Effect of hydrated lime and other mineral fillers on stiffening and oxidative ageing in bitumen mastic

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Abstract

The bituminous binder's ageing process is the primary reason behind the decrement in the pavement's in-service life, which can lead to cracking as a result of extreme hardening of the binder. In order to mitigate this problem, several methods have been used, such as polymer modification, functional improvement and modification with nano-particles. Due to its exceptional performance in the asphalt mixtures, hydrated lime has also been considered the potential antioxidant in recent studies. However, its impacts have not been well understood. Therefore, the aim of this study is to investigate the effect of hydrated lime and other fillers on mastic stiffening and ageing. In this detailed study on the mastics, the effect of hydrated lime on stiffening and ageing mitigation was evaluated by various means involving both physical and chemical properties. The evaluation testing was aimed at understanding the mechanisms of hydrated lime on ageing mitigation. Moreover, special attention was paid to the interactions between hydrated lime and bitumen, which affects bitumen mastics' ageing. The results indicate that hydrated lime reduced the ageing indices more as compared to other fillers. Further, increasing the concentration of hydrated lime resulted in more decrease of ageing indices just opposite to that of granite filler. Also, the bitumen recovered from the hydrated lime mastics showed less carbonyl index and asphaltenes content than granite mastics which prove the ability of hydrated lime to reduce the ageing products. Moreover, it is noticed that the mastics stiffness increased with an increase in the ageing time. The fillers can increase or decrease the ageing of the mastics as the time in the TFOT proceeds.

Keywords: hydrated lime; oxidative ageing; asphalt mastic; ageing index; mineral fillers

1. Introduction

The ageing process in the bituminous binders is the critical factor in assessing the asphalt pavement's lifespan. The excessiveness of the bitumen ageing will substantially affect the durability properties of the asphalt mixtures. In case that bitumen binder is extremely aged, the asphalt mixture will develop more brittle behaviour and decrease its capability to resist the stresses or strains induced by the traffic. Consequently, it can cause the development of cracking distress in the bound layer of asphalt pavement. Further, it would reduce the adhesion property between the aggregates and bitumen, causing the loss of materials at the upper surface layer [1]. The ageing process mainly involves changes in the physical and chemical properties, making the bituminous binder more brittle, leading to the pavement's ultimate failure. The failure modes in the pavement due to the ageing process include ravelling and the cracking induced by thermal or traffic loads. The development of the cracks on the top layer of pavement may further increase into binder's ageing due to more exposed surface to atmospheric conditions [2].

Commonly, the bitumen's ageing process takes place in two phases: short-term ageing, which occurs at elevated temperatures during different processes that include paving, storage and mixing of the bituminous binder; long-term ageing happens in service at ambient temperatures. Further, the process of ageing involves two kinds of mechanism; the first one is the irreversible one recognised by the chemical changes in the bituminous binder, which affect the rheology of the bitumen. This process includes oxidation, evaporation of volatile components and escaping of oily constituents from the bituminous binder into the aggregate [3]. The other mechanism is the reversible one, known as physical hardening. It may involve molecular structuring, defined as reorganising of bitumen molecules to gain the optimal thermodynamic state subjected to specific conditions.

For a long while, attempts to solve asphalt binder's ageing problem by various methods, including polymer modification, modification with nano-particles [4, 5], or functional improvement, have been undertaken. Through these methods, various anti-ageing additives have been used, such as ultraviolet (UV) absorbers, antioxidants and combinations of these [1, 6-9].

Hydrated lime is one of many potential additives used in bitumen to improve the properties and the performance of asphalt mixtures. Hydrated lime in hot mix asphalt (HMA) creates multiple benefits. A considerable amount of information exists in the literature on hydrated lime's ability to control water sensitivity and its well-accepted ability as an anti-stripping agent to inhibit moisture damage. However, recent studies demonstrate that lime also generates other effects in asphalt mixtures. Specifically, hydrated lime acts as an active filler that has antioxidant effects [10, 11]. These properties create multiple benefits for pavements.

Hydrated lime has been used as an additive for asphalt mixtures for a considerable time. However, its impacts are not fully recognised. With the unique properties, hydrated lime may prove to be an additive with a special impact on the rheology and damage mechanics of asphalt mastics.

The need still exists for developing more effective treatments or additives for controlling oxidative hardening and ageing in asphalt pavements. In order to do so, a comprehensive study is needed to develop a better understanding of the ageing mechanisms, factors affecting bitumen ageing in the presence of different fillers and especially hydrated lime. Thus, understanding the impact of hydrated lime and different fillers on asphalt mixture ageing is of great interest.

In order to investigate the effect of hydrated lime on the stiffening and ageing of mastics, a detailed study was proposed. In this study, mastics with different percentages of hydrated lime were compared to mastics made with other fillers (granite and limestone). The effect of hydrated lime on stiffening and ageing mitigation was evaluated by different means. (1) Basic properties: penetration, softening point, and viscosity, (2) Mechanical and rheological behaviour using a dynamic shear rheometer (DSR), and (3) a Chemical approach with Fourier transform infrared (FTIR) spectroscopy. The evaluation testing aimed to understand the mechanisms hydrated lime employs for ageing mitigation. In addition, this study focuses on interactions between hydrated lime and the bitumen that affect and reduce the ageing in bitumen mastics and mixtures.

2. Materials and testing programme

2.1. Materials

Three types of fillers were used in this study, granite filler (G), limestone filler (LS), and hydrated lime (HL).The properties of the three fillers used in this study are provided in the Table 1. Further, one type of bitumen; a 40/60 Pen bitumen with a penetration of 45dmm and a softening point of 50˚C was used to prepare the mastics. For comparing stiffening effects of hydrated lime with different binders, 50/70 pen bitumen and 100/150 pen bitumen were also used to prepare the mastics.

Table 1. The characteristic properties of fillers used in this research.

	Granite (G)	Limestone (LS)	Hydrated Lime (HL)
Specific Gravity (Mg/m^3)	2.66	2.65	2.22
Surface area (m^2/g)	1.26	1.58	2.24
Rigden voids (%)	46.94	39.82	61.62

2.2. Testing programme

The aim of this study was to individually evaluate the effect of each of the three fillers on the ageing properties of the mastics. In order to understand the mechanisms of these fillers, especially the hydrated lime to mitigate the ageing, this study was performed in two parts. The first part of this research study was to investigate the hydrated lime effect on mastic stiffening and in addition, to understand the reasons and factors behind this phenomenon. The second part of this study was to investigate the effect of hydrated lime on ageing mitigation and the factors that affect ageing at the mastic level. Furthermore, this part attempts to address how hydrated lime affects the mechanisms of ageing of bitumen mastics. In order to achieve these objectives, the ageing study was performed in two stages. The first stage was by ageing the different mastics using standard TFOT (thin film oven test) short-term ageing for 5 hours at 163°C and then the standard long-term PAV ageing for 20 hours at 90°C. The second stage, called the ageing time study, where the mastics were aged in the TFOT oven for extended times of 2, 5, 10, and 15 hours. The stiffening effect was evaluated after mixing the fillers with the bitumen, using the softening point and viscosity at 135°C (measured as per BS EN 13302:2010). In addition, the Dynamic Shear Rheometer (DSR) was used to study the rheological effect of different fillers on the mastics and to quantify the ageing and stiffening effect of the fillers.

The mastics were prepared at three levels of filler volume concentration (filler volume in the mastic to the total volume of the mastic). The filler percentages selected were 5, 15 and 30-vol% of filler in the mastics.

In addition to the evaluation of the ageing of the mastics, the binders and the fillers were recovered from the mastics and the change in their properties was investigated using Fourier transform infrared (FTIR) spectroscopy. In addition to this testing programme, the ageing time study was performed in the TFOT in order to evaluate the effect of each filler on the ageing rate of the bitumen mastics and to understand the behaviour of these mastics after being subjected to extended ageing.

The results for the tests involved in this study are the average of three replicates for viscosity and FTIR ageing indices and two replicates for softening point and complex modulus, and the results were repeatable. The percentage deviation with respect to the mean value representing all the replicates tested was less than 15%. The annotations of samples used in this research are provided in Table 2.

