Abstract

In this thesis an extensive background study on the use of bio-oil modified binder, used in surface dressings in Iceland, was carried out. Surface dressings, or chip seals, are paved by first spraying out binder and then distributing aggregates over the surface before compaction. The bio-oil, most notably fish oil ethyl ester or rape seed oil, is included in a binder mixture to lower its viscosity, enabling the binder to be sprayed out at a lower temperature than unmodified bitumen.

In January 2013, severe bleeding of binder was noticed on road sections paved with bio-oil modified surface dressings in the northern part of Iceland. Following the bleeding, the Icelandic Road and Coastal Administration (IRCA) sent samples of the sections in question, as well as binder samples, for testing at the laboratory of Highway and Railway Engineering at KTH Royal Institute of Technology (KTH) in Stockholm, Sweden. The conclusions of that study were that the fish oil ethyl ester was highly polar and had solubility issues with the bitumen. This was found to have led to the fish oil separating from the binder mixture and covering the stones, preventing bonding between aggregates and binder [1].

The laboratory tests in this thesis extend on the aforementioned research. Through the background investigation it was found that Wetfix N, an adhesion promoter, was used in the binder mixture to facilitate bonding to the aggregates. Based on these findings, previous work and field experience in Iceland, two sample sets were created. The first sample set included 7.5% of either fish oil ethyl ester or rape seed oil by weight, while the second set included 4% of

the same bio-oils by weight. To determine the effect of the adhesion promoter, all samples were tested with and without Wetfix N. Furthermore, all samples were put through a short-term aging treatment to simulate the process during mixing and paving, and tested again.

The findings of this study suggest that the fish oil ethyl ester is more suitable for road constructions, compared to the rape seed oil, and that adhesion promoter should always be included when paving surface dressings in Iceland. Furthermore, the samples tested cannot be recommended for field use due to high polarity in the sample with a fish oil concentration of 7.5% and too high viscosity in the sample which includes 4% of fish oil. Therefore, it can be said that the upper and lower limits have been narrowed to the range between the two concentrations tested. To better understand the properties and behavior of the sample mixtures, a complete adhesion test with aggregates is advisable. Viscosity testing of samples which include between 4.5% and 7% of fish oil by weight are recommended and the mixture with the lowest concentration that passes IRCA's guidelines for spraying viscosity at a desired temperature should be used in practice.

Acknowledgements

I would like to thank my advisor, Prof. Nicole Kringos, for her guidance and helpful advice throughout this thesis work. Furthermore, I am grateful to Abdullah Khan, whose assistance was invaluable during the laboratory investigation and the data analysis following.

I also wish to thank the Icelandic Road and Coastal Administration (IRCA) for their financial support and for providing me with a work area when this thesis work brought me to Iceland. Additionally, I'd like to express gratitude to Daníel Árnason, Einar Gíslason, Ingvi Árnason and Haraldur Sigurþórsson at IRCA for all their help during the background research and the preparations for the laboratory work.

Finally, I would like to thank my family for the support and encouragement given over the course of this thesis work.

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Chapter 1

Introduction

For around 30 years, the Icelandic Road and Coastal Administration (IRCA) has been using surface dressings, or chip seals, to pave smaller roads in the country. The difference between standard flexible asphalt pavements and surface dressings is the paving procedure. In flexible asphalt pavements, aggregates and binder are mixed together, paved and then compacted, usually with more than one compactor [3]. However, when paving surface dressings the binder is sprayed on a surface before aggregates are distributed evenly over it and compacted, first with a small compactor and then regular traffic compacts it further [4]. Surface dressings only add a single layer of stones on top of the existing road structure and therefore add no structural capacity to it. Asphalt pavements, however, are generally a few centimeters thick and are important for the bearing capacity of the road structure. This means that surface dressings are only suited for roads where traffic volume is low and heavy traffic is little to none. In its guidelines, IRCA recommends surface dressings for roads with a maximum annual average daily traffic (AADT) of 3000 cars, with around 10% of the traffic consisting of heavy vehicles (>3.5 tons). For roads expected to exceed that traffic, asphalt pavements are recommended [4, 5]. Surface dressings have considerably lower initial costs than asphalt pavements and are therefore preferred by IRCA when possible [6]. A large portion of the Icelandic road system falls within the maximum recommended AADT for surface dressings and therefore it is the most commonly used paving method in the country.

Unmodified binder is highly viscous and requires high temperatures in order to be fit for spraying. Therefore, IRCA mixes modifiers with the binder to lower its viscosity. In the early days of surface dressings, IRCA used white spirit to lower the binder's viscosity temporarily, as the white spirit evaporates from the binder mixture with time. However, surface bleeding of binder and

environmental concerns called for changes. In 2006, IRCA started to move towards bio-oil modified binder and experimental road sections were paved in the years following [7]. Unlike the white spirit, the bio-oils became a permanent part of the binder and did not evaporate or degrade with time. The most notable bio-oils tested were fatty acid methyl ester from rape seed oil and ethyl ester from fish oil.

In January of 2013, several roads in the north of Iceland were reported to IRCA due to severe damage on their top layer. Most of these roads were paved using the aforementioned experimental bio-oil modifiers mixed in the binder. The damage was described as if the surface was floating in the binder, with the binder sticking to tires of passing vehicles, especially heavy trucks. Following the bleeding, IRCA contacted researchers at the Division of Highway and Railway Engineering at KTH Royal Institute of Technology (KTH) in search for a detailed research of the binder mixtures. The analysis was finished in early November 2013. The modifiers were found to include hydrophilic fatty acids and due to that have solubility problems with the binder, making the mixture vulnerable to moisture damage [1]. Regardless of those results, there is a strong desire at IRCA to continue using these modifiers, especially the fish oil ethyl ester.

In this project, a background investigation on the bleeding section is conducted. The research, carried out with an extensive literature review, site visits and meetings with the people involved, is intended to shed light on the causes of the bleeding in January 2013. Furthermore, on the basis of a hypothesis following the background research, a laboratory analysis is performed to reveal possible solutions to the problem at hand. The main purpose of the laboratory work is to determine the effects the bio-oils and adhesion promoters have on the binder by testing the properties of the mixtures and comparing with previous work. The final product of this thesis will be in the form of recommendations to assist with the design of an ideal binder mixture for Icelandic conditions.

Chapter 2

Background

2.1 Surface Dressings in Iceland

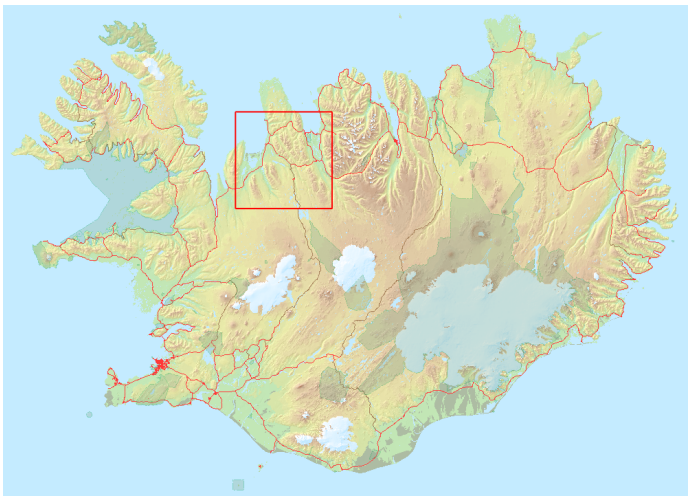
Since 1978, the Icelandic Road and Coastal Administration (IRCA) has been using surface dressing to pave smaller roads, which make up for a large portion of the road system [8]. By using surface dressings, IRCA has been able to cut costs of paving and thus been able to pave a larger part of the road system than would have been possible using standard asphalt pavements. In IRCA's guidlines, surface dressings are recommended for roads with a maximum annual average daily traffic (AADT) of 3000 cars are paved with surface dressings [4]. Roads with higher traffic are usually paved with standard flexible asphalt pavements. When paving new roads with surface dressings in Iceland, two layers are paved, allowing considerable time between paving, oftentimes up to one year if the lower layer is paved late in the paving season [9].

IRCA uses a bituminous binder with a penetration grade 160/220, which has too high viscosity to spray unmodified unless it is heated considerably, to a higher temperature than the paving equipment can withstand [10]. Therefore, some additives are needed to reduce the viscosity and allow spraying at lower temperatures. At first, white spirit was added to the mixture. That practice creates so-called cut-back bitumen, where a volatile solvent is used to reduce viscosity temporarily during paving. Due to its volatility the white spirit evaporates, leaving the bituminous binder in its original form with time [11]. Although this method proved effective to some extent, there were downsides to the use of white spirit. Firstly, frequent winter bleeding of binder was linked to its use. Secondly, the white spirit is very hazardous to the environment and workers. Thus, IRCA pursued possible alternatives. The first alternatives tested were solvents similar to white spirit, but more environmentally friendly. These solvents, Shellsol D60 and Shellsol D40, were found to

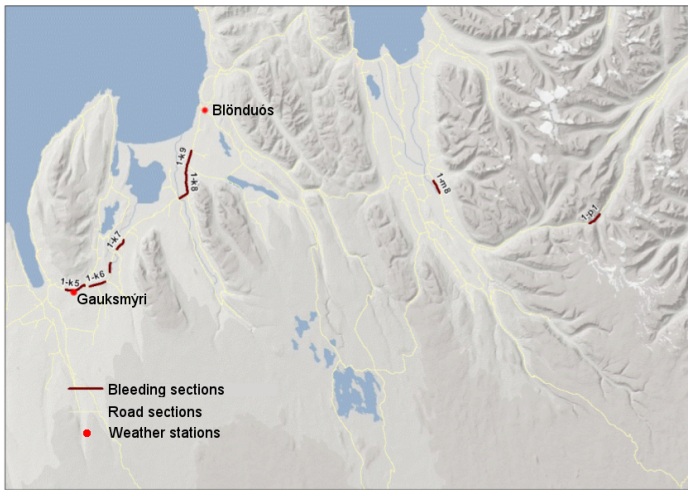
have disadvantages which included bituminous aerosol during spraying (D60) and higher cost (D40) [12]. In 2006, IRCA started to phase out the white spirit by using fluxed bitumen instead, in which a non-volatile diluent is used. The diluent does not evaporate or degrade with time and remains a permanent part of the binder mixture throughout it lifetime [7, 11]. Experiments where performed with bio-oil, at first fatty acid methyl ester from rape seed oil and later ethyl ester from fish oil. The former was a by-product of bio-diesel production in Denmark while the latter is originated in Iceland and falls from a distillation process where omega-3 fatty acids are extracted from fish oil [13].

2.2 Bleeding in January 2013

In January 2013, severe bleeding was reported on roads in the northern part of Iceland. The affected area is shown in Figure 2.1, along with nearby weather stations at Blönduós and Gauksmýri.



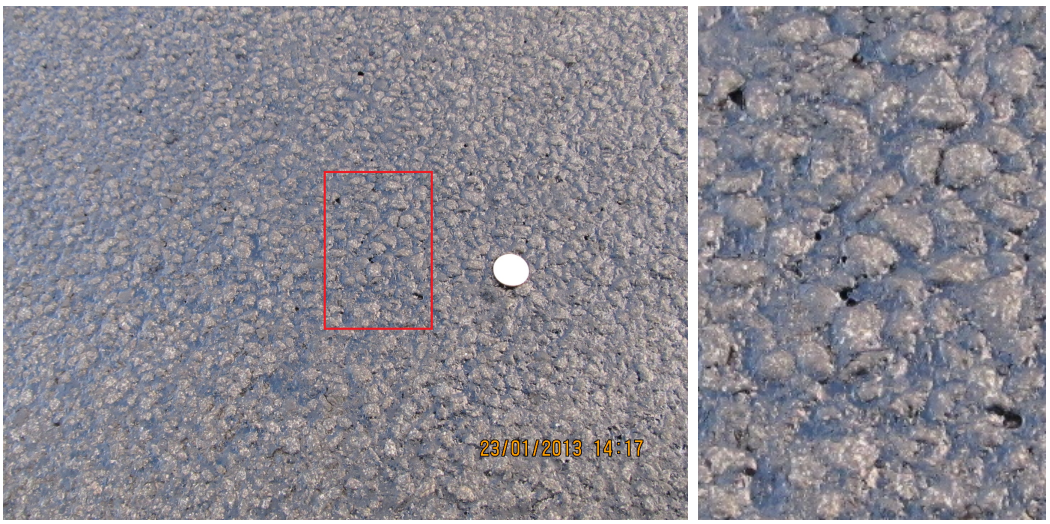
(a) A map of Iceland [14].



(b) A map of the affected area [1].

Figure 2.1: A map of Iceland (a) shows the location of the affected area while (b) shows the area in more detail.

Inspectors from IRCA visited the affected area on January 21st 2013. They observed that bleeding occurred in sections totaling little over 26 km, thereof around 6.5 km of surface dressings with fish oil ethyl esters as a modifier and 19.5 km modified with rape seed oil [15]. Eye-witnesses described this phenomena as if the surface was floating in the binder. When the surface was loaded, a low viscosity fluid oozed out of small holes on the road surface. These holes can be seen in Figure 2.2.



(a) The bleeding surface.

(b) A close up of the bleeding holes.

Figure 2.2: A photo showing the bleeding surface (a) with a detailed close up of the bleeding holes (b) [16].

The fluid stuck to tires of passing vehicles, especially heavy trucks, where it hardened. It was noted that once it melted again it was a binder without any aggregates [17]. An example of the fluid sticking to a tire can be seen in Figure 2.3.

Figure 2.3: A tire that has been driven through an area where severe bleeding has occurred [15, 18].

It should be noted that, according to experts at IRCA, this reported bleeding is not at all typical for the Icelandic road system. The most common winter bleeding is when tiny droplets of binder stick to studs of studded tires, accumulating over a long distance and not noticed until several kilometers after it started. The experts claim that the origins of these kinds of bleeding can be difficult to spot, as no contamination can be seen on the road surface [19].

2.3 Previous Work

2.3.1 Forensic Research on Binder Modifiers

Early 2011, Halldorsson, Torfason and Hjaltason [20] published a report comparing fish oil ethyl esters to rape seed oil as modifiers in bitumen for surface dressings. The report covered an extensive forensic investigation, as well as descriptions of the processes from which these products derive.

The fish oil ethyl ester used by IRCA arises from a ethanol catalyzed transesterification reaction during Omega-3 production, a popular source of vitamin D, which results in corresponding ethyl esters. The ethyl esters are distilled to separate the saturated short-chain fatty acids from the long-chained polyunsaturated ones. The latter substance is used in various health product while the the former is a by-product of the distillation, a clear and pure bio-

oil. From this process around 20 000 tons of fish oil ethyl esters fall annually worldwide, with around 300 tons Iceland alone [13, 21].

The researchers noted that the tests performed on the rape seed oil revealed that the oil that had been used in Iceland was a mixture of methyl esters, monoglycerides, diglycerides from rape seed oil but not pure triglycerides as was expected. Later, it was confirmed by the manufacturer that the alleged rape seed oil was a by-product of bio-diesel production in Denmark. It is essentially a fatty layer that is extracted from another by-product, glycerol [20].

