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The antioxidant effect of grape pomace in asphalt binder

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ABSTRACT
Asphalt binder ages on time mainly due to oxidation during mixing, and in service along the years. The aging effect will diminish material viscoelastic properties until it becomes brittle. Once asphalt binder reaches its brittle stage, the material will reduce its capability to withstand repeated traffic loads while in service, (fatigue). There are four methods to enhance fatigue life of an asphalt pavement; among these methods is the use of antioxidants. The work presented in this paper summarises the research work where grape pomace residue has been used as an antioxidant. The research objectives were to evaluate and understand the antioxidant effect of this additive. Consistency and rheological tests where used to prove the relative effect for reducing aging when adding grape pomace residue. It was possible to demonstrate the antioxidant properties of the additive but at the same time, it was found that the small solid undissolved particles of the additive would produce a secondary effect that will it make more difficult to isolate the pure antioxidant effect.

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Asphalt binder; oxidation; aging; fatigue; grape pomace; antioxidant

1. Introduction

Asphalt binder ages on time mainly due to oxidation during mixing and along the years while exposed to loads and environmental factors. The aging effect will diminish material viscoelastic properties making asphalt binder stiffer and stiffer until it becomes a brittle material. Once asphalt binder reaches high stiffness values and becomes brittle, the material will reduce its capability to withstand repeated traffic loads while in service (fatigue resistance). Asphalt binder stiffens over time mainly through the following primary mechanisms:

- Oxidation and polymerisation: The binder oxidises by interchanging electrons with the oxygen, forming free radicals that react with other free radicals of the binder molecules increasing molecular size (polymerisation) and the oxidation rate is function of temperature and oxygen availability (Petersen 2009). This process is more severe during construction but also continues during pavement service life. While in service pavement is also affected by ultraviolet light but this oxidation effect compromises only few microns of the asphalt surface and not the entire thickness of the asphalt layers.
- Loss of volatiles: The binder is subjected to loss of volatiles mainly during the mixing and compaction process (Lesueur 2009, Traxler 1961) however, the amount of volatile loss is controlled by asphalt binder specification (Mass Loss –[AASHTO T 240–13 2013]). This value ranges from different specifications from 0.3 to 1% so it should not be expected that the primary reason of asphalt pavement hardening will be volatile loss since the AASHTO test conditions are more severe than the conditions during mixing process (Thenoux 1983).
- Absorption: Binder low molecular components are absorbed by the aggregates during mixing. The ratio of low molecular weight (paraffinic components) to asphaltenes is reduced and could be an important factor associated to hardening of the binder film on the surface of the aggregate and upon depending on aggregate properties this may be a short-term effect as well as long-term effect (Read and Whiteoak 2003, (Luo and Lytton 2012, Morian, *et al.* 2012).

The above three processes may be the principal causes of asphalt binder chemical and physical hardening; however, asphalt binder will also harden at low temperature without aging. At low temperatures the binder becomes more rigid until it reaches its transition temperature when it becomes brittle (Thenoux, *et al.* 1985). This process is reversible when temperatures rise back (Steric Hardening). Main problem associated with this last effect is not fatigue, but low temperature cracking.

There are basically four methods to enhance fatigue life of an asphalt pavement:

- Increase binder content (and limit voids content). This will increase binder film thickness reducing the oxidation rate and increase asphalt mix ductility. However, excess amount of binder may affect the stability of the mix and produce binder exudation. The loss of stability in most asphalt mixes may result in major risk when pavement is

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Table 1. Main components of grape pomace (Source: Zuñiga).

Skin	Seed
Water (78–80%)	Water (25–45%)
Organic Acids (08–16%)	Carbohydrate Compounds (34–36%)
Tannins (04–3%)	Taninns (4–10%)
Anthocyanins (0–05%)	Nitrogenous Compounds (4–65%)
Nitrogenous Compounds (15–2%)	Minerals (2–4%)
Minerals (15–2%)	Lípids (13–20%)
Waxes (1–2%)	
Aromatic substances (1%)	

Table 2. Physical properties of powdered grape pomace.

Test	Result
Bulk Density (kg/m^3)	1.650
Absorption (%)	8
Loose bulk density (kg/m^3)	682

subjected to heavy and steady loads and/or high environmental temperatures so, to improve performance on early years of pavement it may be recommended the use polymer modified asphalt(Kandhal and Chakaraborty 1996).

- Use of warm mix asphalt: The temperature used on asphalt mixing process is the main contributor to the early aging process. In the last decades different techniques have been developed to produce warm asphalt mixes reducing temperatures up to 70 °C less.(Capitao, *et al.* 2012, Mallick and El-Korchi 2013).
- Increase asphalt layer pavement thickness: Increasing layer thickness will reduce pavement strain and stresses thus, extending fatigue life (general knowledge).
- Use of antioxidant: Antioxidants are reducing agents that interact with oxygen, and inhibit oxidation reactions by oxidising themselves instead of binder. It is not a very common technique used in the asphalt industry but in more recent years several studies have researched into different antioxidant materials (Apeagyei 2006, Bishara, *et al.* 2006, Ouyang, *et al.* 2006, Bianchetto, *et al.* 2007, Huang and Zeng 2007, Apeagyeig, *et al.* 2008, Williams and McCready 2008, Pan 2012, Peiliang, *et al.* 2012, Plancher and Petersen 1976, Xinde, *et al.* 2011).