Table 2. The samples' combinations and respective annotations used in this research

Combinations with 40/60 bitumen			
Sample	**Un-aged**	**TFOT aged**	**PAV aged**
Mastic with 30% Granite	30%-G	30%-G-TFOT	30%-G-PAV

Mastic with 30% Hydrated lime	30%-HL	30%-HL-TFOT	30%-HL-PAV
Mastic with 15% Granite	15%-G	15%-G-TFOT	15%-G-PAV
Mastic with 15% Hydrated lime	15%-HL	15%-HL-TFOT	15%-HL-PAV
Combinations with different binders			
Sample	**40/60 Bitumen**	**50/70 Bitumen**	**100/150 Bitumen**
Hydrated lime	HL+B2(40/60)	HL+B3(50/70)	HL+B4(100/150)
Granite	G+B2(40/60)	G+B3(50/70)	G+B4(100/150)
Limestone	LS+B2(40/60)	LS+B3(50/70)	LS+B4(100/150)

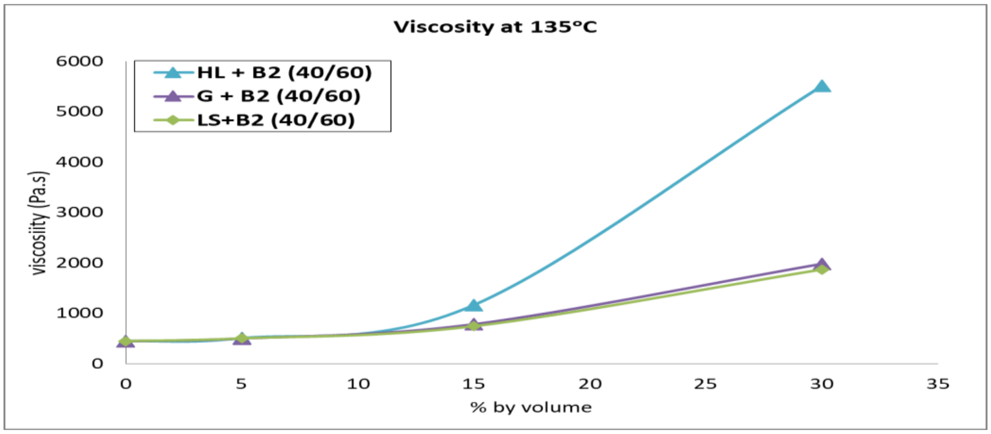
3. Results and discussion

3.1. Stiffening effect of Hydrated Lime

The stiffening effect of mineral fillers in the bitumen mastics and mixtures has been studied by several researchers [12-15]. The researchers evaluated the stiffening effect by looking at stiffening indicators such as the increase in the softening point and viscosity in addition to using modern rheological techniques.

Heukelom and Wijga stated that the volume fraction of the filler is the key parameter that controls the stiffening of the mastics [15]. In practice, the filler to binder ratio in a mastic can be controlled based on either weight or volumetric concentrations. Moreover, many studies have shown that in addition to volumetric concentration, the interactions between the filler and the bitumen binders have an important role affecting the performance of the mastic and consequently the mixture performance. Researchers have proposed that in order to better understand the influence of the fillers on the mastic performance, it is important to carefully study the effects of the physicochemical interactions happening between fillers and bitumen [16].

In order to investigate the stiffening effect of the hydrated lime on the mastics, different volume percentages of fillers (HL, G, LS) were mixed with the (40/60) bitumen and the relation between the increase in stiffening and volume percentages is presented in Figure 1.



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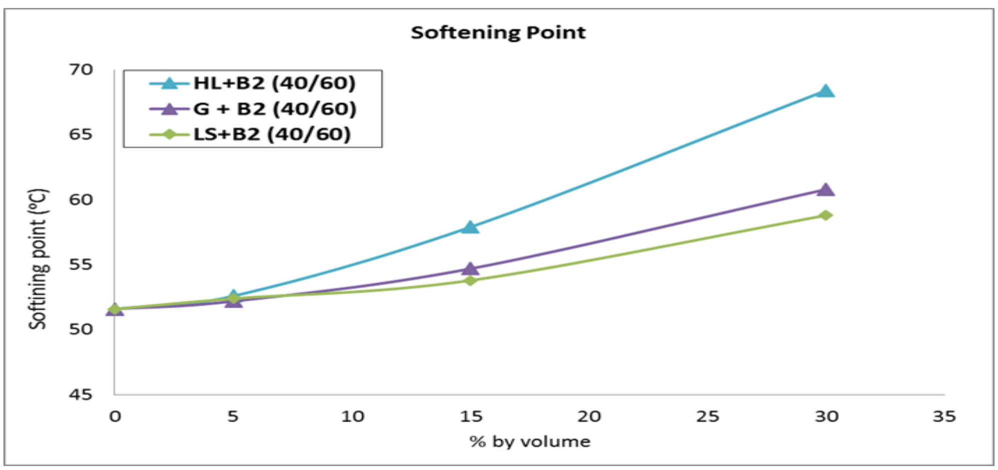

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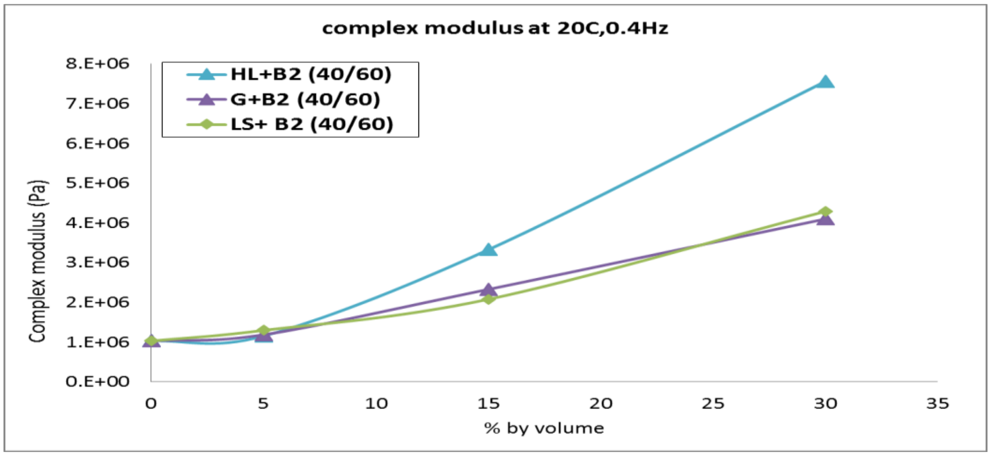
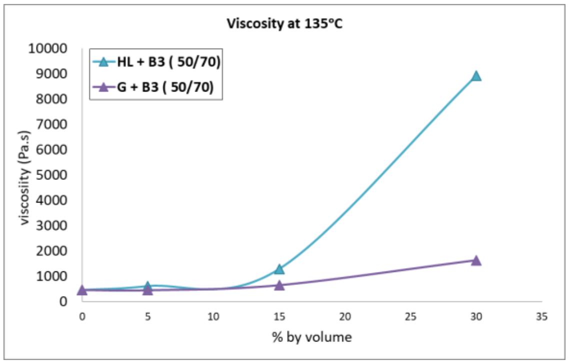


(c)

Figure 1. Stiffening effect of hydrated lime for mastics with 40/60 bitumen on (a) viscosity (b) softening point (c) the complex modulus

Clearly, the stiffening effect of hydrated lime is greater compared to the other fillers. This effect is more pronounced at higher concentrations. However, it can be noticed that the stiffening effect of both granite and limestone fillers are almost the same as can be observed from the indicators used (softening point, viscosity and complex modulus). Some researchers have indicated that the stiffening effect of hydrated lime is more pronounced at higher temperatures. However, in this study, it can be noticed that this stiffening effect of the hydrated lime can be seen at different temperatures as these tests were performed at different testing temperatures. It is also worth noting that the stiffening effect of hydrated lime on the complex modulus of the mastics was investigated by the DSR frequency sweep test at different temperatures and similar results were observed at all tested temperatures.

Furthermore, in addition to the B2 (40/60) bitumen mastics, mastics with two other bitumen binders were used to further investigate this stiffening effect of the hydrated lime with different binders. Mastics with B3 (50/70) bitumen and B4 (100/150) bitumen were prepared with different filler percentages. The stiffening effect was evaluated. The results for the stiffening effect with these binders are shown in Figure 2.