When testing the physical properties of the two modifiers, the researchers found them to be quite similar. They found that the alleged rape seed oil had physical properties closer to the fish oil ethyl esters than to pure rape seed oil. Table 2.1 shows the comparison of the physical properties of the fish oil ethyl esters, the alleged rape seed oil and expected values for pure rape seed oil.

Table 2.1: A comparison of the physical properties of the fish oil ethyl esters, the alleged rape seed oil and expected values for pure rape seed oil [21].

Parameter	Fish Oil Ethyl Ester	Alleged Rape Seed Oil	Pure Rape Seed Oil
Flash point (°C)	176	186	310
Viscosity at 20°C (cStoke)	6	15	40
Density at 14°C (kg/L)	0.88	0.89	0.92
Refractive index at 20°C	1.45	1.46	1.47
Cloud point (°C)	5	-	-
Cold filter plugging point (°C)	0	-	-

Through a chemical analysis, the researchers found the differences between the modifiers. Table 2.2 shows the comparison.

Table 2.2: A comparison of the chemical properties of the fish oil ethyl esters and the alleged rape seed oil [21].

Parameter	Fish Oil Ethyl Esters	Alleged Rape Seed Oil
Monoesters [%]	100	63
Color [Gardner]	0.3	10.6
Water content [%]	0.04	>2.0
Long chain polyunsaturated fatty acids [%]	15-20	0

Finally, the researchers tested mixtures which included bitumen and 7.5% of fish oil ethyl ester and alleged rape seed oil, respectively, to determine their viscosity. Their results can be seen in Table 2.3.

Table 2.3: A comparison of the viscosity of mixtures containing 7.5% of the fish oil ethyl esters and the alleged rape seed oil, respectively [21].

Temperature [°C]	Fish Oil Ethyl Esters [cStoke]	Alleged Rape Seed Oil [cStoke]
105	449	501
120	192	223
135	125	136

Alongside these laboratory tests, an experimental road section was paved with fish oil ester modified binder. The field trial was found to be so successful that IRCA paved over 4 million square meters in 2011 with binder which included fish oil ethyl esters [21].

After the bleeding, IRCA sent samples of the rape seed oil and the fish oil ethyl esters used in the bleeding sections for forensic investigation. In the report for the rape seed oil research, it was concluded that the oil was not pure rape seed oil and was had very different properties to pure oil that was tested earlier. Around 25% of the rape seed oil consisted of hydrophilic fatty acids, monoglycerides and diglycerides, all of which where thought to have contributed to emulsification of the binder and eventually bleeding. Furthermore, the report mentioned nothing unusual or unfavorable with the fish oil ethyl ester [22].

The fish oil ethyl ester was sent to CST Colas [23] for further investigation. In the report, two mixtures were recommended. The mixtures are shown in Table 2.4.

Table 2.4: Recommendations made by CST Colas for the use of fish oil ethyl ester in surface dressings. The recommendations are based on binder with penetration grade 160/220 [23].

Traffic	Heavy Vehicles	Binder	Fish Oil Ethyl Ester	Adhesive
Very low	None	91.6%	7.5%	0.9%
Low	Few	94.1%	5%	0.9%

It was further advised that paving should be performed in June through August and that two layered surface dressings were not recommended due to risk of bleeding. Please note that in Table 2.4, no quantification is given on what is considered low and very low traffic.

2.3.2 KTH Investigation Following the Bleeding in January 2013

To better understand the causes of the bleeding, IRCA sent samples of binder mixtures and surface dressings to researchers at KTH Royal Institute of Technology (KTH) in Stockholm, Sweden. The binder samples were classified based on the basis of Superpave Performance Grading (PG) and chemical characterization. The surface dressing samples were inspected visually and put through X-ray tomography. The information in this section is taken from the report published following that research [1]. The binder samples and their PG are described in Table 2.5.

Table 2.5: Samples used for testing at KTH. The binder mixtures are based on bitumen with penetration grade 160/220. Their Superpave Performance Grade (PG) is also shown [1].

Binder	Modifier	Modifier concentration	PG
N	None	-	52-28
K8	Fish Oil Ethyl Esters	7.5%	Did not meet standards
K9	Rape Seed Oil Fatty Acid Methyl Esters	7.5%	Did not meet standards

As can be seen from Table 2.5, Superpave tests revealed that the bio-oil modified binder did not meet the requirements. It is noted in the report that the modified binder mixtures showed better low temperature performance than unmodified binder. However, the high temperature performance is reduced, causing the mixtures to fail the Superpave grading requirements.

The researchers found that the fish oil ester had solubility issues with the bitumen. That resulted in enhanced surface polarity which led to the aggregates being covered in polar oil instead of bitumen. The poor contact with the bitumen resulted in reduced bonding between stones and binder. Furthermore, the investigation revealed that the problem can be aggravated when surface dressings are exposed to water.

From the X-ray tomography analysis performed on the samples, the researchers identified two major problems. Firstly, debonding between binder and aggregates was noticed and secondly, severe binder bleeding was noticed. These problems are thought to have significant negative effect on the structural capacity of the surface dressings.

2.3.3 Adhesion Promoters

IRCA adds adhesive agents to binder mixtures before paving to increase bonding between binder and aggregates. While IRCA and its contractors use several types of agents from various manufacturers, they all yield similar effects on the binder mixture. Apart from improving bonding directly, adhesion agents make the binder mixture less sensitive to moisture and freeze-thaw effect [24].

Petursson [25] investigated adhesion promoters by performing lab tests on three adhesive agents. The products were Wetfix N from AkzoNobel, TPH from Chemoran and Impact 8000 from MeadWestvaco. Petursson found that the concentration of the adhesive agent in the binder mixture seems to play a large role in bonding. He noted that using insufficient quantities of any of the tested agents has a severe negative effect on the bonding. Furthermore, he noted that the storage of a binder mixture with adhesive agents at high temperatures reduces its bonding capabilities. Tests revealed that Wetfix N showed the worst performance after storage at 130°C for 2 days. The mixture in which it was included was noted to have lost 50% of the adhesion between the binder and the aggregates during that time. After being treated similarly, the TPH mixture showed 80% adhesion while the mixture in which Impact 8000 was included showed adhesion close to 95%.

As of now, Wetfix N is the most commonly used adhesive agent in Iceland. IRCA has leftovers in large quantities that will be used for paving in 2014. However, once it runs out TPH or Impact 8000 will be used as alternatives [26]. Wetfix N is designed for mixing with cold aggregates, as is the case with surface dressings [27]. TPH is an adhesive agent designed for hot-mix asphalt and surface dressings [28]. Impact 8000 is the successor of Impact 7000. The agent is designed for asphalt mixes and cut-back surface dressings and is claimed to improve adhesion between binder mixtures and a wider range of aggregates than its predecessor [29].

2.4 Site Description

2.4.1 Paving Conditions and Structure

The bleeding occurred on two road sections where fish oil ester was partly used. They are named 1-K8 and 1-K9 and are located in the northern part of Iceland on Highway 1, the main ring-road around the country. A road section where no bleeding was reported, section 75-02, is described for comparison. That section is located on Highway 75, which connects Highway 1 to the town of Sauðárkrókur. Road section 75-02 services considerably less heavy traffic than the bleeding sections, which should be kept in mind when observing the data. The comparison is shown in Table 2.6.

Table 2.6: A description of the sections where bleeding occurred, compared to a section where no bleeding was documented [1, 15, 30, 31].

Parameter	Section 1-K8 5400 1-K8 8600	Section 1-K8 11070	Section 1-K9	Section 75-02
Year	2011	2011	2011	2012
Status	Bleeding	Bleeding	Bleeding	No bleeding
Binder Mixture				
Penetration grade	160/220	160/220	160/220	160/220
Quantity (ltr/m^2)	1.7-2.3[1]	1.7-2.3[1]	N/A[2]	1.4-1.9
Modifier	Rape Seed Oil	Fish Oil Ethyl Esters	Rape Seed Oil	Fish Oil Ethyl Esters
Modifier (%)	8.0	7.0	7.5	6.0-7.0
Adhesion agent	Wetfix/TPH	Wetfix/TPH	Wetfix/TPH	Wetfix
Adhesion agent (%)	0.8[3]	0.8[3]	0.8[3]	1
Paving Conditions				
Spraying temperature (°C)	N/A[2]	N/A[2]	N/A[2]	132-148
Ambient temperature (°C)	N/A[2]	N/A[2]	N/A[2]	12
Rain (mm)	N/A[2]	N/A[2]	N/A[2]	6-7
Aggregates				
Size				
- Upper layer	8/11	11/16	8/11	8/11-11/16
- Lower layer	N/A[2]	N/A[2]	N/A[2]	N/A[2]
Quarry				
- Upper layer	Neðri-Mýri	Neðri-Mýri	Neðri-Mýri	Vallholt
- Lower layer	Uppsalir	Uppsalir	Uppsalir	Vallholt
Adhesion (%)				
- Upper layer	100	100	100	100
- Lower layer	As low as 30	As low as 30	As low as 30	100

[1] Quantity requested by IRCA [15].
[2] Not documented at the time of paving.
[3] Not documented at the time of paving. Retrieved from IRCA during research [31].

As can be seen from Table 2.6, documentation at IRCA was severely lacking at the time of paving. Road section 1-K9 was paved before IRCA implemented a system to register properties of mixtures and conditions during paving. Therefore, most data that is available is not as detailed as with sections paved after the system's implementation. There is also some information missing for the road sections within 1-K8. Some data was lost by IRCA's site inspector and detailed information was hard to obtain from the contractor. Furthermore, there was an error in the measurements of the binder quantity in section 1-K8. The quantity requested by IRCA was documented and is listed in the table instead.

According to IRCA it is possible that the binder used had been stored at around 150°C for around 9 months [32]. Nynas, the supplier of the bituminous binder used, recommends storage conditions to be in the range 130-150°C for bitumen of paving grade 160/220. Storing the binder at high temperatures may alter its characteristics by hardening it, resulting in shorter lifetime of the pavement [33].

2.4.2 Subgrade

Iceland's geology is documented by the Icelandic Institute of Natural History [34]. According to a geological map, the bedrock in the area where the bleeding occurred is a basic and intermediate extrusive rock with intercalated sediments. It is from the upper Tertiary period and is believed to be older than 3.3 million years. The subgrade in the area is considered to be made up by this bedrock.

The road sections in question are all built up similarly. The top layer is a 3-5 cm surface dressing. Beneath that is a 7-15 cm layer of stabilized bitumen (75-02), stabilized cement (1-K8 5400/8600), crushed rock (1-K8 11070) or crushed gravel (1-K9). At the bottom there is a 50 cm thick gravel layer, which was laid in 1980-1982, except for 1-K9 where it was laid in 1992.

2.4.3 Traffic

In 2004, transportation of goods via coastal shipping was abandoned in Iceland. With no railroad system in the country, all heavy transportation was transferred onto the road system. Heavier trucks added additional loads on the road system, especially on Highway 1 which connects the most populous areas in the country. The road section 75-02, however, is outside of the ring road and is believed to have significantly less heavy traffic than the other road sections investigated.

Mannvit Consulting Engineers performed a traffic survey for IRCA on section 1-K9 in September 2011 and published a report on it in August 2012 [35]. The study was performed over two days, a typical weekday and a Saturday. In the report it is noted that the traffic, both from personal vehicles and trucks, was found to be significantly lower on weekends. Therefore, only the typical weekday is taken into account here. Heavy vehicles are defined by IRCA as any vehicle exceeding a weight of 3.5 tons. From the report, it can be seen that the average traffic cannot be considered heavy by any means. However, it can be quite concentrated on certain time periods which results in more continuous loading on the road during that time. Counted vehicles were around 1300, with heavy traffic little less than 13% of that. The total number of trucks was 207, with 27 (or 10%) passing by between 10 and 11 in the morning. During the three busiest hours from 10 in the morning to 1 in the afternoon 29% of the day's heavy traffic passed by. The total heavy traffic during that time period was 60 trucks, which equals to one truck every three minutes. No further data is available on the traffic.

2.5 Literature Review

There are numerous products available that utilize waste materials or renewable sources in asphalt binder. Most of the information at hand about these binders or modifiers comes from the manufacturers themselves, where their advantages are emphasized while the drawbacks are ill-documented or underplayed.

2.5.1 Plant-Based Binders

Metwaly and Williams [36] performed the most in-detail research on bio-based binders and modifiers to date. They split the binders into three categories based on their concentration of bio-materials: (1) bitumen modifiers (<10% bitumen replacement), (2) bitumen extenders (25-75% bitumen replacement) and (3) alternative binders (100% bitumen replacement). The research was based on comparing bio-binders from three different resources (corn stover, switchgrass and oakwood) to known bituminous binders. The bio-binders were produced from bio-oils, which were the results of fast pyrolosis of the resources.

After the laboratory evaluation Metwaly and Williams concluded that some pre-treatment is required so that bio-oils can be used as bio-binders, as they were found to include a substantial quantity of both water and volatile contents. They concluded that the procedure of transforming bio-oils to

bio-binders should be determined on a case-to-case basis since the chemical composition of bio-oils, their production process and sources can vary significantly. The researchers also studied the Superpave standard with respect to bio-binders and reached the verdict that some modifications to the standard are necessary to comply with different behavior concerning temperature susceptibility and aging. From a chemical characterization, they concluded that the bio-binders start behaving viscously at temperatures 30-40°C lower than bituminous binders. Through a study of the rheological behavior, the authors observed a significant difference in properties of the bio-binders compared to the bituminous binders, notably in temperature and shear susceptibilities. Moreover, they noted that by polymer modification of the bio-binders, their rheological properties were found to change drastically. Furthermore, Metwaly and Williams carried out a performance test on the bio-binders, from which they concluded that the high temperature performance grade of the bio-binders did not differ considerably from the bituminous binders. However, they noted that the high oxygen content in the bio-binders, compared to bitumen, can affect the low temperature performance grade considerably, as well as accelerating aging. From a master curve comparison, the authors found that the bio-binders generally had higher complex moduli at low temperatures compared to the bituminous binders. They noted that it indicated risk of thermal cracking at low temperatures. Furthermore, they found polymer modified bio-binders to behave very differently to the unmodified ones. In light of that, the researchers recommended thorough investigation on the effect of various polymers and their concentration in bio-binder mixtures in order to create an optimized binder mixture for specific in-service conditions.

Colas has been developing a plant based binder called Vegecol since 2003 [37]. The manufacturer claims that the binder, which is produced from vegetable oils and resins, can essentially replace bituminous binders. Furthermore, it is claimed the use of Vegecol can reduce CO_2 due to its lower melting point compared to bituminous binders, therefore requiring less heating of the binder mixture before mixing [38]. As of 2007, Vegecol is claimed to have been utilized worldwide in over 450 projects [37]. Colas also produces a plant-based fluxing agent, claimed to lower the melting point of bitumen by around 25°C. It is designed for use with hot-mix asphalt and surface dressings, as well as with slow setting emulsion pavements [37].