The work presented in this paper summarises the research where grape pomace residue has been used as an antioxidant. The only work reported using grape pomace is presented by (Calabi-Floody and Thenoux 2012) and is part of the first stage of the work presented here. Consistency and rheological tests were used to prove the relative effect for reducing aging when adding grape pomace residue. It was concluded that grape pomace has antioxidant effect on binder however, later it was found necessary to understand how grape pomace interacts with binder since it was not clear if grape pomace completely dissolves and reacts with asphalt binder during mixing process. If grape pomace does not fully dissolve in asphalt binder, then the additive may be acting as an antioxidant and as a filler.

2. Background

2.1. Oxidation process

Overall, binder oxidation is the interaction (by means of electron exchange) between oxygen and binder. Currently, Petersen's theory on binder oxidation (1998) is the most widely accepted. Petersen indicates that binder oxidation has two phases: a Short Term Aging phase followed by a Long Term Aging phase. The first phase occurs at high temperatures during mixing, transport and laying (Read and Whiteoak 2003, Lesueur 2009). Free radicals and sulfoxides are produced during this oxidation process. Free radicals are chemical elements that have one or more free electrons, which make molecules very reactive to each other, interchanging electrons to achieve chemical stability producing longer and stiffer chains. This process is known as binder polymerisation and may be controlled by adding an antioxidant.

Alongside this initial reaction, a slower Hydrocarbon reaction begins (Long Term Aging). Sulfoxides and ketones are formed during this process increasing binder viscosity on time. The proportion of ketones and sulfoxides formed during this process are highly dependent on temperature and oxygen availability (Martin 1966, Read and Whiteoak 2003). During this second stage, the aging effects continue at a lower rate (Bell, *et al.* 1991) but it has not been found in the literature whether the antioxidants will produce a similar effect as in the short-term aging.

2.2. Grape Pomace

Grape pomace is residue from the wine production process. In a Chile produced 1.282 million litres of wine (Chilean agricultural

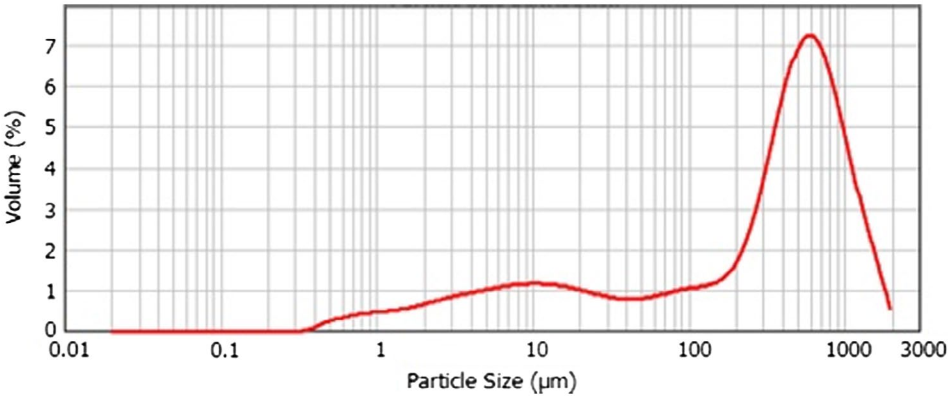

Figure 1. Grape pomace gradation.

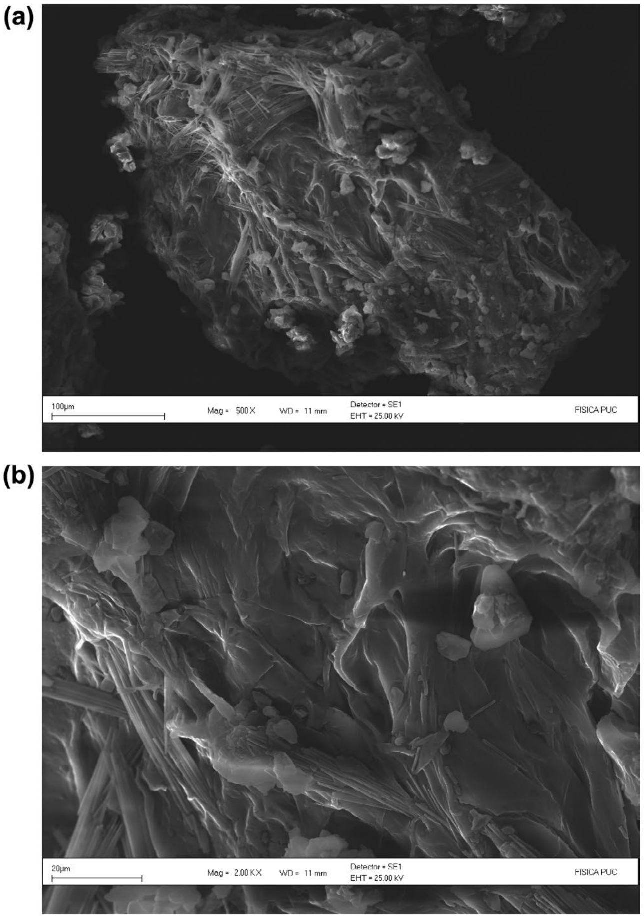

Figure 2. SEM powder grape pomace images. (a) Mag = 500X, (b) Mag = 2000X.