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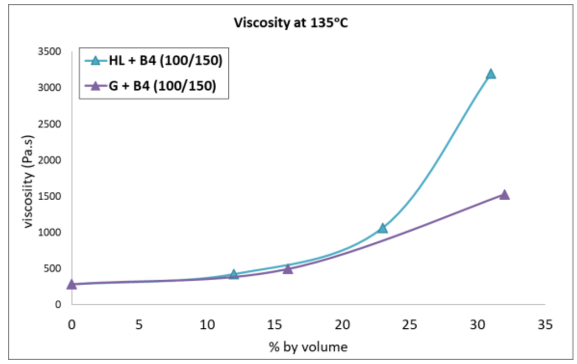

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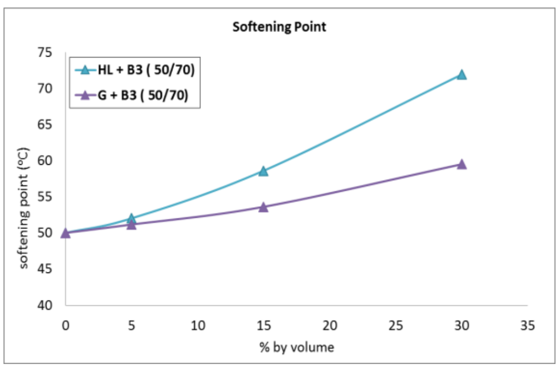

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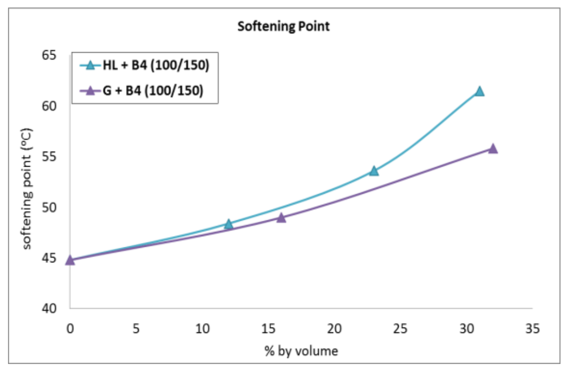


(d)

Figure 2. Stiffening effect of hydrated lime for mastics with different binders on (a) viscosity-B3 (b) viscosity-B4 (c) softening points-B3 (d) softening points-B4

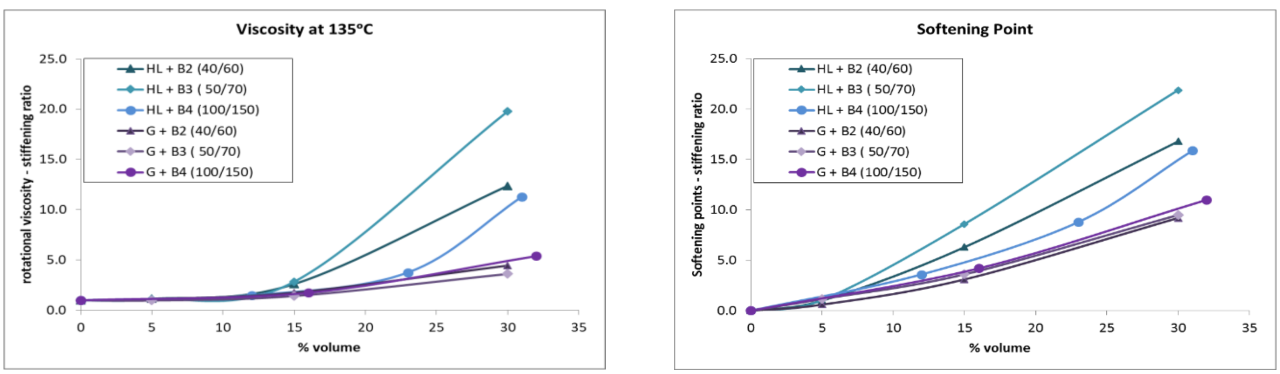
The results above show that similar to the 40/60 bitumen, hydrated lime has a higher stiffening effect than the granite filler. This effect seems to be bitumen specific. In order to show this effect more clearly the stiffening ratios were calculated for each bitumen mastic as follows (Equation 1 and Equation 2):

$$\text{viscosity stiffening ratio} = \frac{\text{Viscosity of mastics}}{\text{viscosity of base bitumen}} \qquad \text{Equation 1}$$

$$\text{Softening point stiffening ratio} \qquad \text{Equation 2}$$

$$= \text{SP of mastic} - \text{SP of bitumen}$$

The results for the stiffening ratios of softening point and viscosity for the mastics with different binders are shown in Figure 3. It can be noticed from the results that the granite fillers have almost the same stiffening effect with the three different bitumen binders used in preparing the mastics in this study. However, this effect is different for the hydrated lime. It can be seen that similar hydrated lime concentrations can result in significantly different stiffening ratios with different binders.



(a) **(b)**

Figure 3. Stiffening ratio of fillers in different bitumen mastics (a) Viscosity (b) Softening point

These properties of the hydrated lime on mastic stiffening effect could indicate that there is a significant interactive effect between the bitumen used and hydrated lime. These properties can affect ageing as well as the rheological properties of the mastics and asphalt mixture as concluded in previous studies by Petersen et al.,1987 [16]. Furthermore, Kim et al.,2003 [17] suggested that, since the behaviour of bitumen mastics with hydrated lime is highly binder dependent then this could indicate that the effectiveness of hydrated lime in a mastic is controlled by physiochemical interaction.

Moreover, an investigation by Wang et al.,2011[18], on the effect of mineral filler characteristics on the stiffening of mastics and mixtures, found that the Rigden voids (RV) in the filler, fineness modulus and possibly the CaO content are the most significant properties to affect mastic performance. This effect was varied based on the type of bitumen binder, and they refer to the possibility of bitumen-filler interactions.

From the results presented in Figure 1 to Figure 3, it can be concluded that the effectiveness of hydrated lime on mastic stiffness is different from limestone and granite fillers and it is highly bitumen dependent. Hydrated lime was more effective than granite and limestone filler, which implies that mechanisms other than a volume filling effect could be occurring. Therefore, further investigation into this phenomenon is needed to understand the mechanisms and the factors affecting this behaviour of mastics containing hydrated lime.

In order to understand the effect of hydrated lime on mastics and to compare with the behaviour of granite filler, the bitumen was recovered from mastics just after mixing and a DSR frequency sweep was performed on the recovered bitumen in order to evaluate the stiffening of the recovered bitumen using the dynamic complex modulus. To make a comparison between mastics containing hydrated lime and granite fillers, complex moduli for the mastics and the recovered binders tested at 20°C and 0.4 Hz are shown in Table 3.

Table 3. Complex moduli for granite and hydrated lime mastics (a) Mastics (b) Recovered bitumen

Sample	G*-Mastics	G*-Recovered binder
30%-G	4103600	1509150
30%-HL	7565600	1214950
15%-G	2331800	1532100
15%-HL	3330400	1503900
40/60 bitumen(un-aged)	1032400	1032400

The results in Table 3 show that the complex modulus of the hydrated lime mastics is much higher than those for granite mastics. This effect is more pronounced at the higher filler concentration of 30% by volume. In contrast, the recovered bitumen from hydrated lime mastics is softer than the bitumen recovered from granite mastics. This effect is more obvious at the higher concentration of 30% filler by volume as well. These results indicate that there could be an interaction between bitumen and hydrated lime and this does not happen with the granite fillers. This effect will be further investigated in the following sections with the ageing results.

3.2. Stage 1: Long and short-term ageing of mastics

The effect of hydrated lime on ageing mitigation was studied. Two ageing simulation tests were used in this stage: TFOT ageing for short-term simulation and the PAV was used to simulate the long-term ageing. The tests were conducted according to the British Standards as mentioned earlier. Different ageing indicators, namely viscosity, softening point and the dynamic complex modulus were used to evaluate the effect of ageing on mastics. The ageing index (AI) was calculated for each mastic after ageing by dividing the aged property values by the unaged values for the same mastic. The results of the mastic stiffening ratios are presented in Figure 4. The effects of TFOT and PAV ageing on mastics are shown in Figure 5 and Figure 6 respectively.