Ecopave GEO320 MRH, produced by Ecopave Australia, is another example of a bio-material based binder. The manufacturer claims it can be produced from various sources, such as sugar canes, tree resins, vegetable oil and starch from potatoes or rice [39]. The product is delivered in a dry and granulated form, intended to make storage and transportation less sensitive

to diverse conditions. The delivered form is also claimed to save energy and lower CO_2 emission since, allegedly, no heating is necessary until at the mixing stage [40].

Aforementioned Williams has taken part in the development of a binder called Bioasphalt, developed at the University of Iowa and Avello Bioenergy. The binder was tested on a bike trail in Des Moines in Iowa, USA, in 2010, where it was used as a modifier with 5% strength [41]. No results have been published from the experimental sections.

Other binders include Floraphalte, a plant-based binder developed by Shell [40]; Mobimix, a plant-based binder from in Belgium [42]; and Alfa Ecology, a asphalt release agent made in Italy [43]. No documented tests on high-traffic roads are available for any of these binders.

2.5.2 Binders from Waste

Fini et al. [44] performed an extensive study on the effects of using bio-oil from swine manure as a modifier in bituminous binder mixtures. The bio-oil binder is produced through a thermo-chemical liquefaction process, which utilizes the carbon from the manure. The binder is produced by placing manure in a reactor, heating it to a high temperature and keeping it constant under pressure for a specific length of time, using nitrogen as processing gas. After the specified time, the reactor is cooled rapidly to room temperature and the gas released to reach atmospheric pressure. The binder is then acquired by separating the sticky residue from aqueous solutions. The leftover water is claimed to include nitrogen, phosphorous and potassium nutrients, which can be used as a fertilizer, according to the researchers. Tests were performed to determine the chemical characterization of the bio-oil and compare to asphalt binder.

The chemical experiments did not provide any measurable results of the compatibility of the bio-oil binder with bituminous binder. However, the authors noted that the weight percentage of resins in the bio-oil binder indicates potential. Furthermore, they concluded that the high concentration of polar compound (such as oxygen and nitrogen) in the bio-oil binder hints at a possibility that it could improve the moisture resistance of a bituminous binder mixture.

For the rheological experiments Fini et al. used a binder with performance grade PG 64-22. Four different mixtures were tested, unmodified binder and mixtures consisting of 2%, 5% and 10% of bio-oil by weight, respectively. From the results they concluded that the viscosity was significantly reduced as more

bio-oil binder was added, thus lowering the temperature needed for mixing. Similarly, the authors found the cracking temperature to have lowered, indicating enhanced performance in colder climates. They also found that the rut resistance was increased with added bio-oil binder, making bio-modified binders a feasible choice for recycled asphalt pavements, where rutting due to compactability is a concern.

Fini et al. noted that on of the main benefits of producing binder from swine manure compared to other biomass sources is its wet nature, which they claim to reduce costs as external water resources are not needed. The authors estimate in their study that the cost of binder from swine manure is \$0.13/L, compared to \$0.53/L for bituminous binder. It should be noted that the estimated cost is not accurately measured, but is based on a similar manufacturing process. However, since the use of external water is claimed to be unnecessary, the authors believe that the prices will be further reduced. It is concluded in the study that the price, availability and environmentally friendly nature of the swine manure based bio-binder, along with its usability, will make it a feasible option for future asphalt pavements.

According to the United States Environmental Protection Agency, hotels and restaurants in the United States produce around 11 billion liters of waste cooking oil every year [45]. H. Wen, S. Bhusal and B. Wen [46] performed a laboratory evaluation of the use of waste cooking oil based binder as an alternative to bituminous binder for hot mix asphalt. In their experiments they used bio-binder that was produced by thermochemical process, in which the waste oil was heated and put through a polymerization process to create bio-binder. In the laboratory experiments, bituminous binder of three different Superpave performance grades (PG 58-28, PG 76-22 and PG 82-16) were mixed with the bio-binder at different concentrations, ranging from 10% to 60% of the base binder's weight. The mixtures were put through various chemical and rheological tests to determine their performance. They concluded that the addition of bio-binder increased the resistance to thermal cracking, while resistance to fatigue and rutting was decreased.

Other binders from waste include Biophalt, made from waste from the paper industry. According to the manufacturer, Eiffege TP, it is a transparent binder and can easily be pigmented in order to better fit into its environment, such as parks and green areas in cities. Compared to bituminous binders, Biophalt is claimed to reduce the emission of green house gasses due to its lower mixing temperature. Researchers which analyzed Biophalt concluded that the bio-binder's disadvantages included high initial costs, low bearing capacity, which yield it unusable for roads with high traffic, as well as sensitivity to

mixing and paving temperature and moisture during paving [40].

2.5.3 Binders from Fish Oil

Outside of Iceland, fish oil is not widely used in road construction. Currently, several kilometers of surface dressings around the country which include fish oil ester modified binder are being tendered by IRCA for completion in the summer of 2014 [47]. In Iceland, extensive research has been performed on certain aspects of the usage of fish oil ethyl ester in surface dressings, while others are not as well researched.

A Swiss-based company called Modern By-Products (MBP) focuses on utilizing by-products from several industries for various uses [48]. Among other products, MBP produces MBP TP 93 and MBP TP 95, fluxing-agents derived from the anchovy industry, for use in road construction. The aforementioned products were evaluated by AMEC Environment & Infrastructure [49] in 2012. A laboratory analysis was performed on binder with pavement grade PG 58-28 mixed with the two types of bio-oil fluxing agents. Tests were conducted on modified warm-mix asphalt (WMA) and the results compared with hot-mix asphalt (HMA) standards set by the Nova Scotia Transportation and Infrastructure Renewal (NSTIR). The tests carried out were performance graded asphalt binder test, to determine the modified binder's performance grad (PG) rating, aggregate tests and tests on the asphalt mix using the modified binder and chosen aggregates. The researchers concluded that MBP TP 95 met all requirements provided by NSTIR for additives in WMA, while MBP TP 93 did not comply with compaction requirements.

In an ongoing project in Denmark, researchers are observing road sections with ethyl ester modifiers from fish oil. Due to the sensitive stage at which the research is, no further information is available. In Norway, the contractor NCC has been using fish oil as fuel to heat up binder mixtures for several years. In the year 2008, NCC estimated that around 25% of the asphalt produced by the company was heated with fish oil [50].

2.5.4 Surface Dressings

Surface dressings, or chip seals, are used worldwide on low volume traffic roads with little to no traffic of heavy vehicles. In design guidelines from Iceland and Norway, the heavy vehicle traffic is assumed to be around 10% of the total traffic [5]. Generally, there are three types of binder mixtures used for surface dressings; cut-back bitumen, fluxed bitumen and bitumen emulsion. Cut-back bitumen is where a volatile solvent is used to reduce viscosity temporarily

during paving. Due to its volatility the white spirit evaporates, leaving the bituminous binder in its original form with time [11]. In fluxed bitumen, a non-volatile diluent is used to lower the viscosity of the mixture. The diluent does not evaporate or degrade with time but rather remains a permanent part of the binder mixture [7, 11]. The third type, bitumen emulsion is where the bituminous binder is mixed with water and an emulsifying agent (soap) to lower its viscosity. The soap releases an electric charge so that the binder does not mix with the water. After the mixture has been laid down, the water evaporates and in 1-2 hours the emulsion is set [11, 51].

In Scandinavia, surface dressings are widely used. Petursson [52] researched practices and procedure regarding surface dressings in Scandinavia by sending a questionnaire to the countries involved. He found the degree of use and practices to vary significantly between countries. In Finland and Norway, 500-600 000 square meters of surface dressings were laid in 2012, while road authorities in Denmark laid 5-6 million square meters and in Sweden around 12 million. In Sweden and Norway, dressings with polymer modified emulsified binder are used almost exclusively. In Denmark, all three types of dressings are used, with cut-back bitumen being the most common (around 70% of total), while cut-back bitumen is the sole type used in Finland. In comparison, IRCA paved around 2.5 million square meters in 2012, only using fluxed bitumen with fish oil ester modifier. It is interesting to note that of the Nordic nations, only Denmark and Sweden use washed aggregates. Petursson notes that mining and preparation of aggregates in Iceland could be revised with respect to experience in those countries, especially if experiments with emulsified bitumen continue.

Surface dressings are also used as a preventive maintenance treatments on flexible pavements. The dressings allow protection and water resistance to pavements which show little distress, but provide no added structural capacity to roads which show severe distress. Countries which use surface dressings as a wearing course include the United States, Canada, New Zealand, the United Kingdom and Australia, the last of which had 450 000 lane kilometers with surface dressings as of 2005 [53].

Chapter 3

Hypothesis

3.1 Scenario

In the days leading up to the bleeding event, several freeze-thaw cycles were documented [54, 55]. The thaw periods of these cycles did not last for long, so it can be assumed that although the surface was above freezing, the subsoil was frozen throughout the period. This caused water to seep through parts of the paved layer but stop on top of a frozen layer, where it collected and mixed with the binder. When vehicles, especially heavy trucks, drove over the section, it created a pumping effect where the water and binder formed a soap-like emulsion which was pumped up to the surface, sticking to tires. A scenario in which the bleeding event is likely to have occurred can be seen in Figure 3.1.

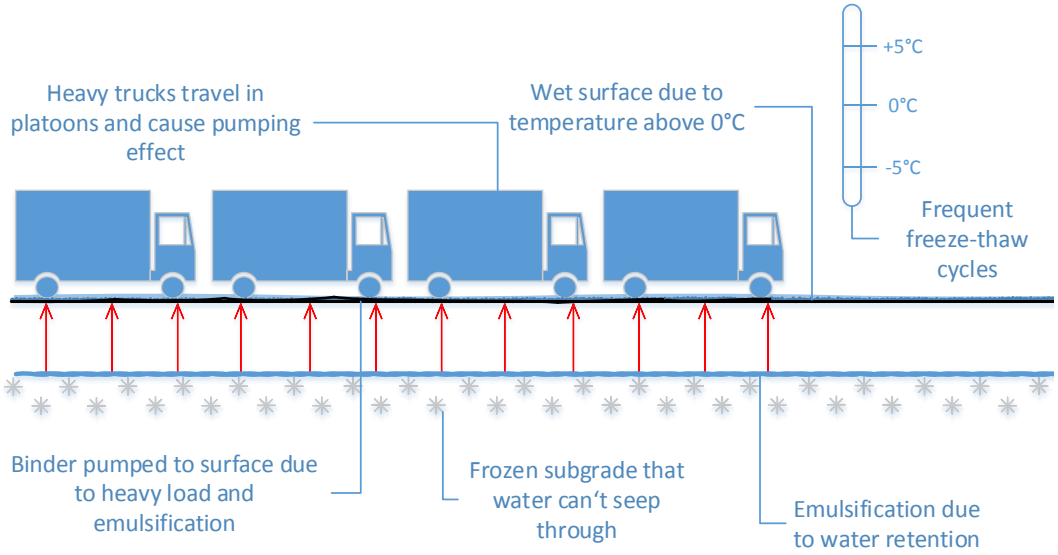


Figure 3.1: A scenario in which the bleeding event is likely to have occurred.

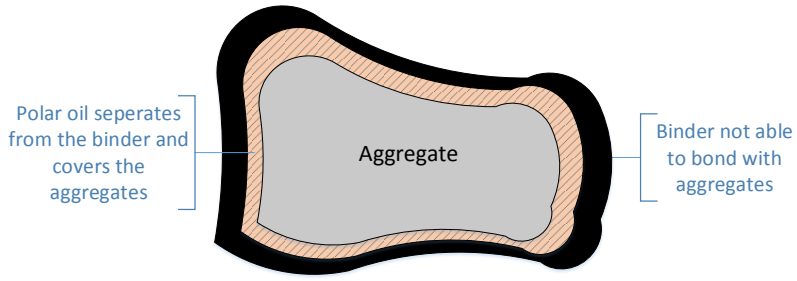
3.2 Causes

Although the weather can be seen as a catalyst for the bleeding event, there is an underlying issue that needs to be identified and investigated. Tests have revealed that the adhesion between aggregates used in the lower layer of the surface dressings in question and the binder may have been as low as 30%, where 100% is desirable.

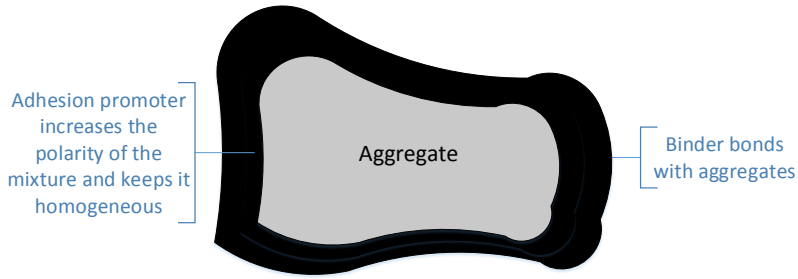
It is likely that these factors contributed to the bleeding. However, their contribution may have been minor and could prove difficult to define. The effect of the fish oil ethyl esters on the binder mixture is largely unknown. The esters have been tested, both individually and as a part of a binder mixture. The individual tests revealed no unfavorable characteristics, while tests where the esters were used as a part of a binder mixture identified some problems. In the laboratory investigation by Guarin et al. [1], the researchers found that binder mixtures which included the fish oil esters did not pass the Superpave standard testing. Furthermore, through chemical characterization they revealed issues with the use of fish oil ester in the bitumen. From a surface energy test, they found the fish oil esters to be highly hydrophilic. Moreover, researchers noted that tests on the aggregates showed that the fish oil esters separated from the bitumen and covered the stones. These results suggest that the fish oil esters may have some solubility issues with the bitumen, which is

likely to have had a major contribution to the bleeding event. To confirm this, further testing is required.

Additionally, Wetfix N, the adhesion promoter used, may have shown decreased performance due to storage, as tests have shown it to be very sensitive to storage at high temperature for as short as 24 hours [25]. In Figure 3.2, the effect of the adhesion promoters is explained. When no adhesive agent is used, the highly polar bio-oil modifier can separate from the binder mixture, cover the stones and prevent bonding between the binder and the aggregates. This enables water to penetrate into the surface dressing which can lead to bleeding. The work of the adhesion promoters is essentially to compete with the polar oil, that is to ensure that the aggregates prefer bonding with the binder mixture rather than the polar oil.



(a) Polar oil covers the stone surface and prevents bonding between the binder and aggregates.



(b) Adhesion promoter facilitates bonding between the binder and the aggregate, without the polar oil separating.

Figure 3.2: The work of adhesion promoters, where (a) shows problems that arise when adhesion promoters are not included and (b) shows how they work.

Please note that the adhesion promoter does not cover the stones, but rather is a part of a homogeneous mixture with the binder and bio-oil. The layer shown around the stone in Figure 3.2 (b) is merely to explain the effect of the adhesion promoter and does not accurately depict reality.