and Livestock service 2013), leaving 192.314 tons of grape pomace in 2013 (Palma, *et al.* 2007).

Grape pomace is made up of the skin and seed of grape. Fresh grape pomace from wine production have a high water content (about 80% in the skin and 20% in the seed) as shown in Table 1, and it has a high antioxidant capacity (Pia, *et al.* 2008). The antioxidant capacity of grape pomace depends on the grape type (red or white wine). In general, red grape pomace have a higher antioxidant capacity than white grape pomace, as red grapes are subjected to a fermentation process during red wine production before being discarded. In white wine production grape pomace is eliminated prior to the fermentation process, thus white grape pomace has a higher sugar content, and red grape pomace has a higher antioxidant capacity.

Red grape pomace from Cabernet Sauvignon was selected for this research, due to its high antioxidant content in relation to other grapes (Pia, *et al.* 2008). Main components are shown in Table 1 (Zuñiga 2005).

Grape pomace was dehydrated at a relative low temperature (40 °C for 9 to 11 days), to keep its antioxidant properties. This byproduct (dehydrated grape pomace) is rich in antioxidants. It has an antioxidant capacity of 650 umol TE/g, determined with ORAC (Oxygen Radical Absorbance Capacity) Test, which is the most commonly used test in this type of materials. It was reported that further drying time at 40 °C does not significantly affect the antioxidant capacity however higher drying temperatures reduces antioxidant capacity (Calabi-Floody and Thenoux 2012).

Table 3. Properties of asphalt binder.

Test	Result
Viscosity 60 °C (P)	3.210
Penetration, 25 °C, 100 g, 5s (0,1 mm)	60
Ductility 25 °C, 5 cm/min (cm)	>150
Softening point (°C)	504
Penetration index (IP)	−07
After RTFOT	
Mass loss (%)	02
Absolute viscosity 60 °C (P)	9.016
Ductility 25 °C, 5 cm/min (cm)	150
Durability index (ID)	28
Mixing temperature (°C)	155
Compaction temperature (°C)	146

The dry material was powdered to a maximum size of 0,63 mm (#30 sieve), vacuum sealed and stored at -24 °C and avoiding exposure to light. That storage temperature was selected in order to avoid any potential degradation of the byproduct, although this research demonstrated that it was not necessary, since store at vacuum and avoiding exposure to light was enough. Figure 1 presents the gradation of powder grape pomace. Physical properties of powder grape pomace are shown in Table 2.

The microstructure of powdered grape pomace was studied by using a Scanning Electron Microscope (SEM) under high vacuum condition. To make the sample electrically conductive, a 10 to 15 nm thick gold coating was applied to the sample by sputtering with a sputter-coater. Grape pomace images are presented in Figure 2.

SEM analysis (Figure 2(a)) indicated that powdered grape pomace particles have a rough surface morphology and also an irregular shape. Figure 2(b) shows a close-up with a higher resolution where surface interlacing fibres were observed. The rough surface creates a large surface area, but it was not possible to determine.

3. The research work and results

Early research reported by (Calabi-Floody and Thenoux 2012), proved the effectiveness of the antioxidant based on the following series of tests performed before and after short-term aging (RTOFT) and long-term aging (PAV): asphaltenes content, Fraass test, Viscosity at 60 °C and Superpave tests (complex shear modulus, fatigue parameter and m-value). Although, the main conclusion of this work was that grape pomace reduces rate of hardening, further research was proposed in order to better understand the effect of grape pomace powder. Some of the results will indicate that dry grape pomace will not fully dissolve and since it has a high active surface, its filler effect may be important (Calabi-Floody and Thenoux 2012). For better understanding the effect of the grape pomace as antioxidant and as filler, a new test program that will include three additional experiments was follow. Results are reported in this paper.

3.1. Asphalt binder used for the present research and sample preparation

The asphalt binder selected for this research was a CA 24 (Table 3) complying with Chilean specification. This is the equivalent to a PG 64–10.