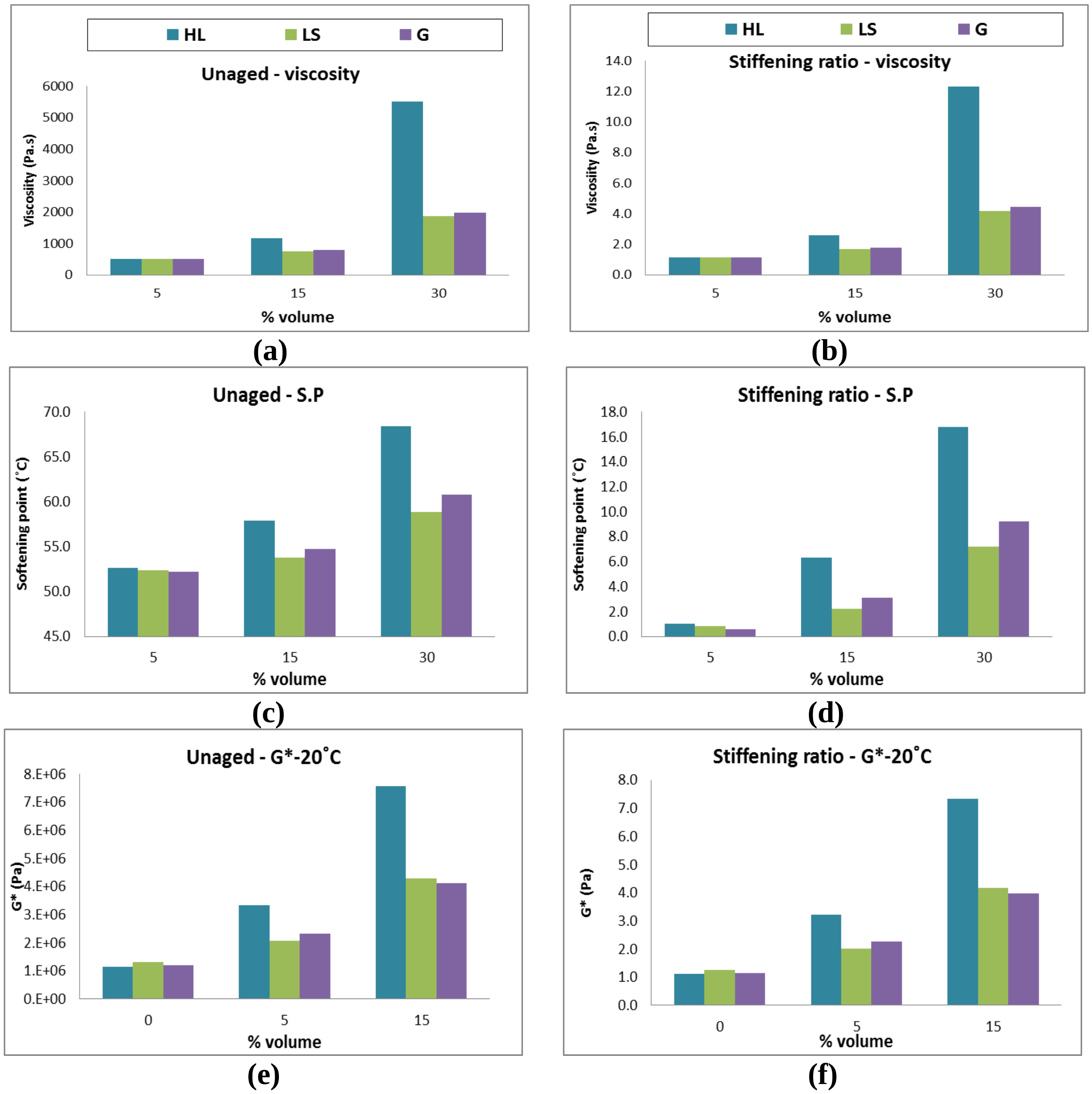
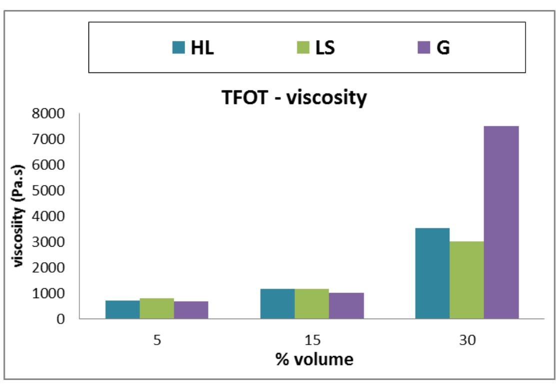


Figure 4. Unaged mastic properties and filler stiffening ratios (a) Viscosity-unaged (b) Viscosity-stiffening ratio (c) Softening point-unaged (d) Softening point-stiffening ratio (e) G*-unaged (f) G*-stiffening ratio

From the results presented in Figure 4, it can be noticed that the stiffening effect of hydrated lime is much larger compared to granite and limestone fillers for all the evaluating indicators (viscosity, softening point and the complex modulus). The stiffening effect of hydrated lime is almost three times that of the limestone and granite at 30% volume of filler in the mastics. In addition, it can be noticed that the stiffening effect of both limestone and granite fillers are similar. At the lower filler concentration, the stiffening effect of all fillers is almost the same in all the mastics. However, even though these tests were performed at different testing temperatures, the stiffening effect of hydrated lime is clear and pronounced in all these tests.

From the results in Figure 5, it can be observed that although, before TFOT ageing, the hydrated lime mastics were much stiffer than the granite and limestone mastics, after TFOT ageing they are either softer or the same stiffness as other mastics, especially at higher concentrations. This means that the hydrated lime mastics exhibit the lowest ageing increase rates.



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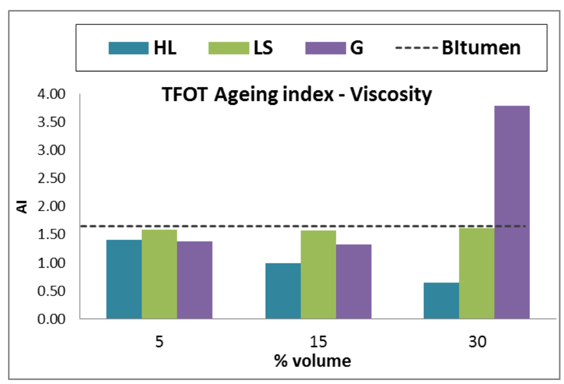

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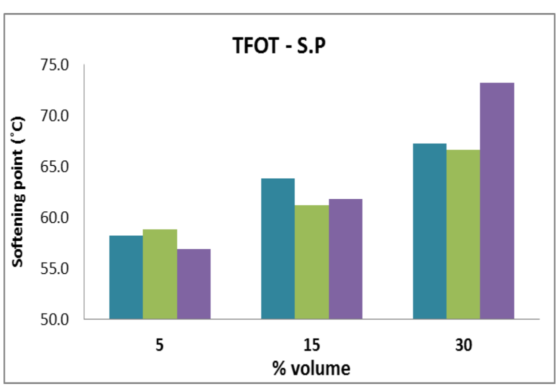

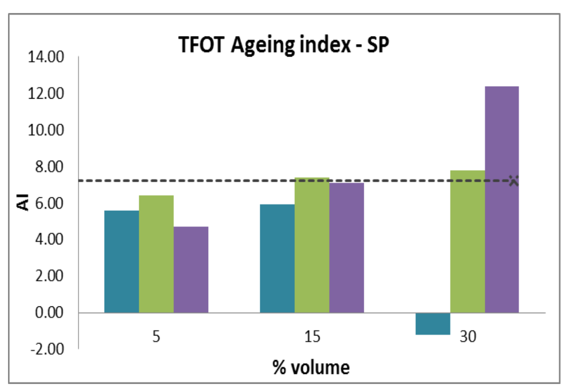

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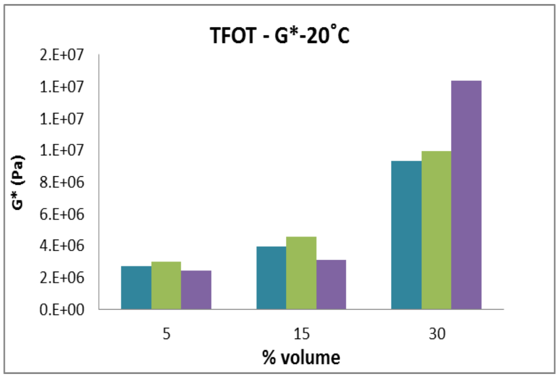
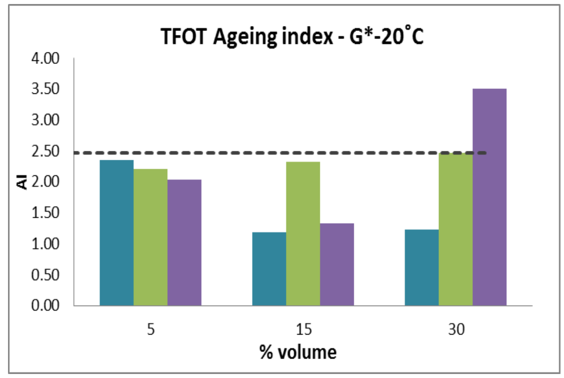




(e) (f)

Figure 5. mastics ageing indices after TFOT ageing (a) Viscosity-TFOT (b) Viscosity-TFOT ageing index (c) Softening point- TFOT (d) Softening point- TFOT ageing index (e) G*- TFOT (f) G*- TFOT ageing index

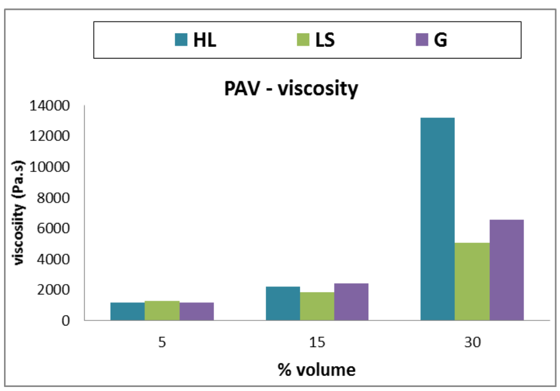
The calculated ageing indices after TFOT ageing show that hydrated lime always has the lowest ageing indices compared to the other mastics. Moreover, when the concentration of hydrated lime in the mastics is increased, the ageing index after TFOT decreases.