3.3 Testing

In this thesis, tests performed by Guarin et al. will be extended. Background investigation has revealed that the adhesion promoter Wetfix N was used in the paving mixtures, which was not clear at the time of testing by Guarin et al. Adhesion promoters decrease the effect of moisture by modifying the binder mixture so that it bonds better with aggregates. With stronger bonding the risk of water reaching the interface between the binder and stones, and causing debonding is lessened. Therefore, the presence of adhesion promoters is an important factor that needs to be tested. By testing mixtures with and without Wetfix N, it is possible to determine the effect it has on the binder. A surface energy test can be used to reveal the adhesive capabilities of the binder. Furthermore, the test can reveal whether or not the fish oil esters are compatible enough with the bitumen to be used in road construction and if they are, in which quantity. With a lower concentration of fish oil esters in the mixture, the solubility issue becomes less severe and thus it is possible to determine an upper limit of quantity with the surface energy test. The lower limit of the concentration can be found with a viscosity test. Since the esters have lower viscosity than the bitumen, it is possible to determine the lowest concentration required for the mixture to become fluid enough to be sprayed at a desired temperature. From the surface energy and viscosity tests it is possible to provide practical recommendations to IRCA. These recommendations can be seen in Chapter 6.

Chapter 4

Methodology

4.1 Theoretical Background

4.1.1 Aging

With time, binder mixtures become stiff and brittle. The process is called aging and is divided into two categories, short-term and long-term. Short-term aging occurs during production, mixing and paving. The aging is caused by vaporization of volatile molecules due to high-temperature treatment and oxidation, leading to increased viscosity in the binder mixture [56]. Long-term aging is the change in properties of the binder during the lifetime of the road structure. In this research, only the short-term effect is examined. The long-term aging is considered non-essential, since the focus of this study is the mixture itself as well as the procedure during mixing and paving.

4.1.2 Surface Energy

The surface free energy of a material is defined as the work required to create a new surface area, that is to separate molecules in the bulk of the material to obtain two surfaces. Within the bulk each molecule is surrounded by other molecules and thus forms a stronger bond to the material than the surface molecules, which are not completely surrounded, see Figure 4.1.

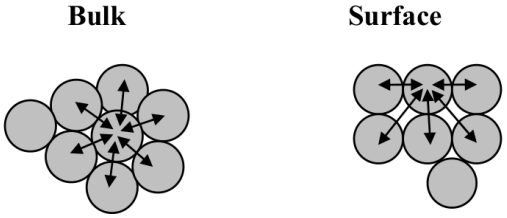


Figure 4.1: A comparison of the forces between molecules on the surface and in the bulk [2].

From the figure it can be seen that the molecules in the bulk are in balance, as each force working on a molecule has a counteracting one in the opposite direction. For surface molecules however, there is a certain imbalance as forces working inwards are not counteracted. This causes surface tension, which requires a force to break through the surface. Surface tension and surface energy are most commonly expressed in the units mN/m or mJ/m^2, which are equal since 1 J= 1 Nm. Surface free energy is a term used to emphasize that it is based on the work performed, not the total excess energy. However, the terms surface tension, surface energy and surface free energy are most commonly used interchangeably when referring to liquids [2].

In practice, the surface energy of a material is seldom attainable directly through measurements. For that, the work of adhesion between the material and another one with known surface energy components is measured [57]. Several theories with methods to calculate the surface energy have been put forth. The most notable theories are described here, separated with regards to how many surface energy components they describe.

Work of Adhesion and Cohesion

The basis for the thermodynamic theory of adhesion is that an adhesive material (here a liquid) will adhere to a substrate (a solid) through intermolecular forces at the interface between the materials. Surface free energy is one way of quantifying these forces. The Gibbs free energy model describes the Gibbs free energy (G) in terms of; the enthalpy (H), the amount of energy given off or absorbed during a process; the entropy (S), the system's increase in randomness; and the temperature (T), presented in Kelvins [58].

$$\Delta G = \Delta H + T\Delta S \tag{4.1}$$

The Gibbs free energy can be said to express the change in a system's energy during a process. If $\Delta G < 0$, energy will be relased and the process

occurs spontaneously. With $\Delta G > 0$, the process requires energy from the environment to occur, while if $\Delta G = 0$ the process is in an equilibrative state. The work of adhesion (W^a), also known as the surface energy of the interface (γ), is described as the work required to break the adhesive bonding, or

$$W^a = -\Delta G^a \tag{4.2}$$

When two diverse materials bond, the work required to set them apart can be described with Dupré's equation

$$W^a = -\Delta G^a = \gamma_1 + \gamma_2 - \gamma_{12} \tag{4.3}$$

where γ_1 and γ_2 represent the surface energy of the adhesive and the substrate, respectively, and γ_{12} is the surface energy at the interface between the two materials. Similarly, the cohesion of a material can be described by simplifying Equation 4.3, where $\gamma_1 = \gamma_2 = \gamma$ and $\gamma_{12} = 0$.

$$W^c = 2\gamma \tag{4.4}$$

where γ is the surface energy of the material in question.

Thomas Young described γ_{12}, relating it to the contact angle (θ) at which the two materials meet, see Figure 4.2 [59].

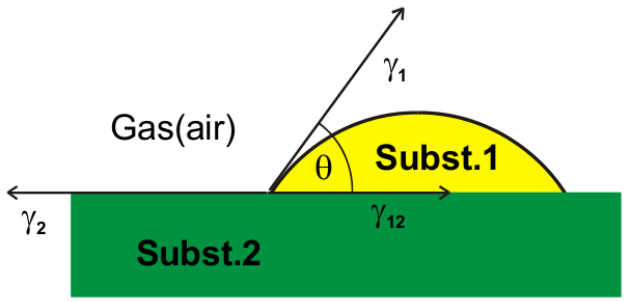


Figure 4.2: The contact angle (θ) of a droplet to a solid surface [59].

Young concluded that with the contact angle closer to $\theta = 0°$ the surface became more favorable towards the liquid which results in it covering, or wetting, a larger area, whereas a contact angle higher than $\theta > 90°$ is considered unfavorable and the droplet will minimize contact with it [58]. When relating to water, it can be said that with $\theta < 90°$ the surface is hydrophilic while $\theta > 90°$ indicates a hydrophobic surface. By assuming that equilibrium has been reached in Figure 4.2, Young's equation is valid

$$\gamma_2 = \gamma_{12} + \gamma_1 \cos\theta \tag{4.5}$$

By combining Equations 4.3 and 4.5, it is possible to obtain the Young-Dupré equation.

$$W^a = \gamma_1 (1 + \cos\theta) \tag{4.6}$$

The Young-Dupré model is the basis for the theories described in this section and the most important relationship in the data analysis of the tests performed for this thesis.

One Component Theory

Zisman described a one component theory. The theory is based on a critical surface tension approach, in which the contact angle (θ) of a droplet of a probe liquid, a homogeneous liquid which does not chemically react or dissolve with the solid and has known surface energy components, is utilized to find the surface energy of the solid [2]. Using a smooth solid surface, he concluded that there was a linear relation between the cosine of the contact angle ($\cos\theta$) and the surface tension of the known liquid (γ_{lv}) [58].

According to the Zisman theory it is useful to plot the known liquid surface tension (γ_{lv}) versus the cosine of the contact angle ($\cos\theta$) and extrapolate a straight line to $\cos\theta = 1$. From that, Zisman concluded, it is possible to determine the highest surface tension liquid which will completely wet the surface. According to Zisman, the surface energy of the solid can be assumed to be the same as the surface tension of this particular probe liquid. Figure 4.3 shows an example of a $\gamma_{lv} - \cos\theta$ plot, or a Zisman plot, for a low density polyethylene film. From the figure it can be seen that the material, polyethylene, has a surface energy of 22.8 $\mathrm{mJ/m^2}$ [60].

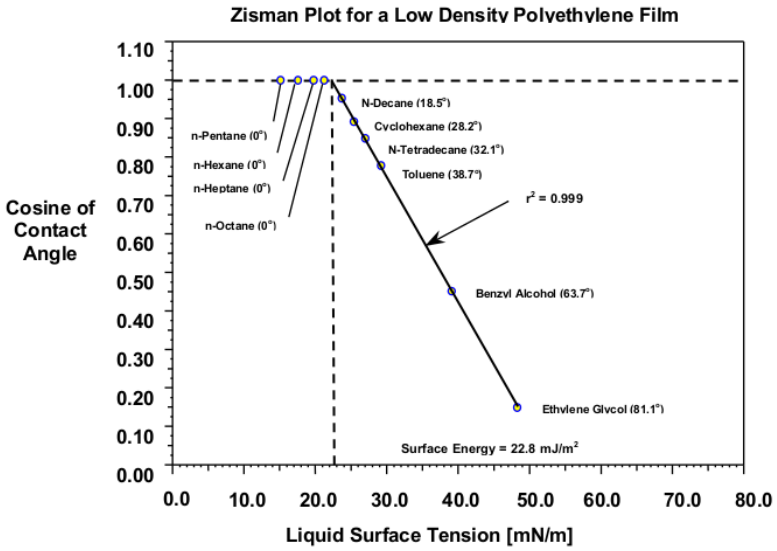


Figure 4.3: An example of a Zisman plot for a low density polyethylene film [60].

The Zisman theory is most commonly used for non-polar surfaces, as it will yield inaccurate results if the surface has the slightest polarity. The theory is based on only one component and can therefore not describe the complex nature of the liquid-solid interaction [60]. In the research by Guarin et al. it was concluded that pure binder was almost completely non-polar whereas binder modified with fish oil ethyl esters showed increased polarity [1]. Since the polarity is an important factor with regards to bonding ability with aggregates, the Zisman theory is inadequate for the work at hand.

Two Component Theory

Frederick M. Fowkes introduced a theory of determining surface energy components. The theory is based on a two component model, whereas the surface free energy is split into two components, dispersive and non-dispersive. In his work, Fowkes calculated the interfacial tension γ_{sl} in terms of the tension of the two surfaces, γ_l and γ_s, as well as the geometric mean of their dispersive γ^d and non-dispersive γ^{nd} parts [61].

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\left(\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^{nd} \gamma_l^{nd}}\right) \tag{4.7}$$

In his derivation of the surface free energy, Fowkes [62] only calculated the dispersive component. The derivation started with the Young-Laplace

equation, which describes the contact angle θ of a liquid l on a plane surface s

$$\gamma_l \cdot \cos\theta = \gamma_s - \gamma_{ls} - \pi_e \tag{4.8}$$

Where γ_l and γ_s is the surface free energy of the liquid and the solid, respectively, θ is the contact angle between the liquid and the surface, π_e is the adsorbed vapor on the solid surface and γ_{ls} is the solid-liquid interaction between the two material, expressed as

$$\gamma_{ls} = \gamma_l + \gamma_s - 2\sqrt{\gamma_l^d \gamma_s^d} \tag{4.9}$$

Using that $\pi_e = 0$ for a liquid l on a given solid s with low surface energy where $\gamma_l > \gamma_s$ and inserting Equation 4.9 into Equation 4.8 it is possible to get the contact angle θ

$$\cos\theta = -1 + 2\sqrt{\gamma_s^d}\left(\frac{\sqrt{\gamma_l^d}}{\gamma_l}\right) \tag{4.10}$$

where γ_l^d and γ_s^d are the dispersive components of the liquid and the solid, respectively. From this derivation it is easy to find the non-dispersive component when both the total surface free energy and the dispersive component are known.

Owens and Wendt [63] put forth an extension on the Fowkes model. In their model, the polar forces of the materials were calculated, as seen in Equation 4.11

$$\gamma_{ls} = \gamma_l + \gamma_s - 2\sqrt{\gamma_l^d \gamma_s^d} - 2\sqrt{\gamma_l^h \gamma_s^h} \tag{4.11}$$

where γ_l^h and γ_s^h are the surface free energy components due to hydrogen bonding and the dipole-dipole interactions of the liquid and the solid, respectively.

The theory was later disproven by researchers, as it is only applicable where one of the interacting materials has an acidic character and the other one basic [64]. The polar component is of interest in this thesis. For practical purposes it is not necessary to divide it further. Therefore, to simplify the data analysis the Fowkes theory is used to find the surface energy components.

Three Component Theory

A three component theory was put forth by van Oss, Chaudbury and Good [65]. Their model can be said to be an extension of the two component theories put forth by Fowkes and Owens and Wendt. It separates the components into disperse and polar, similar to the aforementioned theories, but further separates the polar component into two acidic and basic components. Basing their derivation on the Young-Dupre equation on work of adhesion, they started with Equation 4.6. The work of adhesion can also be expressed as

$$W^a = W^d + W^p \tag{4.12}$$

where W^d and W^p are the work of adhesion due to dispersive and polar forces, respectively. The work of adhesion due to dispersive forces can be described as

$$W^d = 2\sqrt{\gamma_l^d \gamma_s^d} \tag{4.13}$$

and the work of adhesion due to polar forces as

$$W^p = 2\sqrt{\gamma_l^+ \gamma_s^-} + \sqrt{\gamma_l^- \gamma_s^+} \tag{4.14}$$

By inserting Equations 4.6, 4.13 and 4.14 into Equation 4.12, the general form of the model can be expressed as

$$(1 + \cos\theta) = 2\left(\sqrt{\gamma_l^d \gamma_s^d} + \sqrt{\gamma_l^+ \gamma_s^-} + \sqrt{\gamma_l^- \gamma_s^+}\right) \tag{4.15}$$

By using three liquids with known surface free energy components and equipment to measure the contact angle, it is possible to obtain the three unknown surface energy components of the solid in question. The three component model is based on the assumption that the two components within the polar component of water, acid and base, are equal. Based on this, van Oss, Chaudbury and Good calculated the acid and base components for numerous liquids. However, this approach has been criticized and several researchers have put forth their own scale. Despite this criticism, the van Oss, Chaudbury and Good model is still frequently used. This should be kept in mind when dividing the polar component into two, as they are relative to the water polar component scale model used [2]. In this study, the acid-base division is considered to be non-vital and thus the van Oss, Chaudbury and Good theory is not used for calculations.

4.2 Laboratory Methods

4.2.1 Samples

The samples sets created for the laboratory work in this thesis were thought to provide an extreme in either direction of the concentration of the bio-oils. Sample set A, based on the previous work by Guarin et al. [1], is considered at the upper limit while sample set B was designed as a lower limit extreme. A significant difference on the concentration was considered vital in order to gain significant variations in the measurements for different samples. The samples can be seen in Table 4.1.

Table 4.1: The samples used for the laboratory analysis.

Sample	Sample Set	Binder N [%]	Fish Oil Ethyl Ester [%]	Rape Seed Oil [%]	Wetfix N [%]
F	A	92.5	7.5	-	-
FW	A	91.7	7.5	-	0.8
R	A	92.5	-	7.5	-
RW	A	91.7	-	7.5	0.8
F	B	96	4	-	-
FW	B	95.2	4	-	0.8
R	B	96	-	4	-
RW	B	95.2	-	4	0.8

Binder N is a sample of bitumen which was sent by the Icelandic Road and Coastal Administration (IRCA) to KTH Royal Institute of Technology (KTH) for the previous research by Guarin et al. It was initially believed to be of penetration grade 160/220, however research showed that it fell somewhere between penetration grades 100/150 and 160/220. It was noted in the report following the testing that it is possible that the binder N was originally of penetration grade 160/220, but after unknown handling procedure and heating history it became stiffer. Furthermore, it was noted that the difference between the two penetration grades is relatively small and it can prove hard to distinguish between them in real conditions [1].