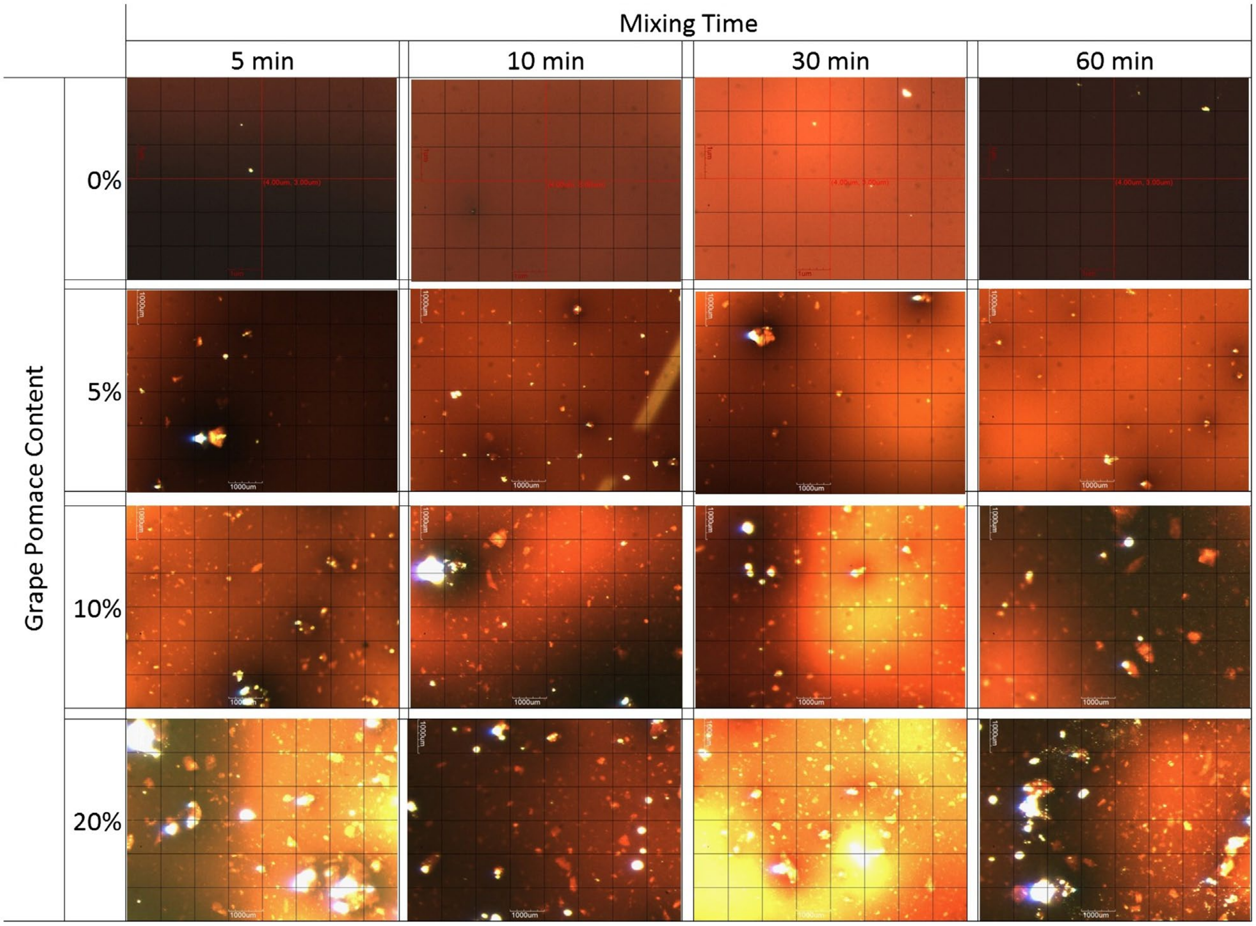

Figure 3. (4X) Microscopic evaluation of N°100 – N°200 fraction sized particles with different grape pomace content and different mixing time.

The asphalt binder samples were heated to 95 °C to achieve viscosities of 7000–8000 Poises (Calabi-Floody and Thenoux 2012). Grape pomace powder was added and mixed from five to ten minutes, until a homogeneous mixture was obtained. Three percentages were used: 5, 10 and 20% by weight.

3.2. Experiment number 1. Grape pomace dissolve evaluation

In order to find out if the grape pomace powder dissolves in the binder, a microscopic experiment was performed. Different microscopes were considered (SEM, ATR, epifluorescence and optic) and different forms of evaluation also were considered (qualitative and quantitative). Quantitative analysis considers the use of image software to measure the area covered by undissolved grape pomace. Since the objective of this experiment was to determine the presence or not of undissolved particles, but not necessarily to quantify them, image analysis software finally was not used, and an optical microscope was selected.

Three samples of the same asphalt binder with 0, 5, 10 and 20% grape pomace content were mixed during 5 min, 10 min, 30 min and 60 min. The experiment was performed for #100 – #200 and #50 – #100 size fraction particles. Although the optical microscope has a limited resolution, it was high enough to observe the proportion of undissolved particles.

Figure 3 shows pictures of #100 – #200 fraction size of grape pomace. Microscopy evaluation showed in all cases that grape pomace does not dissolve on binder, even for finer sieve fractions (N°50 –- N°100 or N°100 – N°200).