Furthermore, the ageing indices for granite mastics are the highest at higher filler concentrations. It can be noticed that the ageing indices for 30%vol. granite mastics are higher than the pure bitumen ageing index, which means that the addition of this percentage of granite increases the ageing. In contrast, the hydrated lime at 30% vol. concentration reduces the mastic stiffness from what it was before the TFOT ageing. As can be seen, the ageing indices are lower for the viscosity and negative for the softening point. The softening point decreases by about two degrees after TFOT ageing and the viscosity dropped to 64% of the unaged mastic viscosity.

The strange effect of the granite filler at higher volume concentrations needs more investigation to understand the factors and the reasons for this behaviour.

In order to establish the causes for these interesting results, the bitumen binder was recovered from the mastics and the chemical changes in the bitumen during ageing were investigated using FTIR. In addition, the rheological changes of the recovered binder were tested using the DSR. The results and discussion of these tests will be presented later.

However, the results for the long-term ageing in the PAV will be discussed and presented first. Figure 6 shows the mastic ageing indices after the PAV ageing.



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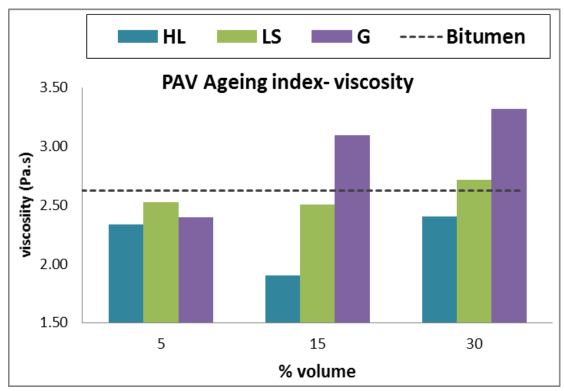

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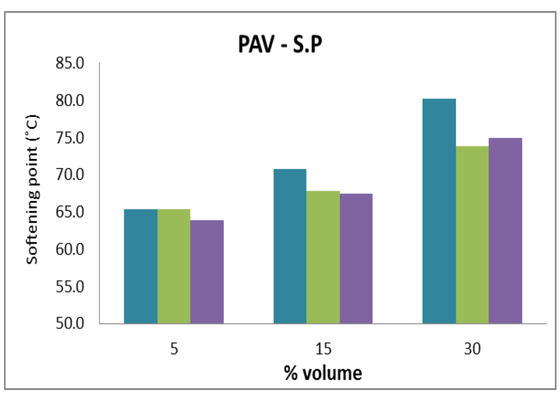

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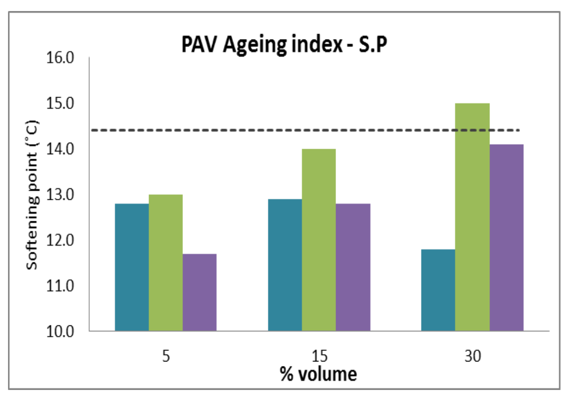

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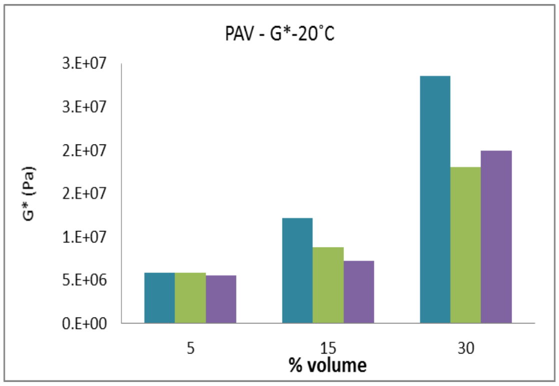
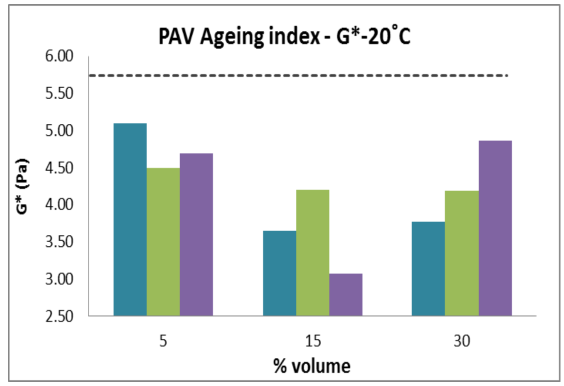




(e) **(f)**

Figure 6. Mastic ageing indices after PAV ageing (a) Viscosity-PAV (b) Viscosity-PAV ageing index (c) Softening point- PAV (d) Softening point- PAV ageing index (e) G*- PAV (f) G*- PAV ageing index

These results show that despite the hydrated lime mastics being softer than the granite mastics after TFOT, they became stiffer than the granite mastics after PAV ageing. According to the ageing indices after PAV, it can be noticed that hydrated lime has lower ageing indices than granite and limestone at 30% vol. concentration. However, at lower filler concentrations, it can be seen that the ageing indices are not consistent in ranking the mastic ageing.

In general, from both the short-term and long-term ageing results, it can be concluded that the ageing indices are affected by the concentration of the filler, especially at higher concentrations. In addition to that, the filler type had a very significant effect on the ageing indices, as it was seen that hydrated lime decreased the ageing indices more than the other fillers. Furthermore, the ageing evaluation indicators used can in some cases rank the mastics differently; this effect was more pronounced after PAV ageing than after the TFOT ageing.

From the results above, it was also observed that increasing the granite filler concentration in the mastics resulted in increasing the ageing rather than reducing it. In contrast, generally, increasing the concentration of hydrated lime in the mastics decreases the ageing. These findings indicate that for each filler there will be a different optimum filler concentration that will result in the best stiffening effect on the mastics, as well as better ageing mitigation. This optimum depends on the filler properties and the possible interaction between the filler and the bitumen.

In a study done by Wu,2009 [1], mastics made with 40 vol.% of mineral filler (limestone and gritstone) after TFOT ageing were tested. The result showed that the ageing index of the mastics after 1 hour ageing was lower than that of the neat bitumen. Their findings were explained by the combination of the adsorption of the lighter fractions of the bitumen on the surface of the fillers and the catalytic effect of the mineral fillers. This corresponded to an increase in polar components after bitumen was recovered and tested by FTIR. The study suggested that the adsorption action of the acidic gritstone did not last as long as that of the basic limestone. This is why the ageing indices of limestone mastics were lower than those of gritstone.

3.3. Recovered bitumen - DSR analysis

In order to investigate the adsorption and catalytic effect of fillers on the bitumen mastics, the fillers and the bitumen were recovered after different ageing stages. They were tested for their changes in their chemical and rheological properties using FTIR and the DSR respectively.

In order to investigate the effect of the fillers on the rheological properties of the recovered bitumen, the results from the DSR are presented in the form of isochronal plots for the complex modulus and the phase angle. The isochronal plots were used to compare the effect of ageing for the recovered bitumen from the hydrated lime mastics and the granite mastics. The isochronal plots presented in Figure 7 show the complex modulus and the phase angle of the recovered bitumen at different testing temperatures up to 50°C.