4.2.2 Short-Term Aging

Short-term aging behavior of the binder mixture is determined using the Rolling Thin Film Oven Test (RTFOT). The test is performed with an unaged

binder mixture. Samples of the mixture are heated, put in bottles, weighed and then cooled down. The bottles are then put in a rotating carousel in a rolling thin film oven. The samples are kept at a steady temperature and airflow within the oven for 85 minutes, after which the bottles with the samples are removed. The samples are cleaned out of the bottles and cooled down. Finally, the samples are weighed and their mass change is documented. The final results are the mass change as a percentage of the initial mass of the samples. Typical values are within the range of 0.05-0.5% and should never exceed 1%. Following the RTFOT, the short-term aged binder can be tested for long-term aging [56].

For this research, the short term aging itself is not important. Therefore, the samples are not weighed after aging, but are tested for surface energy and viscosity. The results from these tests will be compared to outcome of tests on unaged samples.

4.2.3 Viscosity

The viscosity of the binder mixture is an important factor when paving surface dressings, as it has to be fluid enough to be sprayed over the surface at a desired temperature. Adding fluxing or cut-back agents to a binder mixture lowers its viscosity, making it possible to spray it at lower temperature. By measuring the viscosity of the samples, it is possible to determine the required spraying temperature for a given concentration. The samples will be tested at two different temperatures, 80°C and 135°C. The lower temperature is common for the mixing of warm-mix asphalt while the higher is an ideal spraying temperature for surface dressings according to IRCA's guidelines [4]. The viscosity is measured with a Brookfield Rotational Viscometer (RV), shown in Figure 4.4.

Figure 4.4: The equipment used for the rotational viscosity test [66].

The test is performed by first preheating the equipment and the binder mixture until it is fluid enough to pour into a sample chamber, which then is inserted into the environmental chamber. The sample is then heated up to the testing temperature and the rotating spindle put to work. Once the sample has reached the testing temperature, readings are taken from the RV. The readings indicate the torque required to maintain a constant rotation, which can be used to find the viscosity through the following derivation. The torque readings can be used to find the shear stress with

$$\tau = \frac{T}{2\pi R_s^2 L} \tag{4.16}$$

where T is the torque, R_s is the spindle radius and L is the effective spindle length. The shear rate is also needed and can be obtained with

$$\gamma = \frac{2\omega R_c^2 R_s^2}{x^2 \left(R_c^2 - R_s^2\right)} \tag{4.17}$$

where ω is the rotational speed, R_c is the container radius, x radius at the location (at the spindle surface) of calculations. The viscosity can then be calculated with

$$\eta = \frac{\tau}{\gamma} \tag{4.18}$$

where the SI unit of viscosity is Pa·s [66]. In its guidelines IRCA reports the desired viscosity in terms of the kinematic viscosity, in the unit cStoke. The kinematic viscosity can be obtained with Equation 4.19

$$\nu = \frac{\eta}{\rho} \tag{4.19}$$

where ν is the kinematic viscosity and ρ is the density of the liquid. For the purpose of this thesis work, the density of a given sample is assumed to be $\rho = 1000$ kg/m^3. That results in the units for viscosity, mPa·s, and kinematic viscosity, cStoke, taking the same numerical value for any given measurement.

4.2.4 Surface Energy

The surface energy of the binder mixture samples is tested with a drop shape analyzer, using a so-called sessile drop technique. The test can be used for all asphalt binders, except ones that include crumb rubber or other particulate additives. In short, the testing method involves a drop shape analyzer, where a drop of pure, homogeneous probe liquid falls on a smooth binder surface, where a camera captures an image of the liquid on top of the surface. From the image it is possible to measure the contact angle between the liquid and the binder surface. The contact angles between the binder surface and different probe liquids can then be used to determine the unknown surface energy components of the binder [2]. Figure 4.5 shows a photograph of a Krüss Drop Shape Analyzer DSA100s, the equipment used to determine the contact angle.

Figure 4.5: A photo of a drop shape analyzer, the equipment used for the sessile drop technique [67].

The testing procedure, as described by Little and Bhasin [2], can be divided into three categories:

Sampling

Firstly, the binder mixture samples are prepared, modifiers added, and they moved to small aluminum containers. If aging is required, the samples are put through the aging procedure at this stage. The samples are then heated and when they are fluid enough, they are poured onto a glass slide and spread evenly. Each sample is used to cover one slide for each probe liquid tested. Finally, the samples are allowed to cool down to room temperature before testing. It is advisable to keep the samples covered to keep their surface clean.

Testing

Once the samples are firm, the drop shape analyzer is set up. For this test, three or more probe liquids are used to determine the unknown surface energy components. The probe liquids used in this laboratory analysis are Diiodo-Methane, Formamide and water, see Table 4.2.

Table 4.2: The probe liquids and their total interfacial tension (IFT), dispersive tension and polar tension.

Probe Liquid	Total Liquid IFT [mN/m]	Dispersive Tension [mN/m]	Polar Tension [mN/m]
Diiodo-Methane	50.80	48.50	2.30
Formamide	58.20	39.50	18.70
Water	72.80	21.80	51.00

A sample is placed on a platter. When the sample has been properly adjusted, so that the drops will fall on its center line, a drop is released from a syringe above it. The sample is lit up by a light source on one side of it, while a camera on the opposite side records the drop. This procedure is repeated for all samples and all probe liquids, where 5-6 repetitions for each liquid on each sample are sufficient to obtain a reliable average reading. The setup of the drop shape analyzer is shown in Figure 4.6.

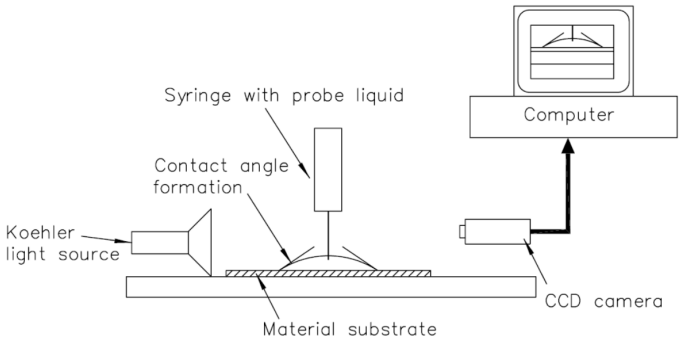


Figure 4.6: A schematic illustration of the sessile drop technique [2].

Data Analysis

Determining the contact angle between the probe liquid and the binder can prove to be the most time consuming task of the test. From the images generated from the recordings, it is possible to determine two contact angles for each droplet, see Figure 4.7.

Figure 4.7: An image of a drop captured by the camera on the drop shape analyzer [2].

The contact angles are calculated with an automated process using computer software. For this thesis work two methods were used, the circle method and the height-width method. Both methods assume that the sessile drop takes a form of a circular arc on the surface. In the circle method, the whole arc is considered compared to only a few points of significance in the heigh-width method [68]. Once contact angles have been established between a given sample and all three probe liquids, it is possible to calculate the surface energy components for the sample. This is also done using a computer software. These surface energy components are then compared and adhesion to aggregates for each sample is determined.

Chapter 5

Results

5.1 Surface Energy

The bio-oils are included in the mixture to lower its viscosity and ensure that spraying is possible at a lower temperature than for an unmodified binder. However, they also modify the surface energy components. From these alterations, several conclusions can be drawn. Most notably, an increase in the polarity indicates that the mixture is hydrophilic and more vulnerable to moisture damage than a mixture which has total surface energy almost exclusively consisting of a dispersive component. Guarin et al. [1] found that the aggregates used in the bleeding sections had a highly polar surface and had a strong inclination to bond with polar liquids, compared to dispersive ones. Therefore, it can be said that the more polar the bio-oil is, the more likely the aggregates are to prefer bonding with it over the binder. The high polarity of the bio-oil can cause it to separate from the mostly dispersive binder and cover the stones, preventing bonding between the binder and the aggregates. Furthermore, the hydrophilic oil covering the aggregates allows water to penetrate into the pavement and build up at the interface between the binder and the aggregates, further preventing bonding. The effect of adhesion promoters, such as Wetfix N, is to increase the polarity of the binder mixture and change the properties of it so that the aggregates prefer bonding with the binder.

By comparing the two different concentrations of the two modifiers, the increase in effects of the bio-oils on the surface energy should be clear. Additionally, the measurements of the samples which include Wetfix N should show its effect with a surge in the polar forces.

The samples tested are F with fish oil; FW with fish oil and Wetfix N; R with rape seed oil and; RW with rape seed oil and Wetfix N. The sample sets

A and B include 7.5% and 4% of the bio-oil, respectively. The remainder of the samples consist of binder N. All samples were tested unaged and after a short-term aging process. Further explanation of the samples can be seen in Table 4.1 in Chapter 4.

The surface energy components were calculated using two methods, the circle method and the height-width method. The results were in good agreement and no significant difference was seen between the two methods. Therefore, only the results for the surface energy components found using the circle method are shown here. Furthermore, for simplification, the results from the contact angle measurements are not shown here. The full results from the sessile drop test are shown in Appendix A.

5.1.1 Binder N

Guarin et al. [1] tested the unaged binder N using the sessile drop method. The results, which are included in this section to compare with the tests performed on the modified binder mixtures, can be seen in Table 5.1.

Table 5.1: The surface energy components of unaged binder N, as tested by Guarin et al [1].

Component	Surface Energy	
	[mN/m]	[%]
Total	43.5 ± 1.2	
Dispersive	43.4 ± 0.8	99.8 ± 1.9
Polar	0.1 ± 0.4	0.2 ± 0.8

As can be seen from Table 5.1, the polarity of the unmodified binder N was found to be very low, if any.

5.1.2 Unaged Binder Samples

The results from the surface energy tests for the unaged binder samples can be seen in Tables 5.2-5.5. Furthermore, the results are compared in Figures 5.1-5.2.

Table 5.2: The surface energy components of unaged sample F.

Component	Surface Energy			
	Sample Set A		Sample Set B	
	[mN/m]	[%]	[mN/m]	[%]
Total	39.2 ± 1.4	-	45.2 ± 2.8	-
Dispersive	34.1 ± 0.6	87.0 ± 1.5	44.9 ± 1.78	99.3 ± 4.5
Polar	5.3 ± 0.8	15.5 ± 2.3	0.3 ± 1.0	0.7 ± 2.8

From Table 5.2 it can be seen that the addition of fish oil esters increases the polarity, compared to the unmodified binder N. When comparing sample set A and B it is clear that with higher concentration of fish oil, the polarity increases significantly.

Table 5.3: The surface energy components of unaged sample FW.

Component	Surface Energy			
	Sample Set A		Sample Set B	
	[mN/m]	[%]	[mN/m]	[%]
Total	41.4 ± 2.8	-	44.1 ± 0.7	-
Dispersive	34.2 ± 1.6	82.6 ± 3.8	44.1 ± 0.7	100.0 ± 1.6
Polar	7.3 ± 1.2	17.6 ± 3.5	0.0 ± 0.0	0.0 ± 0.1

Adding Wetfix N to the mixtures results in an increase in the polarity for the sample from sample set A, while it is decreased to a negligible level for sample set B.

Table 5.4: The surface energy components of unaged sample R.

Component	Surface Energy			
	Sample Set A		Sample Set B	
	[mN/m]	[%]	[mN/m]	[%]
Total	41.5 ± 1.6	-	44.8 ± 2.8	-
Dispersive	37.5 ± 1.1	90.4 ± 2.7	44.8 ± 2.3	100.0 ± 5.6
Polar	4.0 ± 0.5	9.6 ± 1.3	0.0 ± 0.5	0.0 ± 1.2

The effects of the rape seed oil are similar to that of the fish oil esters for the sample with higher concentration, where an increase in the polarity is noticed compared to binder N. The sample from sample set B, however, shows

a decrease in the polarity, although an increase is possible as it is within the margin of error.

Table 5.5: The surface energy components of unaged sample RW.

Component	Surface Energy			
	Sample Set A		Sample Set B	
	[mN/m]	[%]	[mN/m]	[%]
Total	41.5 ± 4.2	-	45.5 ± 0.5	-
Dispersive	37.7 ± 3.0	90.8 ± 7.3	45.2 ± 0.5	99.3 ± 1.1
Polar	3.8 ± 1.2	9.2 ± 3.1	0.4 ± 0.1	0.9 ± 0.1

Adding Wetfix N to the mixture with rape seed oil does not seem to have a significant affect on the surface energy. The polarity is lowered somewhat for sample set A, while a small increase is seen for sample set B. These changes are not as dramatic as seen when adding Wetfix N to the samples which include fish oil.

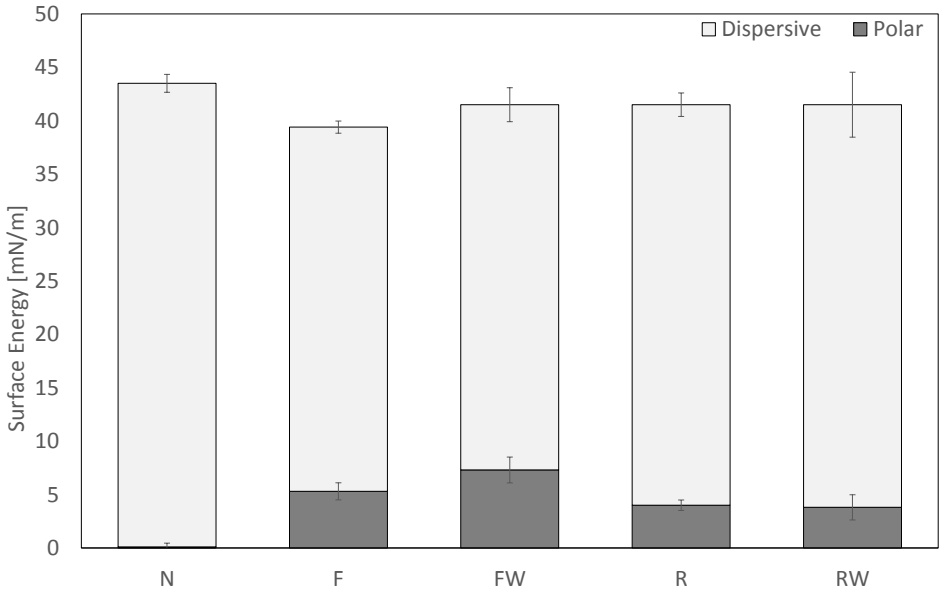


Figure 5.1: A comparison of the surface energy components of the unaged samples in sample set A.

Figure 5.1 shows a comparison of the results from the surface energy tests on the unaged samples from sample set A, as well as the unaged binder N. The polarity is highest in sample FW and is relatively higher than for sample

F. The polarity of the samples which include the rape seed oil is significantly lower than for the fish oil ester samples and no considerable change is seen when Wetfix N is added. It should be noted that the margin of error is large for sample RW, so it is possible that the polarity is somewhat higher or lower. From the figure it is clear that the polarity of the fish oil is higher than the rape seed oil, making it more feasible to use in a binder mixture which is to bond with aggregates with a polar surface.