3.3. Experiment number 2. Effect of dissolved and undissolved grape pomace

Binder samples (10 mm thick), with grape pomace content of 0, 5, 10 and 20% were placed on flat trays and left in oven at 60 °C up to 6 months (Figure 4). Temperature of 60 °C was selected in order to achieve softening point (and to simulate maximum pavement temperature), and allow the particles to sink. Prior to collect the samples, the try was taken off the oven and cooled at ambient temperature. Once it had cooled to ambient temperature and binder had stiffened enough, samples were collected with a chisel from the surface and from the bottom to perform the following comparative tests: Fraass (NLT 182/84), Viscosity (AASHTO T316-13) and Dynamic Shear Modulus (AASHTO T315-12). It was observed that the undissolved part of grape pomace will sink to the bottom of the layer.

3.3.1. Fraass test

Visually the difference between samples taken from the surface layer and bottom layer may be noticed, as shown in Figure 5. These figures were captured with a high resolution digital camera attached to the microscope. This is a stability issue, which means that there are two phases in this modified binder, where one of these phases is the undissolved grape pomace.

Figure 4. Binder-grape pomace mixes stored on a tray in a 60°C oven.

Figure 6 presents the average Fraass results of three replicates for each point. Figure 6(a) shows that at an initial stage (immediately after mixing binder with grape pomace) there is no effect from the antioxidant and, the additive is homogeneously distributed. Figure 6(b) shows that grape pomace produces a positive effect in aging at the surface level where grape pomace is fully dissolved. Figure 6(b) (bottom layer points) is much more difficult to evaluate since the bottom layer is not exposed to Oxygen and at the same time it is hard to discriminate between the 'filler effect' and the 'antioxidant effect'; the grape pomace is not fully dissolved in the bottom.

Regarding the response of the upper layer, it was not evaluated for a longer period; however, based on other measurements eventually all points will tend to a same aging level regardless the amount of grape powder. It is expected that in the long term all samples (with and without grape) increase their fraass point and converging to the same value since, as seen in the rest of the test, grape pomace reduces short-term aging.

3.3.2. Viscosity test at 60 °C

For viscosity test, samples were pre-mixed prior to the test since it was difficult to obtain the required amount of sample by separating top and bottom layer. Three replicates were considered for this test. Figure 7 shows that for three months aged samples viscosity decreases with the increasing grape pomace content until 10%; a similar behavior was observed for the viscosity measurements performed after six months. These results indicate that undissolved grape pomace may be acting as filler above 10% content. Brookfield viscosity measurement is affected by the presence of undissolved particles, in other words by increasing the amount of powder the asphalt binder becomes a two-phase material affecting the internal flow of the sample.

3.3.3. Dynamic shear modulus and phase angle determination

Same as in Viscosity test, it was also decided to pre-mix upper and bottom layer but in this case was necessary to do it, since a parallel set of test where performed using a non-active grape pomace (the same grape pomace with no anti-oxidant effect).

A limited amount of grape pomace without antioxidant was obtained. In order to achieve this, an extraction of antioxidant was performed on the grape pomace. There are several methods to extract the antioxidant of a sample (Sharapin 2000, Garrido, *et al.* 2007). In this case, the method of extracting hydrophilic solid, which corresponds to the most commonly used method for extracting antioxidants from fruits and herbs was selected. The general procedure is:

- Incorporate 150 ml of extraction solution (ketone/water/acetic in 70/295/05% v/v) in 10 gr of grape pomace.
- Homogenise with mechanical equipment.
- Macerate for 60 min at 23 °C, with agitation (100 rpm).
- Take one aliquot and centrifuge for 10 min at 35 g.

This parallel set of tests was done in order to isolate the filler effect from the antioxidant effect. Samples with 5, 10 and 20%