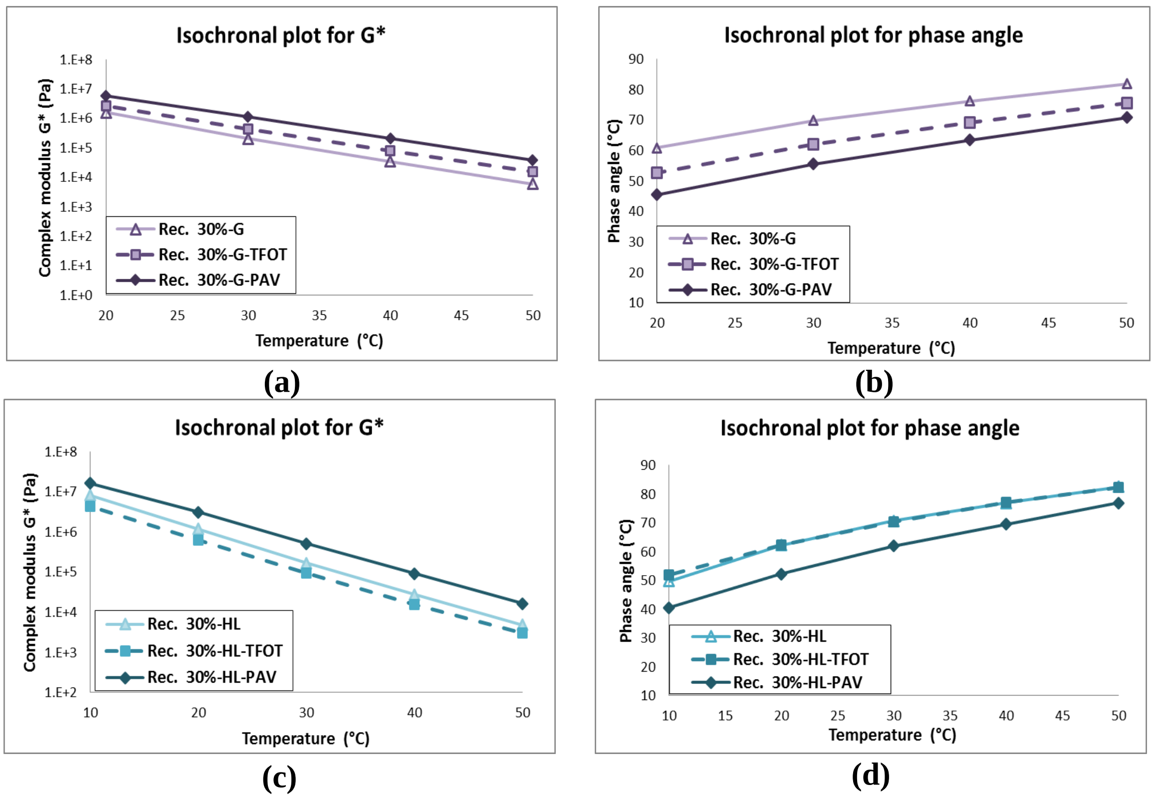


Figure 7. Isochronal plots for G* and δ of the recovered bitumen from granite and hydrated lime mastics after different ageing stages (a) 30%G-G* (b) 30%G-phase angle (c) 30%HL-G* (d) 30%HL-phase angle

The resulting isochronal plots show that, at all testing temperatures, for granite mastics, the complex modulus increases and the phase angle decreases as the ageing proceeds from TFOT and PAV. In contrast, for the bitumen recovered from hydrated lime mastics, it shows that after TFOT it has a lower complex modulus than the bitumen recovered from the unaged mastics. Similarly, the phase angle for the bitumen recovered from the TFOT aged hydrated lime mastics does not show any drop at all tested temperatures. It has phase angles similar to those recovered from the unaged hydrated lime mastics. For further investigation and to make the results more comparable, the complex moduli of the recovered bitumen were compared to the mastic complex moduli after different ageing stages. The mastics and recovered bitumen complex moduli at 20°C and 0.4Hz were chosen for this comparison. The results are presented in Table 4.

Table 4. Mastics and recovered bitumen complex modulus at different ageing stages.

Sample	G*-Mastics	G*-Recovered binder
Un aged		
30%-G	4103600	1509150
30%-HL	7565600	1214950
15%-G	2331800	1532100
15%-HL	3330400	1503900
40/60 bitumen(un-aged)	1032400	1032400
TFOT-aged		
30%-G-TFOT	14348000	2915200
30%-HL-TFOT	9325600	1070985
15%-G-TFOT	3083500	2980900
15%-HL-TFOT	3929800	1403000
40/60 bitumen- TFOT	2551100	2551100
PAV-aged		
30%-G-PAV	19948000	5962400
30%-HL-PAV	28525000	3112500
15%-G-PAV	7175300	5211900
15%-HL-PAV	12132000	6277050
40/60 bitumen- PAV	5929800	5929800

Comparing the complex modulus for the recovered bitumen and the mastics it can be noticed that, for the unaged mastics at the same filler concentrations, the mastics with hydrated lime have higher complex modulus than the granite mastics. However, the recovered bitumen from the hydrated lime mastics is softer than that recovered from the granite mastics. After TFOT, the hydrated lime mastics became softer than granite mastics and, similarly, the recovered bitumen was still much softer than bitumen recovered from granite mastics. Similarly, after PAV, the recovered binder from the hydrated lime mastics is always softer than that recovered from the granite mastics. In general, after TFOT and PAV ageing, the recovered bitumen from hydrated lime mastics is the softest and is softer than the aged bitumen at the same ageing stage. The effect of the fillers on the rheological properties of the mastics and the recovered bitumen was further studied. The phase angle for both the mastics and recovered bitumen are shown in Table 5.

Table 5. Mastics and recovered bitumen phase angle at different ageing stages.

Sample	**G*-Mastics**	**G*-Recovered binder**
	PAV-aged	
30%-G-PAV	43.87	45
30%-HL-PAV	42.59	52
15%-G-PAV	45.26	46
15%-HL-PAV	45.46	46
40/60 bitumen-PAV	46.03	46.03
	TFOT-aged	
30%-G-TFOT	53.81	52.685
30%-HL-TFOT	54.37	60.09
15%-G-TFOT	55.16	53.33
15%-HL-TFOT	55.61	58
40/60 bitumen-TFOT	55.72	55.72
	Unaged	

30%-G	63.93	60.94
30%-HL	60.87	62.27
15%-G	63.37	62
15%-HL	61.24	60
40/60 bitumen	64.94	64.94

The results show that, as expected, the phase angle decreases as ageing proceeds. For the mastics, adding filler to the bitumen slightly decreases the phase angle, which indicates a more elastic behaviour. It is clear that the addition of the mineral fillers to bitumen decreases the phase angle in all cases. With ageing, the phase angle of the mastics decreases more. However, for the recovered bitumen, the bitumen recovered from hydrated lime mastics shows significantly higher phase angle than bitumen recovered from granite mastics. Furthermore, this recovered bitumen from hydrated lime mastics has a higher phase angle than that of the pure bitumen at the same ageing stage. This significantly higher phase angle (δ) for the recovered bitumen from hydrated lime mastics, could be a relative measure of the ability of asphalt to dissipate energy, in aged HL-treated pavements, which should be beneficial in reducing cracking in aged pavements [19].

In order to compare the results quantitatively, the ageing indices for both the mastics and recovered bitumen were calculated. The ageing indices for mastics and the recovered bitumen were calculated according to the equation 3 and equation 4, respectively.

$$Aging\ index\ of\ mastic = \frac{G*\ of\ \ aged\ mastic}{G*of\ un\ aged\ mastics} \qquad \text{Equation 3}$$

$$Aging\ index\ of\ recovered\ bitumen = \frac{G*\ of\ Recovered\ bitumen}{G*of\ base\ bitumen - unaged} \quad \text{Equation 4}$$

The results for the calculated ageing indices for the granite and hydrated lime mastics and their recovered bitumen after different ageing stages are presented in Table 6.

Table 6. Complex modulus ageing indices for mastics and the recovered bitumen after different ageing stages

Samples	unaged	TFOT-aged	PAV-aged
	Mastics		
15%-G	1.00	1.32	3.08
30%-G	1.00	3.50	4.86
15%-HL	1.00	1.18	3.64
30%-HL	1.00	1.23	3.77
40/60 bitumen		2.47	5.74
	Recovered binder		
15%-G	1.48	2.89	5.05
30%-G	1.46	2.82	5.78
15%-HL	1.46	1.36	6.08
30%-HL	1.18	1.04	3.01
40/60 bitumen	1.00	2.47	5.74

The results show that, among the recovered binders, the bitumen recovered from hydrated lime 30% vol. concentration always has the lowest ageing index at different ageing stages. It can be noticed that the bitumen recovered from these mastics has significantly lower ageing than that recovered from granite mastics with the reduction in aging index being almost 50%.

These results show that there is a similar ranking for the mastic hardening and the recovered bitumen. For the recovered bitumen, the results revealed that after TFOT the recovered bitumen from 30% vol. HL was softer than that recovered from the unaged mastic. Furthermore, the results indicate that filler type can significantly influence the ageing properties of the bitumen in contact with them, which could prove that some filler types may interact with the bitumen more than others. Hydrated lime has been considered as an active filler, which has the potential to interact with different bitumen binders. Some studies has related this effect to the adsorption of polar components from bitumen [1, 20].