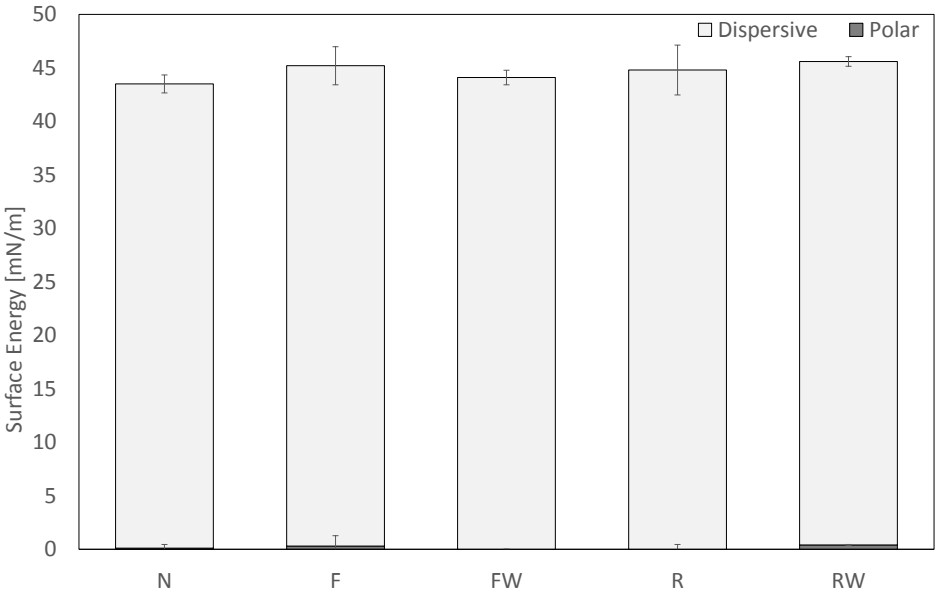


Figure 5.2: A comparison of the surface energy components of the unaged samples in sample set B.

A substantial decrease in the polarity can be seen in the samples from sample set B, shown in Figure 5.2, compared to the samples from sample set A, shown in Figure 5.1. From these results it is clear that the concentration of either of the two tested bio-oils has a significant effect on the surface polarity of the binder mixtures in question. It is possible that the surface polarity does not necessarily represent the polarity in the bulk of the mixture, as it is possible that some separation occurred within the mixture and a higher concentration of bio-oil is seen on the surface. However, it should be noted that no separation was noticed during the laboratory work and it is not believed to be a serious concern here.

5.1.3 Short-Term Aged Binder Samples

The samples were put through a short-term aging process and tested again. The treatment was performed to imitate the aging due to high temperature storage and oxidation during that process. It should be noted that the samples which include Wetfix N were aged with the adhesion promoter already added. Previous studies have shown that Wetfix N is highly sensitive to high-temperature storage and a severe diminish is noticed in its adhesion effect afterwards. Therefore, the differences between the samples with and without the adhesion promoter will not be as considerable as they would have been had the adhesion agent been added after the aging process. The results from the surface energy tests for the short-term aged binder samples can be seen in Tables 5.6-5.9. Furthermore, the results are compared in Figures 5.3-5.4.

Table 5.6: The surface energy components of sample F after having gone through a short-term aging process.

Component	Surface Energy			
	Sample Set A		Sample Set B	
	[mN/m]	[%]	[mN/m]	[%]
Total	41.9 ± 1.3	-	42.7 ± 2.0	-
Dispersive	41.6 ± 1.1	99.3 ± 2.7	42.7 ± 1.2	100.0 ± 2.9
Polar	0.3 ± 0.1	0.7 ± 0.3	0 ± 0.8	0.0 ± 1.8

The aging process seems to affect the binder mixture significantly. When Table 5.6 is compared to Table 5.2, it can be seen that while the total surface energy shows little change, the decrease in polarity is considerable. This could indicate that the polar component of the fish oil is highly volatile and evaporates or diminishes during the aging process.

Table 5.7: The surface energy components of sample FW after having gone through a short-term aging process.

Component	Surface Energy			
	Sample Set A		Sample Set B	
	[mN/m]	[%]	[mN/m]	[%]
Total	41,6 ± 1.8	-	45.0 ± 2.2	-
Dispersive	41.3 ± 1.1	99.3 ± 2.7	44.9 ± 1.2	99.8 ± 2.9
Polar	0.3 ± 0.6	0.7 ± 1.5	0.1 ± 1.0	0.2 ± 2.3

When Tables 5.7 and 5.3 are compared, little change is observed in the total surface energy. The polarity, however, is lowered dramatically. This further supports that the polar properties of the fish oil are lowered during aging. Furthermore, when comparing the short-term aged fish oil ethyl ester modified binder mixtures with and without Wetfix N, it can be seen that the surface energy components are very similar for sample set A. For sample set B, the total surface energy is somewhat increased. However, the increase is mostly due to higher dispersive forces, as very little increase in polarity is noticed.

Table 5.8: The surface energy components of sample R after having gone through a short-term aging process.

Component	Surface Energy			
	Sample Set A		Sample Set B	
	[mN/m]	[%]	[mN/m]	[%]
Total	46.9 ± 1.3	-	43.7 ± 2.4	-
Dispersive	46.7 ± 1.0	99.6 ± 2.0	43.7 ± 2.3	100.0 ± 4.8
Polar	0.2 ± 0.4	0.4 ± 0.8	0.0 ± 0.1	0.0 ± 0.3

A surge in total surface energy is observed in short-term aged binder modified with rape seed oil, Table 5.8, compared to the unaged sample, Table 5.4, for sample set A. The increased energy is observed in the dispersive component, as the polarity is lowered significantly. Sample set B shows no significant change in the surface energy components and the polarity remains close to none, albeit with a lower degree of uncertainty.

Table 5.9: The surface energy components of samples RW after having gone through a short term aging process.

Component	Surface Energy			
	Sample Set A		Sample Set B	
	[mN/m]	[%]	[mN/m]	[%]
Total	43.2 ± 1.4	-	46.7 ± 1.4	-
Dispersive	43.1 ± 1.4	99.8 ± 3.2	46.6 ± 0.9	99.8 ± 2.1
Polar	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.5	0.2 ± 1.0

When comparing Table 5.9 to Table 5.5, it shows that the rise in the surface energy is not as dramatic as was seen for the samples without Wetfix N (Tables 5.4 and 5.8). As observed in the results for other samples, the polarity drops

for sample set A when tested after the aging process, while the samples from sample set B remain with low polarity.

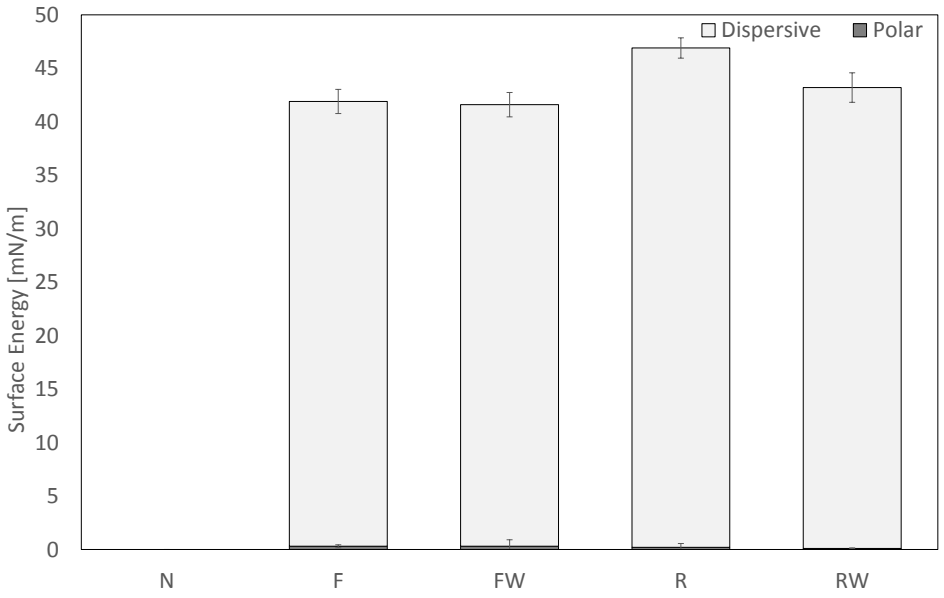


Figure 5.3: A comparison of the surface energy components of the short-term aged samples in sample set A.

Figure 5.3 shows a trend, where the polarity of the samples from sample set A is lowered considerably during the aging process. The samples which include fish oil esters have higher polarity than the samples modified with rape seed oil. This could indicate that the polar component of the rape seed oil is made up of more volatile molecules than the fish oil ester. Furthermore, the addition of Wetfix N does not have a noticeable effect on the polarity of the mixture. That suggest that the adhesion promoter is very sensitive to heat treatment and shows a severely declined effect after being put through the aging process. These findings support the conclusions drawn from earlier research by Petursson [25].

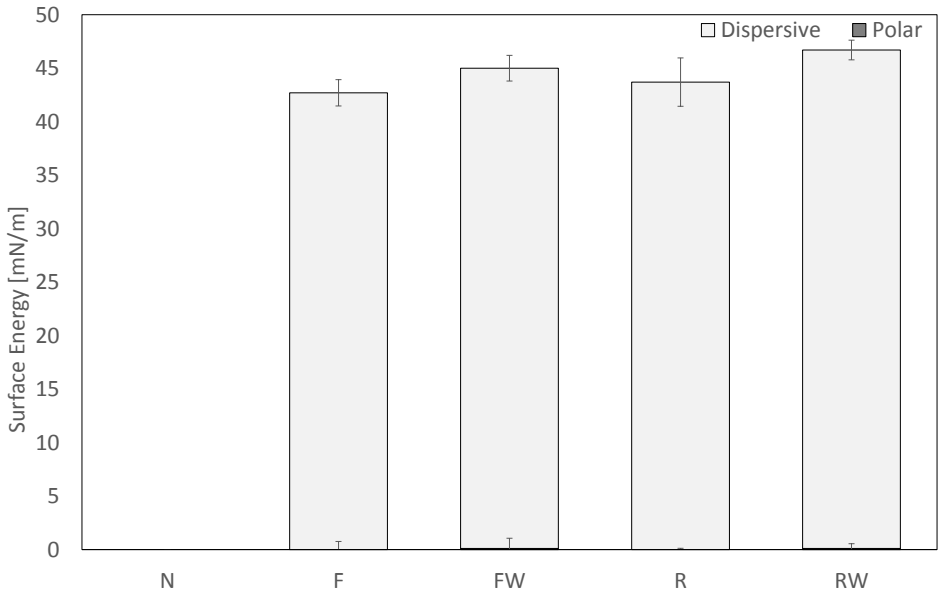


Figure 5.4: A comparison of the surface energy components of the short-term aged samples in sample set B.

Similarly, Figure 5.4 shows that the polarity of the unaged samples from sample set B, see Figure 5.2, is eradicated. The unaged samples had very little polarity, so the change is not as dramatic as seen in sample set A. These results does however support the conclusions drawn for those samples, the poor heat tolerance of Wetfix N and the volatility of the polar components of the bio-oils.

5.2 Viscosity

A Brookfield viscosity test was performed to determine whether or not the sample mixtures are fluid enough to be sprayed out at a desired temperature. In its guidelines, the Icelandic Road and Coastal Administration (IRCA) lists the desired spraying temperature range as 130-140°C and the desired kinematic viscosity in the range 40-100 cStoke [4]. The results from the viscosity tests are shown in Tables 5.10 and 5.11. As stated in Chapter 4, the density of a given sample is assumed to be $\rho_{samples} = 1000$ kg/m^3 and thus the numerical values remain the same when converting from viscosity (mPa·s) to kinematic viscosity (cStoke) with Equation 4.19.

Table 5.10: The viscosity of the unaged binder samples.

	Viscosity at 80°C [mPa · s]		Viscosity at 135°C [mPa · s]	
Sample	Set A	Set B	Set A	Set B
N	-[1]		229.5	
F	1640	3210	96.5	140.5
FW	1500	3040	91.5	134.0
R	2090	3730	107.5	153.5
RW	1950	3520	103.0	145.0

[1] Test not possible due to high viscosity

The purpose of adding bio-oil modifiers to binder is to lower its viscosity, an effect clearly seen in Table 5.10. By adding 4% of the bio-oils, the viscosity is lowered significantly and even further when the concentration is increased to 7.5%. The fish oil ethyl esters are around 10% more effective in lowering the viscosity, compared to the rape seed oil modified binder with the same concentration. Furthermore, the addition of Wetfix N lowers the viscosity of each sample by around 5%.

Table 5.11: The viscosity of the short term aged binder samples.

	Viscosity at 80°C [mPa · s]		Viscosity at 135°C [mPa · s]	
Sample	Set A	Set B	Set A	Set B
N	-[1]		327.5	
F	4520	6950	171.5	212.5
FW	4230	6360	165.0	208.5
R	3880	6180	158.5	202.5
RW	3680	5720	154.4	196.0

[1] Test not possible due to high viscosity

As seen in Table 5.11, the samples respond differently to the short-term aging process, with regards to viscosity. The viscosity of the samples which include rape seed oil does not rise as considerably as the samples modified with fish oil. That indicates that the rape seed oil maintains a larger part of its low viscosity properties compared to the fish oil. As seen with Table 5.10, the viscosity is lowered with the addition of Wetfix N, although not as significantly. This indicates that the adhesion promoter loses some of its

low viscosity properties during the aging process. This further supports that Wetfix N is not suited for high temperature treatment.

From the two viscosity measurements for each sample, it is possible to set up a graph for each of them showing the temperature range at which spraying is possible. Figures 5.5-5.8 show the relationship between the viscosity ad the temperature. When the viscosity is shown on a log-scale and a trendline is extrapolated through the two measured data points, it is possible to determine the spraying temperature range.