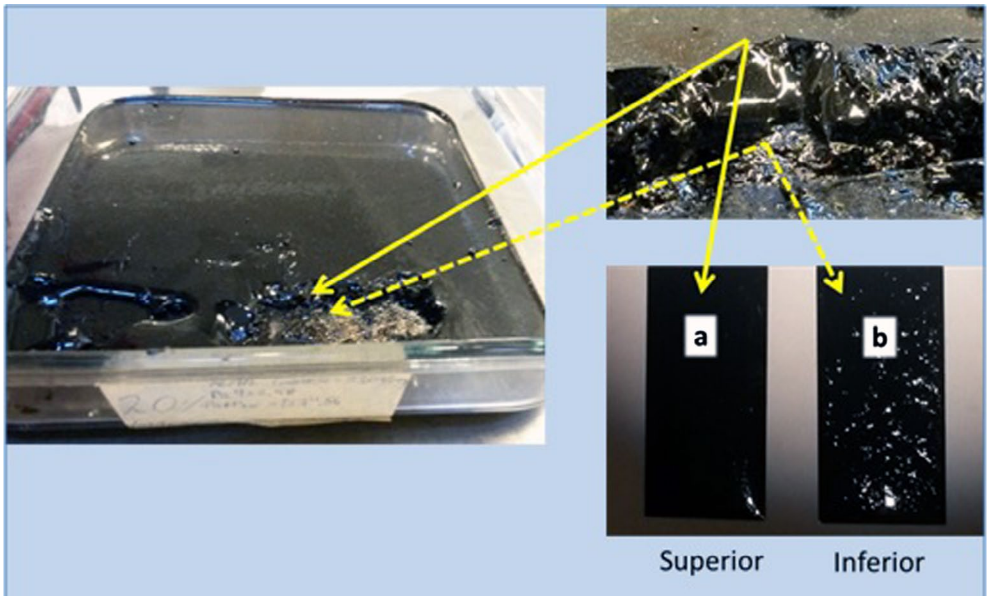

Figure 5. Grape-binder mixes samples taken from Upper layer (a) and bottom layer (b).

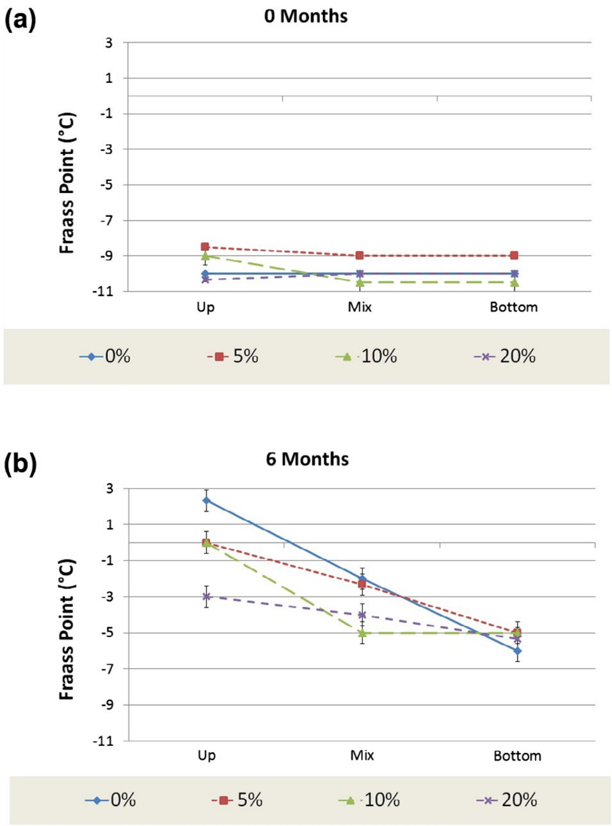

Figure 6. Fraass point test results for (a) unaged samples with 0 to 20% grape pomace content and (b) 6 months aged samples with 0 to 20% grape pomace content.

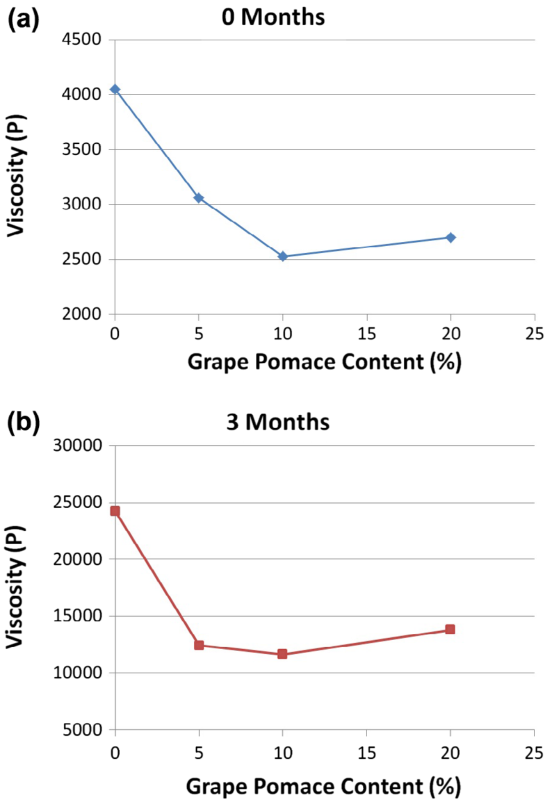

Figure 7. (a) Zero month's viscosity measurements and (b) Six month's viscosity measurements.