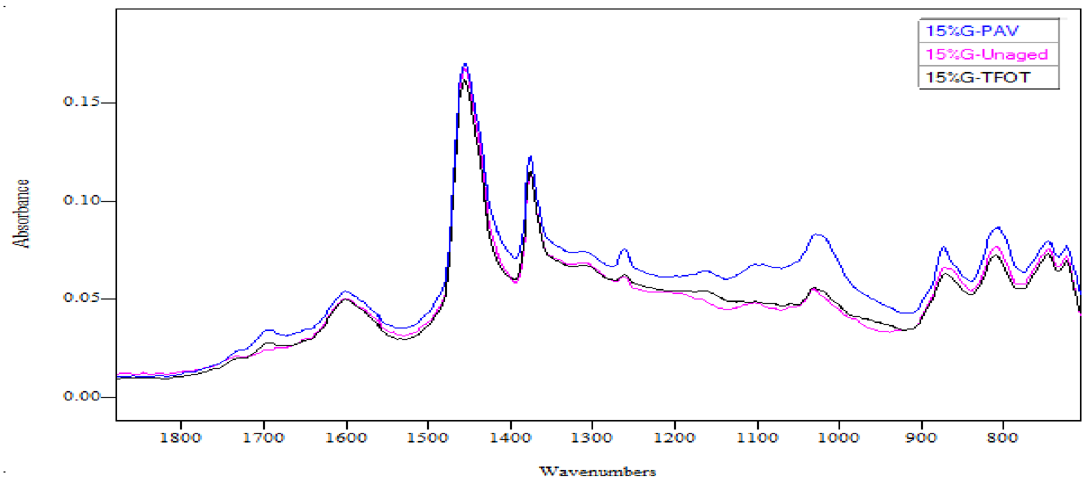
For the higher aging indices, even higher than for pure bitumen, the reason could be due to these fillers exhibiting some catalytic effect which increases the aging. Thus, in order to investigate the adsorption/ absorption effects of the fillers, the chemical changes in the recovered bitumen and the recovered fillers were studied using FTIR. The discussion is presented in the sections below.

3.4. Recovered bitumen- FTIR analysis

The FTIR analysis on the recovered bitumen evaluates the binder age hardening degree according to the carbonyl and sulfoxide formation as a result of bitumen oxidation.
Carbonyl and sulfoxide groups are the most important oxidation products. Both indices are identified as key parameters when studying bitumen ageing. As known, bitumen oxidation causes the formation of functional groups, which are characterised by the growth of groups in the bands at 1700 cm-1 and 1030 cm-1, which represent carbonyl formation (C=O) and sulfoxide formation (S=O), respectively. The carbonyl and sulfoxide ageing indices were calculated for the recovered bitumen after different

ageing stages. A comparison of the recovered bitumen ageing indices with those of the pure bitumen where made.

The carbonyl and sulfoxide ageing indices were calculated as follows: Carbonyl index (C=O) = $A_{1700}/\Sigma A$, Sulfoxide index (S=O) = $A_{1030}/\Sigma A$, Where: the sum of the area ΣA represents: $A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} + A_{(2953, 2923, 2862)}$. Examples of the results for FTIR spectra are presented in Figure 8, while the resultant chemical ageing indices for the recovered bitumen are presented in Table 7.



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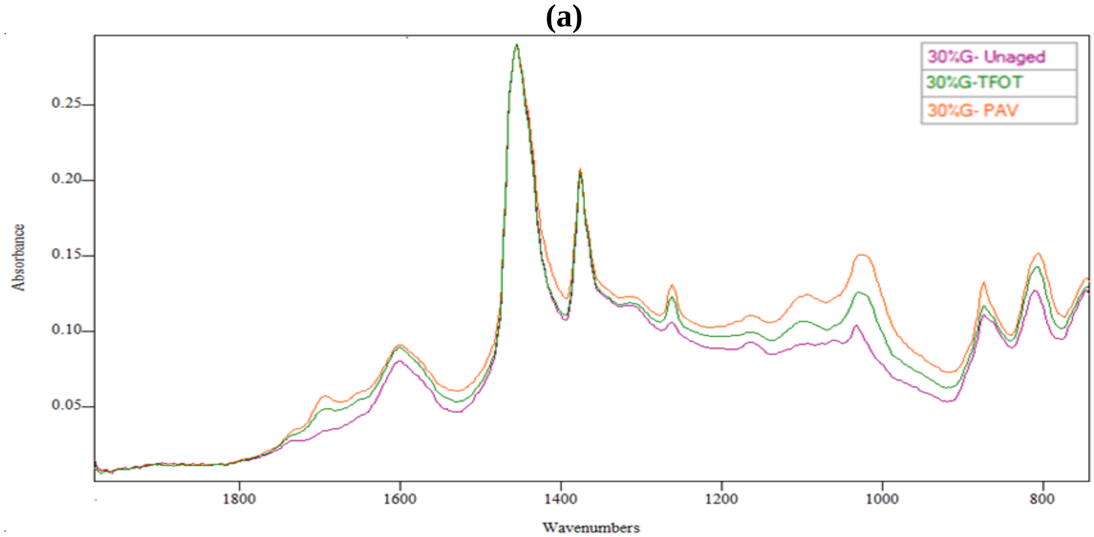

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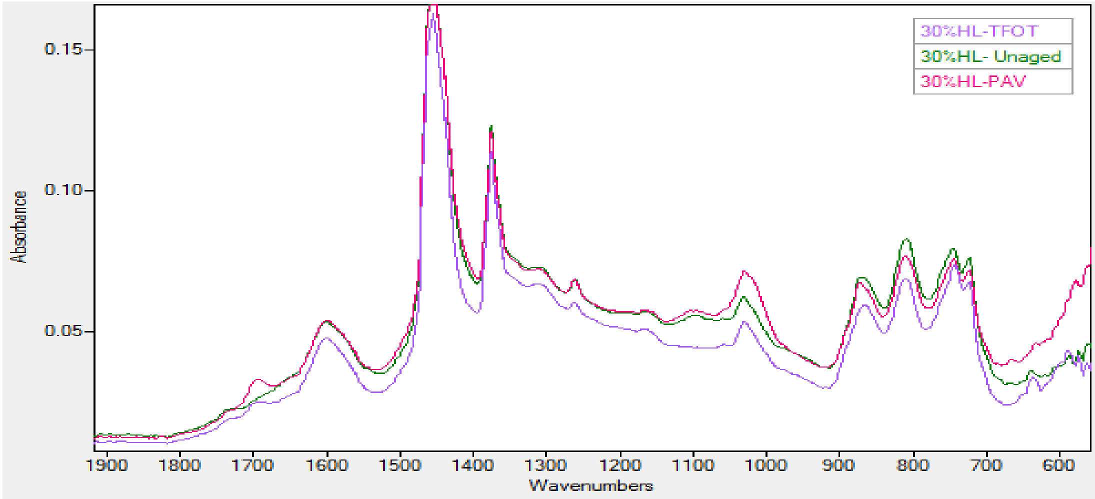


(c)

Figure 8. FTIR spectrums for the bitumen recovered from the mastics after different ageing stages. (a) 15%-G (b) 30%-G (c) 30%-HL

Table 7. Chemical ageing indices for the recovered bitumen after different ageing stages.

Samples	C=O	S=O	C=O + S=O
	Unaged		
15%-G	0.00083	0.01492	0.01574
30%-G	0.00069	0.01365	0.01434
15%-HL	0.00077	0.01671	0.01748
30%-HL	0.00023	0.01588	0.01611
40/60 bitumen	0.0054	0.019	0.0244
	TFOT-aged		
15%-G-T	0.00539	0.02169	0.02708
30%-G-T	0.00452	0.0273	0.03182
15%-HL-T	0.00224	0.01823	0.02048
30%-HL-T	0.0024	0.01662	0.01902
40/60 bitumen	0.0059	0.035	0.0409
	PAV-aged		
15%-G-P	0.00705	0.03267	0.03972
30%-G-P	0.00798	0.03766	0.04565
15%-HL-P	0.00948	0.02668	0.03616
30%-HL-P	0.00648	0.0283	0.03479
40/60 bitumen	0.0076	0.044	0.0516

The results from the FTIR test reveal that the carbonyl C=O index was significantly affected by the fillers mixing with the bitumen. It can be noticed that the recovered bitumen from the unaged mastics has very low C=O index compared to the unaged bitumen. The C=O index for the recovered bitumen from different mastics is about 85% less than that of the unaged 40/60 pen bitumen used to prepare the mastics.

As ageing proceeds, it can be noticed that after TFOT, the bitumen recovered from the hydrated lime mastics is softer than the bitumen recovered from granite mastics of the same filler concentrations. However, all the recovered bitumens after TFOT still have lower C=O indices for the HL mastics. Furthermore, after PAV ageing, bitumen recovered from the 30% HL mastics has the lowest C=O index. These results for the carbonyl C=O indices are in agreement with the previous results from the complex modulus evaluation. This shows that the recovered bitumen from hydrated lime mastic has a lower complex modulus (i.e. it is a softer binder). Similarly, the lower carbonyl index means less oxidation products generated during ageing, which means less ageing for the hydrated lime mastics. These results are in agreement with previous studies [2, 21, 22].