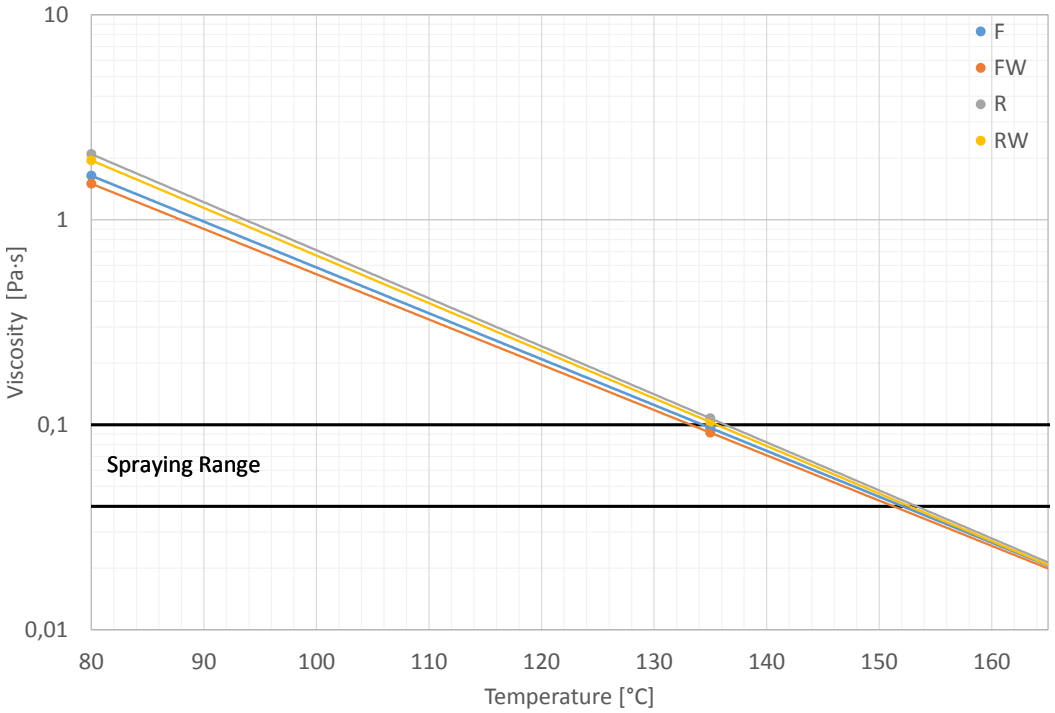


Figure 5.5: The spraying temperature range for the unaged samples from sample set A.

Figure 5.5 shows the spraying temperature range for the samples in the sample set A. The range is quite similar for all samples, with the lower limit close to 135°C and the upper limit around 150°C. All samples fall within the limits IRCA has set for the desired spraying temperature.

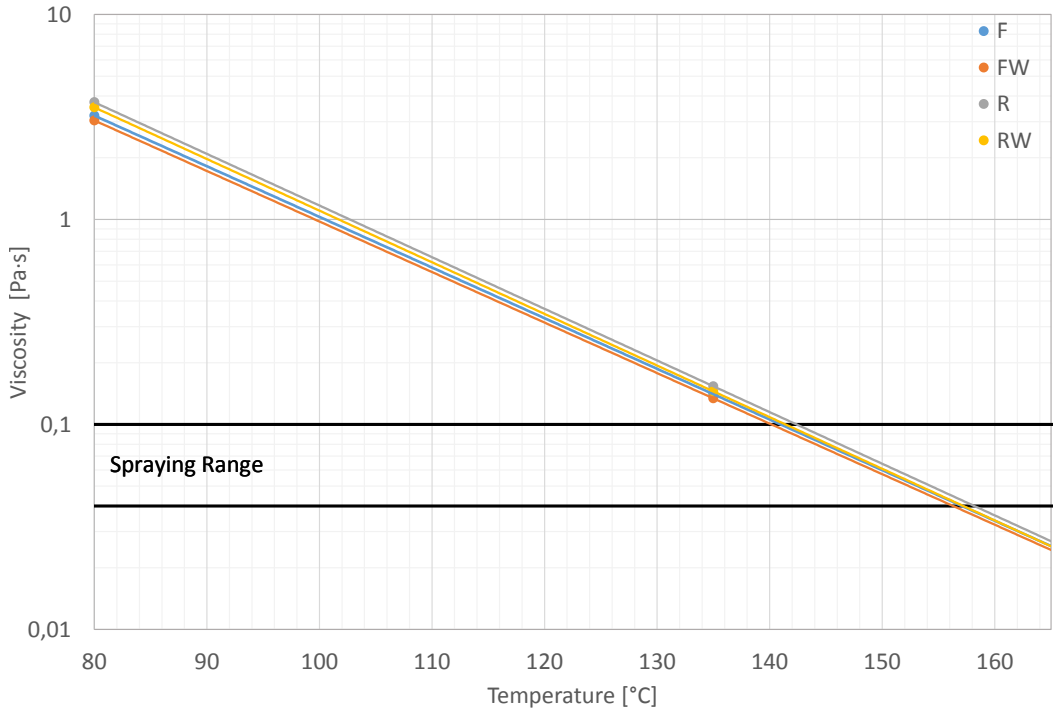


Figure 5.6: The spraying temperature range for the unaged samples from sample set B.

Figure 5.6 shows the spraying temperature range for the samples in sample set B. As for the unaged samples from sample set A, the ranges for the different samples in sample set B are quite similar. The lowest lower limit within the spraying range is for sample FW, which reaches 100 mPa·s at 140°C while the other samples fall within the spraying range at 1-2°C higher. The upper limit of the range is 156-158°C, lowest for sample FW and highest for sample R. A comparison of the spraying temperature range for the unaged samples from sample sets A and B shows clearly the effect of the modifiers, as the lower limit of the range differs typically around 5°C for a given sample.

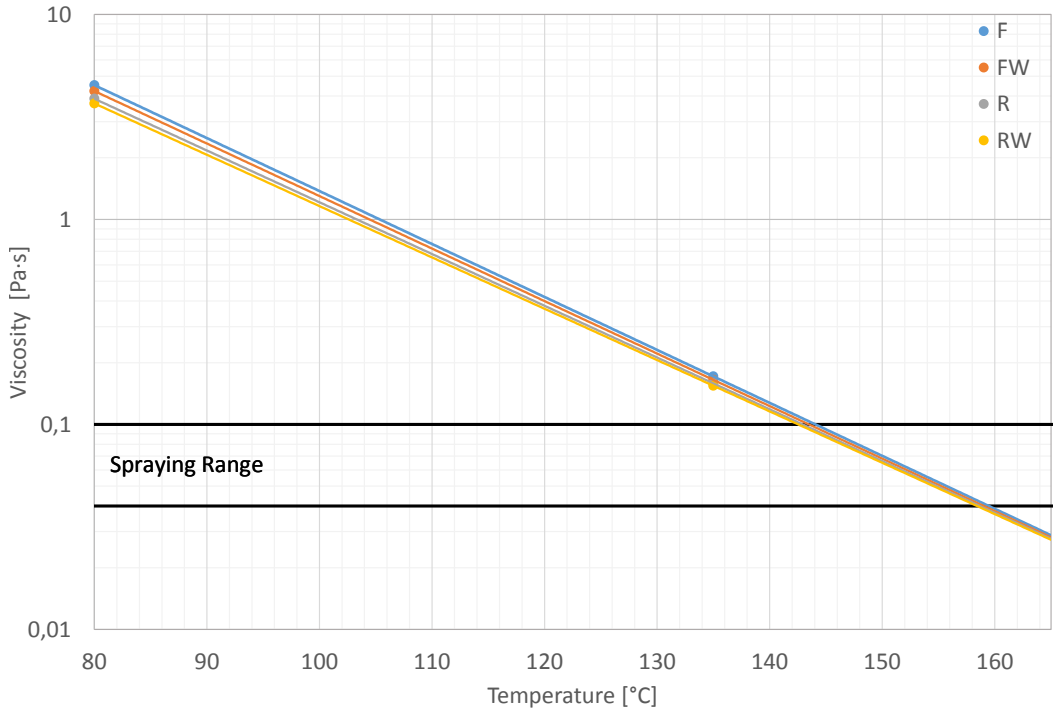


Figure 5.7: The spraying temperature range for the samples from sample set A after they have gone through a short-term aging process.

From Figure 5.7 it is clear that the aging process has an effect on the viscosity. The temperature range for the short-term aged samples from sample set A is between 143°C and 159°C, which is around 10°C higher than for the unaged samples from the same sample set and even lower for the aged samples. Again, the variations of viscosity between samples are very little. All samples fall outside the desired spraying temperature range, as listed in the guidelines from IRCA.

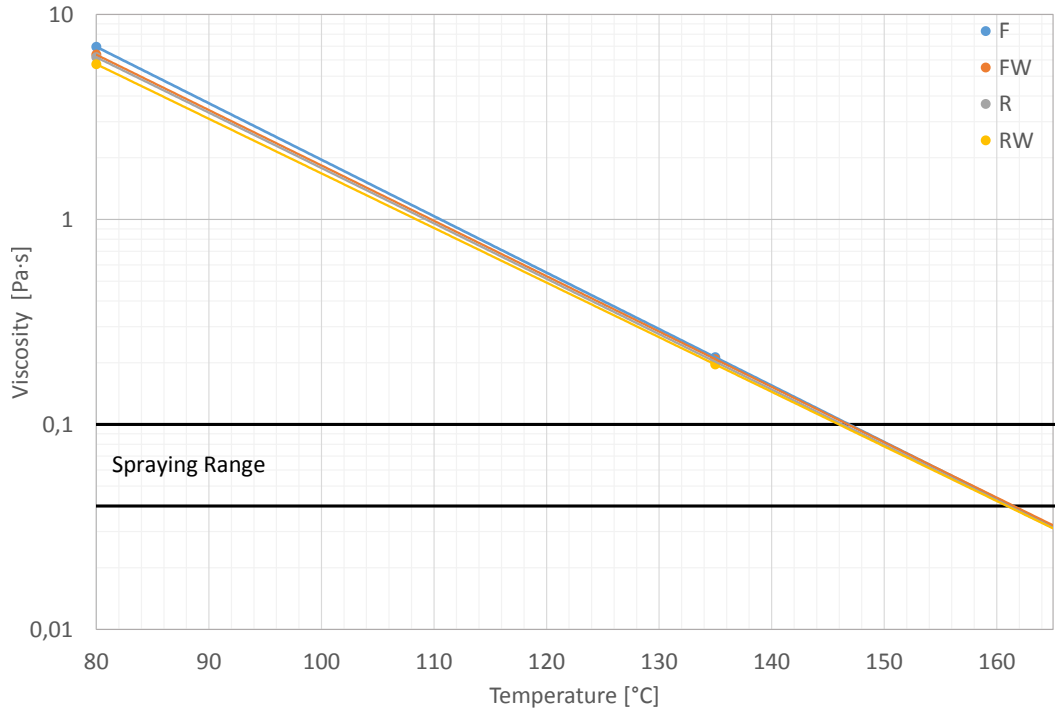


Figure 5.8: The spraying temperature range for the samples from sample set B after they have gone through a short-term aging process.

As with the short-term aged sample from sample set A, all samples in sample set B fall outside the desired temperature range after they have been put through a short-term aging process. The range shown in the graph has a lower limit of around 147°C, which is well outside the desired temperature range.

Chapter 6

Discussion and Conclusions

6.1 Conclusions

In this thesis an extensive background research on road sections located in the northern part of Iceland where severe bleeding occurred early 2013 was undertaken. Following the background study, a laboratory investigation was performed to better understand the behavior of the materials included in the binder mixtures. The laboratory testing consisted of a sessile drop test and a Brookfield viscosity test. The sessile drop test was performed in order to attain the dispersive and polar components of the binder mixture samples. The ratio between the polar component and the total surface energy is referred to as the polarity. The polarity is a vital aspect of the binder mixture, as it can hint at the adhesion with aggregates, which highly favor bonding with polar liquids over dispersive ones. The viscosity test was carried out to obtain a temperature range within which spraying was possible. The spraying temperature range is a very important factor when paving surface dressings, as the binder mixture has to be sprayed out before aggregates are distributed over it. Furthermore, samples which included Wetfix N were tested and compared to similar samples which did not include the adhesion promoter. This was done to show the effect of adhesion promoters on the bonding abilities of the binder mixtures. Moreover, all samples were put through a short-term aging process and tested before and after. These measures were made to investigate the effect of high temperature treatment on the bitumen, the bio-oils and the adhesion promoter.

The results from the surface energy test revealed a direct connection between higher concentration of bio-oils, especially the fish oil ethyl ester, and increased polarity in the binder mixture. The polarity indicates that the bio-oils are highly hydrophilic, which could lead to problems during the lifetime

of the pavement. These problems are likely to arise if separation of the bio-oil from the binder occurs, due to poor mixing or excessive concentration of the bio-oil. Furthermore, the addition of Wetfix N was found to increase the polarity of the mixtures, leading to better bonding between the binder and aggregates. The surface energy tests on the short-term aged samples also yielded interesting results. The polarity of the binder mixtures was severely lessened after the aging process, which indicates volatility of the polar molecules in the bio-oil. Little change was seen on the samples which included Wetfix N compared to those who did not, showing that the adhesion effect is diminished during the high-temperature aging process.

The purpose of the Brookfield viscosity test was to determine the lower limit of the bio-oil concentration. Results from the tests showed that the fish oil ethyl ester is better suited to lower viscosity, compared to rape seed oil at the same concentration. Furthermore, the inclusion of Wetfix N lowered the viscosity by around 2-5%. After the aging process, all samples were seen to have higher viscosity and graphs showing the spraying temperature range placed them outside the recommended temperature range, shown in the guidelines set by th Icelandic Road and Coastal Administration (IRCA) guidelines.

Furthermore, on the basis of these laboratory experiments it was concluded that the fish oil ethyl ester is better suited as a modifier in surface dressings. More detailed reasons are discussed in the section following.

6.2 Recommendations

Based on the findings of this research the following recommendations can be made:

Quality Control

After meetings with experts at IRCA and by reading through documents during the site investigation, it has become clear that the quality control system at the time of paving was insufficient. To minimize the risk of future failure, an efficient documentation system could be implemented in order to identify errors and learn from mistakes. When setting up the site description table (Table 2.6) several issues arose. Firstly, the documents available consisted of non-standardized spreadsheets with large gaps of missing data. Filling these gaps was either subject to the memory of experts at IRCA or not possible at all. Secondly, reports on road section 1-K8 were never found as the site inspector claimed to have lost the data. Thirdly, it was not possible to retrieve the

missing data from the contractor which paved the road, which indicates that IRCA is too lenient on contractors with regards to documentation. Documentation at the time of paving by both site inspectors and contractors reduces the risk of errors. Furthermore, by standardizing the data registration system, IRCA expedites the work of researchers, both internal and external, as they gain understanding of the site description, paving conditions and materials.

According to experts at IRCA, some steps have been taken towards a quality control system since the sections studied here were paved. That is a positive measure and will likely benefit the paving industry in Iceland in the long-term. The author did not have access to this system and thus it is not possible to make judgments on its efficiency here. The only recommendation here is to aspire to a perfect quality control system, making it easier to learn from past mistakes.

Bio-Oil

By comparing the results from the binder modified with fish oil ethyl ester and rape seed oil, respectively, it can be seen that the fish oil is better suited for use in road construction. Firstly, the fish oil is a clear homogeneous liquid, while the rape seed oil is not entirely homogeneous and has some sludge at the bottom. Secondly, the fish oil ester has higher polarity and is thus better suited to aid bonding with aggregates than the rape seed oil at the same concentration. However, separation is a concern with higher concentration of fish oil. Thirdly, the fish oil is more effective in lowering the viscosity, compared to the rape seed oil at a given concentration.