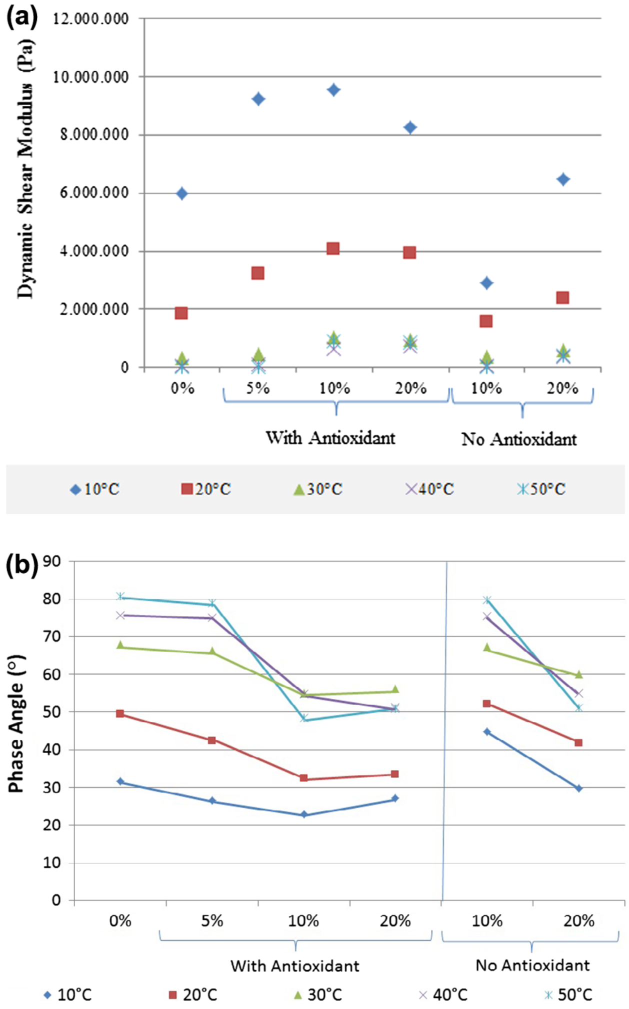

Figure 8. (a) Dynamic shear modulus for binder with different grape pomace content and (b) Phase angle for binder with different grape pomace content.

grape pomace with antioxidant, and with 10 and 20% grape pomace and with no antioxidant were prepared and tested unaged at temperatures of 10, 20, 30, 40 and 50 °C. An additional sample of binder with no grape pomace was tested. A DHR-2 Rheometer was used for this purpose. The test was performed at 10 rad/s frequency; strain controlled (2%). A 25 mm parallel plate Geometry, with 2 mm gap was selected.

Figure 8 shows results for $|G^*|$ and δ for all test temperatures and samples with and without active grape pomace. By comparing $|G^*|$ for 10 and 20% grape pomace content with and without antioxidant in Figure 8, can be noticed that results are different. Since the only difference between these samples is that one has grape pomace with antioxidant and the other has the same grape pomace but its antioxidant was extracted (all the other parameters are the same for both), that $|G^*|$ difference can only be explained by the effect of the antioxidant of the grape pomace. Figure 8 shows evidence that both antioxidant and no-antioxidant (filler) component of grape pomace have an effect on binder Dynamic Shear Modulus. These results may not be compared with Brookfield results, since Brookfield viscosity results are affected by the presence of undissolved particles.

Both, the antioxidant and the filler effect are better depicted at relative lower temperatures or, when asphalt binder is at its elastic or viscoelastic temperature range.

Table 4. 10 °C Dynamic shear modulus *t*-student analysis.

	With antioxidant						Antioxidant v/s No antioxidant			
							10%	10%	20%	20%
Grape pomace content	0%	5%	10%	20%	5%	10%	Ant	No Ant	Ant	No Ant
Average	5,975,343	9,217,335	9,525,522	8,273,899	9,217,334	9,525,521	9,525,522	2,906,238	8,273,899	6,484,476
Variance	9,7E+11	2,6E+12	3,7E+11	7,6E+11	2,6E+12	3,7E+11	3,7E+11	1,3E+11	7,6E+11	3,4E+11
Observations	13	13	13	13	13	13	13	13	13	13
Pooled variance	1,8E+12		5,6E+11		1,5097E+12		2,5E+11		5,5E+11	
T stat	−6		423		−06		338		62	
P(*T* <= *t*) one-tail	0		0.0		03		0		0	
T critical one-tail	2		17		17		17		17	
P(*T* <= *t*) two tail	0		0		05		0		0	
T critical two-tail	2		201		21		21		21	
Significant difference	Yes		Yes		No		Yes		Yes	

Table 5. Two-sample t-test (0% and 10% grape pomace).

	0 months		8 months		13 months		17 months		18 months	
Grape pomace content	0%	10%	0%	10%	0%	10%	0%	10%	0%	10%
Average	7.739	6.664	8.546	7.747	8.688	7.978	9.438	8.831	9.947	9.534
Varianzce	567.259	93.477	791.861	210.888	1.352.130	195.961	1.689.729	500.386	2.148.055	346.664
Observations	4	6	5	4	6	6	6	6	6	6
Pooled variance	271.145		542.873		774.045		1.095.057		1.247.360	
Hypothesised mean difference	00		00		00		00		00	
Df	80		70		100		100		100	
T stat	32		16		14		10		06	
P(*T* <= *t*) one-tail	00		01		01		02		03	
T critical one-tail	19		19		18		18		18	
P(*T* <= *t*) two tail	00		01		02		03		05	
T critical two-tail	23		24		22		22		22	
Significant difference	Yes		No		No		No		No	

Table 6. Two-sample *t*-test (0% and 20% grape pomace).