Adhesion Promoters

The effect of Wetfix N, the adhesion promoter tested in this work, was quite clear. When Wetfix N was added to the unaged samples the polarity was increased, indicating improved adhesion with aggregates, and the viscosity lowered, decreasing the lower limit of the spraying range. However, after the short-term aging process a severe decline was noticed in the influence of the adhesion promoter. That is in agreement with the findings of other studies. Thus, it is recommended that if Wetfix N is used as an adhesion promoter, it should be added to the binder mixture at later stages in the process, that is it should not be stored within the mixture at high temperatures for an extended time.

Mixture

The mixtures tested in this thesis work cannot be recommended for use in the field. The samples which included 4% concentration of the fish oil ethyl ester had little to none polarity, even with the addition of Wetfix N, suggesting poor adhesion with aggregates. Furthermore, the lower limit of the spraying range of the unaged samples is slightly higher than the recommended limit in the guidelines put forth by IRCA. The samples which included 7.5% concentration of the fish oil were within the guideline limits. However, the high polarity of the samples is a concern and could cause separation of the fish oil from the binder mixture. Therefore, a recommended fish oil concentration in the mixture has to be somewhere in between the two tested. Based on that, the recommended mixture should include a 6% concentration of fish oil ethyl ester, which has lower viscosity than the 4% mixture and lower polarity than the 7.5% mixture. The inclusion of Wetfix N proved to have a positive effect on the mixtures, both in regards to surface energy and viscosity. As the variation in the concentration of the adhesion promoter only took to whether or not it was included, the tested concentration is recommended. The remainder of the binder mixture should consist of bitumen with a penetration grade of 160/220.

6.3 Future Work

Due to time constraints the scope of this study was quite narrow. A more generous research time would have allowed for a more extensive study of the samples. Most notably, performing an adhesive test to determine bonding between the binder and the aggregates is a very important test that should be performed in the future. From that test, it is possible to rank binder mixtures based on their effectiveness and select the best suited mixture of binder, bio-oil and adhesion promoter.

Furthermore, in order to establish an ideal mixture, a number of new samples have to be tested. The samples tested in this thesis were seen to provide an extreme on either side of the scale with regards to bio-oil concentration. Therefore, by testing samples which include 4%-7% of bio-oil by weight, at 0.5% increments, it would be possible to optimize the bio-oil concentration in the binder mixture. Moreover, testing samples which include different concentrations of Wetfix N, or other adhesion promoters such as TPH and Impact 8000, could be used to determine the ideal use of adhesion promoters with regards to concentration and storage. It could also be beneficial to test short-term aged samples where the adhesion promoter is added after the aging process. By comparing the results to the ones from this thesis the sensitivity

to high temperature treatment could be determined.

Lastly, through discussions with experts within the paving industry in Iceland it is clear that bleeding has been a serious problem for a long time. Therefore, a comparison to countries with similar conditions could prove beneficial. For example, a questionnaire, sent to countries with similar climates, with respect to the frequency and scale of bleeding events as well as methods used to prevent them could be used to improve techniques and methods used in Iceland. Another possible approach would be to undertake an in-depth investigation focusing on one country where surface dressings are commonly used and learn from the mistakes and successes of the road authorities in that country.

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Appendix A

Results from the Sessile Drop Test

Previous Work

Table A.1: The mean contact angles of the probe liquids on the surface of unaged binder N, as tested by Guarin et al [1].

Probe Liquid	Mean Contact Angle Circle Method [deg.]	Mean Contact Angle Height-Width Method [deg.]
Diiodo-Methane	26.0	24.3
Formamide	71.1	71.9
Water	90.2	91.7

Table A.2: The surface energy components of unaged binder N, as tested by Guarin et al [1].

Component	Surface Energy Circle Method [mN/m]	Surface Energy Height-Width Method [mN/m]
Total	43.5 ± 1.19	44.5 ± 0.90
Dispersive	43.4 ± 0.84	44.5 ± 0.53
Polar	0.1 ± 0.35	0.0 ± 0.37

Samples

The samples used for the tests are shown in Table A.3 which is identical to Table 4.1

Table A.3: The samples used for the laboratory analysis.

Sample	Sample Set	Binder N [%]	Fish Oil Ethyl Ester [%]	Rape Seed Oil [%]	Wetfix N [%]
F	A	92.5	7.5	-	-
FW	A	91.7	7.5	-	0.8
R	A	92.5	-	7.5	-
RW	A	91.7	-	7.5	0.8
F	B	96	4	-	-
FW	B	95.2	4	-	0.8
R	B	96	-	4	-
RW	B	95.2	-	4	0.8

Unaged Binder Samples

Table A.4: The mean contact angles of the probe liquids on the surface of unaged sample F.

	Mean Contact Angle Circle Method [deg.]		Mean Contact Angle Height-Width Method [deg.]	
Probe Liquid	Set A	Set B	Set A	Set B
Diiodo-Methane	28.7	28.4	29.4	27.2
Formamide	70.4	77.2	66.1	79.0
Water	70.2	99.1	71.1	97.8

Table A.5: The surface energy components of unaged sample F, where the samples from sets A and B include 7.5% and 4% of fish oil ethyl esters, respectively, while the remainder consists of binder N.

	Surface Energy Circle Method [mN/m]		Surface Energy Height-Width Method [mN/m]	
Component	Set A	Set B	Set A	Set B
Total	39.3 ± 1.37	45.2 ± 2.75	40.4 ± 2.26	44.8 ± 2.66
Dispersive	34.1 ± 0.57	44.9 ± 1.78	35.5 ± 1.27	44.6 ± 1.81
Polar	5.3 ± 0.80	0.3 ± 0.97	4.9 ± 0.99	0.3 ± 0.85

Table A.6: The mean contact angles of the probe liquids on the surface of unaged sample FW.

	Mean Contact Angle Circle Method [deg.]		Mean Contact Angle Height-Width Method [deg.]	
Probe Liquid	Set A	Set B	Set A	Set B
Diiodo-Methane	31.9	27.9	30.7	27.5
Formamide	60.4	70.5	61.3	71.2
Water	67.6	93.5	69.3	94.7

Table A.7: The surface energy components of unaged sample FW.

	Surface Energy Circle Method [mN/m]		Surface Energy Height-Width Method [mN/m]	
Component	Set A	Set B	Set A	Set B
Total	41.4 ± 2.80	44.1 ± 0.71	41.3 ± 3.55	44.6 ± 1.62
Dispersive	34.2 ± 1.59	44.1 ± 0.68	35.1 ± 2.31	44.6 ± 1.03
Polar	7.3 ± 1.21	0.0 ± 0.02	6.3 ± 1.23	0.0 ± 0.59

Table A.8: The mean contact angles of the probe liquids on the surface of unaged sample R.

	Mean Contact Angle Circle Method [deg.]		Mean Contact Angle Height-Width Method [deg.]	
Probe Liquid	Set A	Set B	Set A	Set B
Diiodo-Methane	28.8	29.7	26.8	28.8
Formamide	62.3	68.2	62.2	70.5
Water	74.2	96.1	73.2	95.3

Table A.9: The surface energy components of unaged sample R.

	Surface Energy Circle Method [mN/m]		Surface Energy Height-Width Method [mN/m]	
Component	Set A	Set B	Set A	Set B
Total	41.5 ± 1.59	44.8 ± 2.77	42.0 ± 1.62	44.5 ± 2.68
Dispersive	37.5 ± 1.10	44.8 ± 2.33	37.9 ± 0.93	44.5 ± 2.01
Polar	4.0 ± 0.49	0.0 ± 0.45	4.2 ± 0.69	0.0 ± 0.67

Table A.10: The mean contact angles of the probe liquids on the surface of unaged sample RW.

	Mean Contact Angle Circle Method [deg.]		Mean Contact Angle Height-Width Method [deg.]	
Probe Liquid	Set A	Set B	Set A	Set B
Diiodo-Methane	31.1	27.7	30.2	28.2
Formamide	59.8	78.0	59.8	78.4
Water	76.2	99.3	76.7	98.0

Table A.11: The surface energy components of unaged sample RW.

	Surface Energy Circle Method [mN/m]		Surface Energy Height-Width Method [mN/m]	
Component	Set A	Set B	Set A	Set B
Total	41.5 ± 4.22	45.5 ± 0.50	41.8 ± 4.10	44.6 ± 1.99
Dispersive	37.7 ± 3.04	45.2 ± 0.45	38.2 ± 2.83	44.3 ± 1.89
Polar	3.8 ± 1.18	0.4 ± 0.05	3.5 ± 1.27	0.2 ± 0.10

Short-Term Aged Binder Samples

Table A.12: The mean contact angles of the probe liquids on the surface of samples F after they have gone through a short term aging process.

	Mean Contact Angle Circle Method [deg.]		Mean Contact Angle Height-Width Method [deg.]	
Probe Liquid	Set A	Set B	Set A	Set B
Diiodo-Methane	28.6	29.4	27.0	29.1
Formamide	71.6	74.4	73.5	75.8
Water	88.7	93.4	87.2	92.8

Table A.13: The surface energy components of sample F after they have gone through a short term aging process.

	Surface Energy Circle Method [mN/m]		Surface Energy Height-Width Method [mN/m]	
Component	Set A	Set B	Set A	Set B
Total	41.9 ± 1.27	42.7 ± 1.99	41.6 ± 1.22	42.3 ± 2.71
Dispersive	41.6 ± 1.13	42.7 ± 1.23	41.3 ± 1.07	42.3 ± 1.82
Polar	0.3 ± 0.14	0.0 ± 0.76	0.3 ± 0.15	0.0 ± 0.89

Table A.14: The mean contact angles of the probe liquids on the surface of sample FW after they have gone through a short term aging process.

	Mean Contact Angle Circle Method [deg.]		Mean Contact Angle Height-Width Method [deg.]	
Probe Liquid	Set A	Set B	Set A	Set B
Diiodo-Methane	27.4	28.8	26.7	28.1
Formamide	73.3	74.6	73.1	76.5
Water	87.6	98.1	88.3	96.1

Table A.15: The surface energy components of sample FW after they have gone through a short term aging process.

	Surface Energy Circle Method [mN/m]		Surface Energy Height-Width Method [mN/m]	
Component	Set A	Set B	Set A	Set B
Total	41.6 ± 1.75	45.0 ± 2.16	42.2 ± 1.52	44.0 ± 2.17
Dispersive	41.3 ± 1.14	44.9 ± 1.20	41.9 ± 0.99	44.0 ± 1.35
Polar	0.3 ± 0.61	0.1 ± 0.96	0.2 ± 0.54	0.1 ± 0.82

Table A.16: The mean contact angles of the probe liquids on the surface of samples R after they have gone through a short term aging process.

	Mean Contact Angle Circle Method [deg.]		Mean Contact Angle Height-Width Method [deg.]	
Probe Liquid	Set A	Set B	Set A	Set B
Diiodo-Methane	26.2	31.4	25.8	28.1
Formamide	72.9	71.3	69.8	75.1
Water	93.5	96.7	94.1	97.2

Table A.17: The surface energy components of sample R after they have gone through a short term aging process.

	Surface Energy Circle Method [mN/m]		Surface Energy Height-Width Method [mN/m]	
Component	Set A	Set B	Set A	Set B
Total	46.9 ± 1.31	43.7 ± 2.38	45.3 ± 1.94	44.8 ± 1.75
Dispersive	46.7 ± 0.95	43.7 ± 2.26	45.3 ± 1.24	44.7 ± 1.07
Polar	0.2 ± 0.36	0.0 ± 0.12	0.0 ± 0.71	0.1 ± 0.68

Table A.18: The mean contact angles of the probe liquids on the surface of sample RW after they have gone through a short term aging process.

	Mean Contact Angle Circle Method [deg.]		Mean Contact Angle Height-Width Method [deg.]	
Probe Liquid	Set A	Set B	Set A	Set B
Diiodo-Methane	27.5	28.1	28.0	27.1
Formamide	70.8	69.0	69.9	71.6
Water	90.9	98.9	89.7	99.8

Table A.19: The surface energy components of samples RW after they have gone through a short term aging process.

	Surface Energy Circle Method [mN/m]		Surface Energy Height-Width Method [mN/m]	
Component	Set A	Set B	Set A	Set B
Total	43.2 ± 1.44	46.7 ± 1.37	42.8 ± 1.97	47.1 ± 1.99
Dispersive	43.1 ± 1.38	46.6 ± 0.92	42.6 ± 1.83	46.9 ± 1.13
Polar	0.1 ± 0.05	0.1 ± 0.45	0.2 ± 0.14	0.3 ± 0.86

Appendix B

Results from the Brookfield Viscosity Test

Sample Set A

Unaged

Sample	80°C				135°C			
	Spindle	Spindle Speed [rpm]	Viscosity [mPa*s]	Percentage [%]	Spindle	Spindle Speed [rpm]	Viscosity [mPa*s]	Percentage [%]
F	S21	10	1640	32,8	S21	100	96,5	19,2
FW	S21	10	1500	30	S21	100	91,5	18,3
R	S21	10	2090	41,7	S21	100	107,5	21,5
RW	S21	10	1950	39	S21	100	103	20,6

Short-term aged

Sample	80°C				135°C			
	Spindle	Spindle Speed [rpm]	Viscosity [mPa*s]	Percentage [%]	Spindle	Spindle Speed [rpm]	Viscosity [mPa*s]	Percentage [%]
F	S21	5	4520	45,2	S21	100	171,5	34,3
FW	S21	5	4230	42,2	S21	100	165	33
R	S21	5	3880	38,8	S21	100	158,5	31,7
RW	S21	5	3680	36,8	S21	100	154,4	30,9

Sample Set B

Unaged

Sample	80°C				135°C			
	Spindle	Spindle Speed [rpm]	Viscosity [mPa*s]	Percentage [%]	Spindle	Spindle Speed [rpm]	Viscosity [mPa*s]	Percentage [%]
F	S21	5	3210	32,1	S21	100	140,5	28,1
FW	S21	5	3040	30,4	S21	100	134,0	26,8
R	S21	5	3730	37,3	S21	100	153,5	30,6
RW	S21	5	3520	35,2	S21	100	145,0	29,0

Short-term aged

Sample	80°C				135°C			
	Spindle	Spindle Speed [rpm]	Viscosity [mPa*s]	Percentage [%]	Spindle	Spindle Speed [rpm]	Viscosity [mPa*s]	Percentage [%]
F	S21	5	6950	69,5	S21	100	212,5	42,5
FW	S21	5	6360	63,6	S21	100	208,0	41,6
R	S21	5	6180	61,8	S21	100	202,0	40,4
RW	S21	5	5720	57,2	S21	100	196,0	39,2

Sample Set N

Unaged

Sample	80°C				135°C			
	Spindle	Spindle Speed [rpm]	Viscosity [mPa*s]	Percentage [%]	Spindle	Spindle Speed [rpm]	Viscosity [mPa*s]	Percentage [%]
N	-	-	-	-	S21	100	229,5	45,9

Short-term aged

Sample	80°C				135°C			
	Spindle	Spindle Speed [rpm]	Viscosity [mPa*s]	Percentage [%]	Spindle	Spindle Speed [rpm]	Viscosity [mPa*s]	Percentage [%]
N	-	-	-	-	S21	100	327,5	65,5