	0 months		8 months		13 months		17 months		18 months	
Grape pomace content	0%	20%	0%	20%	0%	20%	0%	20%	0%	20%
Average	7.739	5.668	8546	7378	8688	7443	9438	9304	9947	8970
Varianzce	567.259	93.072	791,861	92,325	1,352,130	338,142	1,689,729	454,535	2,148,055	84,905
Observations	4	6	5	6	6	6	6	6	6	6
Pooled variance	270.892		403,230		845,136		1,072,132		1,116,480	
Hypothesised mean difference	00		0		0		0		0	
Df	80		9		10		10		10	
T stat	62		30		23		02		16	
P(*T* <= *t*) one-tail	00		00		00		04		01	
T critical one-tail	19		18		18		18		18	
P(*T* <= *t*) two tail	00		00		00		08		01	
T critical two-tail	23		23		22		22		22	
Significant difference	Yes		Yes		Yes		No		No	

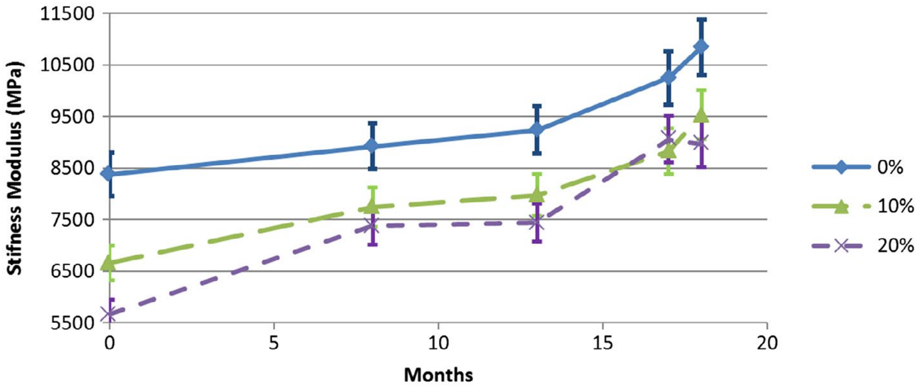

Figure 9. Stiffness modulus evolution for different grape pomace contents.

Table 4 presents statistical analysis for tests performed at 10 °C. Table 4 shows that there is a significant difference between results with different grape pomace content and grape with and without antioxidant. Thus, binder modulus is affected by adding grape pomace, and the antioxidant and undissolved particles have different effects.

3.4. Experiment number 3. Test on asphalt mixes

Asphalt mix samples with 5% asphalt content, were prepared with 0, 10 and 20% grape pomace by weight of binder. These samples were stored at laboratory conditions (23 °C and isolated from direct light) and periodically measured for their stiffness modulus at 15 °C according to EN 12697-26- Annex C (2012) Standard. Six samples were tested for each grape pomace content at 0, 8, 13, 17 and 18 months.

Figure 9 shows Stiffness Modulus results over the 18 month period. **S**tiffness Modulus increases over time as expected, however the grape pomace reduces the initial value. Statistical analysis (Tables 5 and 6) demonstrated that there is a significant difference between the stiffness modulus for samples with 0 and 20% grape pomace content from 0 to 13 months and for samples with 0 and 10% grape pomace content at 0 months. The tests performed in mixes will also prove the effectiveness of antioxidant during the mixing process.

5. Conclusions

In this study, the relative effect for reducing binder aging when adding dehydrated and powdered grape pomace residue was studied. This document presents the result of three experiments from the research. The following findings and conclusions are summarised:

- Dehydrated and powdered grape pomace reduces binder oxidation, mainly short-term oxidation.
- Grape pomace does not dissolve completely producing two different effects on binder; grape pomace acts as an antioxidant and as filler component particularly above 10% addition.
- Fraass test results show that the antioxidant effect is independent from the undissolved grape pomace. The Antioxidant effect of grape pomace improves the Fraass temperature. The grape pomace acting as a filler seems to have no effect on this parameter.
- Brookfield viscosity measurement is affected by the presence of undissolved particles, in other words by increasing the amount of powder the asphalt binder becomes a two-phase material affecting the internal flow of the sample.
- Test with Dynamic Shear Modulus was used to compare the effect of grape pomace as an antioxidant-filler and as a filler without its antioxidant effect. It was demonstrated that there are two combine effects: antioxidant and filler effect.
- Grape pomace reduces the initial mix stiffness modulus (after mixing and compaction), compared with the same mix with no grape pomace.
- Grape pomace needs to be dehydrated at temperatures below 40 °C, otherwise it loses its antioxidant capabilities.
- It is relatively difficult to study the effect of antioxidant in asphalt binder and asphalt mixes since the temperatures used in the production of hot mix asphalt will degrade in different ways the chemical structure of the antioxidant. Antioxidants may have an even better effect in warm mix asphalt.

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