On the other hand, the effect of filler on the sulfoxide index (S=O) is different from the carbonyl (C=O) index. It was observed for the bitumen recovered from the unaged mastics, that the S=O index is not significantly affected by the filler mixing with the bitumen. However, it can be seen that almost all the recovered bitumen and the unaged pure bitumen have lower S=O indices than that of the pure bitumen. After TFOT ageing, it can be noticed that the S=O index of the pure bitumen shows the highest increase. The other recovered bitumen from mastics after TFOT does not show a significant change from the unaged recovered bitumen except for the 30% granite fillers which shows a higher increase in S=O than other recovered binders. Moreover, after PAV ageing a further increase in S=O can be observed for all recovered binders and the pure bitumen. However, in all cases, the bitumen recovered from hydrated lime mastics shows the lowest S=O index.Meanwhile, carbonyl and sulfoxides are the major oxidation products of the ageing process; their sum indicates the relative degree of oxidation in binders.

In general, the FTIR results for the recovered bitumen from mastics show the significant effect of fillers on the ageing of mastics. Furthermore, they indicate that different fillers can affect mastic ageing differently. The results also confirm the beneficial effect of hydrated lime to reduce the age hardening effect on the mastics by reducing the formation of the oxidation products such as carbonyls and sulfoxides as observed from the FTIR indices.

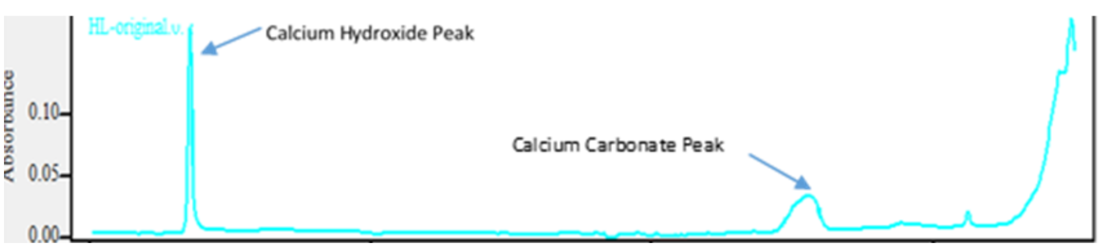
As the rheological and physical characteristics of the bitumen are strongly related to the chemical changes in the bitumen, fewer oxidation products reflect a lower stiffening and hardening in the mastics. Overall, bitumen stiffening and hardening, which was measured by an increase in complex modulus and a decrease in phase angle, was reflected in the growth of the carbonyl and sulfoxide chemical functional groups. These results are in agreement with previous studies, which have confirmed that an increase in viscosity, softening point and stiffening of aged binders is related to an increase in their carbonyl content, [22-26].

In addition to the FTIR test for the recovered bitumen, the asphaltenes content wes used to evaluate the increase in stiffening due to the change in bitumen chemistry after ageing. Table 8 presents the asphaltenes content for the recovered bitumen from the 30% vol. concentration mastics. The results for the asphaltene contents show that the bitumens recovered from the mastics have a lower asphaltenes content than the pure bitumen aged at the same ageing stage. Furthermore, the results show that the bitumens recovered from hydrated lime mastics has the lowest asphaltenes content at different stages. The asphaltenes contents of the recovered bitumen are well correlated with the results of the carbonyl indices and show similar trends for the tested binders.

Table 8. Asphaltenes content of the recovered bitumen from the mastics after different ageing stages

	40/60 bitumen	30%-HL	30%-G
Unaged	16.60	13.70	14.30
TFOT-aged	16.85	15.80	16.75
PAV_aged	18.90	17.10	18.40

The results of the carbonyl indices and the asphaltenes content of the recovered bitumen show a lower carbonyl index and less asphaltenes content for the bitumen recovered from the hydrated lime mastics. These could prove the ability of hydrated lime particles to adsorb polar components of bitumen. In addition, the results could imply that some interactions between the polar components of bitumen and the mineral surface of the fillers may be irreversible. Thus, in order to prove this concept, attempts were made to test the residual filler recovered from the mastics using the FTIR test and to compare the results with those of the original ones. The FTIR spectrum for the original hydrated lime particles and the granite fillers are presented in Figure 9.



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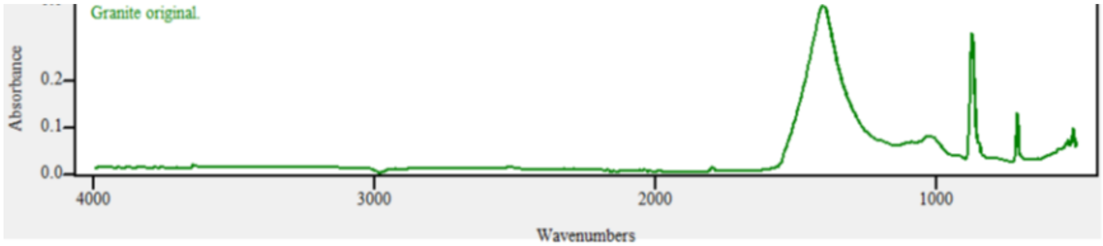


(b)

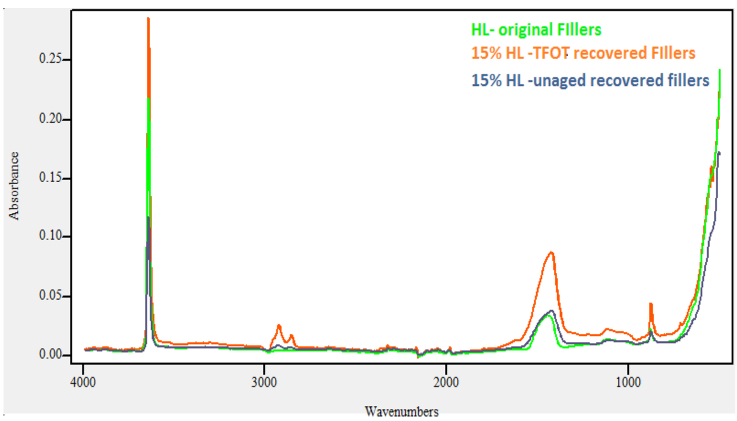
Figure 9. FTIR spectrum of the original hydrated lime and granite filler particles (a) Original hydrated lime (b) Original Granite

It can be noticed that for the hydrated lime particles spectrum there are two main peaks representing the main composition of the hydrated lime, which are the Calcium Hydroxide peak $Ca(OH)_2$ at 3640 cm^{-1} and the Calcium Carbonate peak $CaCO_3$ at 1390 cm^{-1}. These two main components of the hydrated lime comprise 96.00% and 2.77%, respectively, of the total chemical composition of the hydrated lime as provided by the supplier.

The changes in chemical composition of the fillers recovered from mastics after different ageing stages were also observed using the FTIR analysis. The spectrum of the recovered fillers from the unaged, TFOT and PAV aged hydrated lime mastics compared to the original HL particles are presented in Figure 10. From the spectrum in Figure 10(a) and Figure 10(b), it is observed that there are some main peaks affected by the ageing of the asphalt mastics. The intensity of these peaks increases with ageing. These peaks are observed around wavenumbers 1400, 2853, 2920, and 2950 cm^{-1}.

Similarly, the recovered fillers from the granite mastics were analysed and compared with the original granite mastics. The changes in the FTIR spectrum of the original granite fillers and the recovered fillers are presented in Figure 10(c). It can be observed that there is an increase in the intensity at the wavenumbers at peaks around 2850, 2920 and 2950cm^{-1}, which increases as the ageing proceeds.

From the FTIR spectrum for both the hydrated lime and granite fillers, it can be noticed that both fillers share the same increase in the wavenumbers around 2853,2920 and 2950cm^{-1}. These changes could be referred to as interactions between the mineral filler surface and some components of the bitumen. This interaction could be irreversible, as it could be observed there still changes appearing in the recovered fillers after mixing with bitumen. These results could indicate that the fillers adsorbed some of the bitumen components at the corresponding wavenumbers where the changes were observed in the recovered filler spectra.



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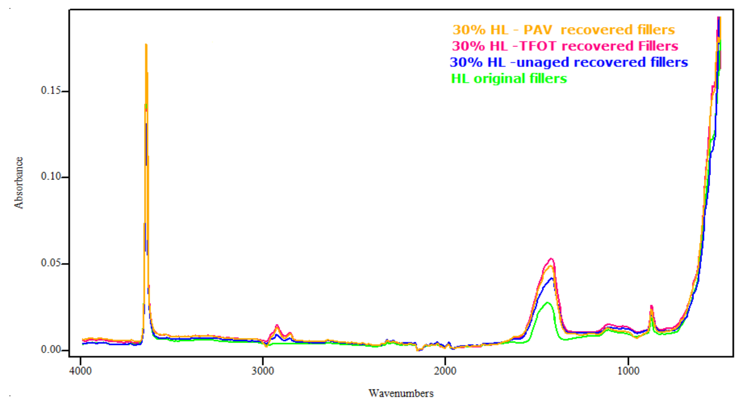

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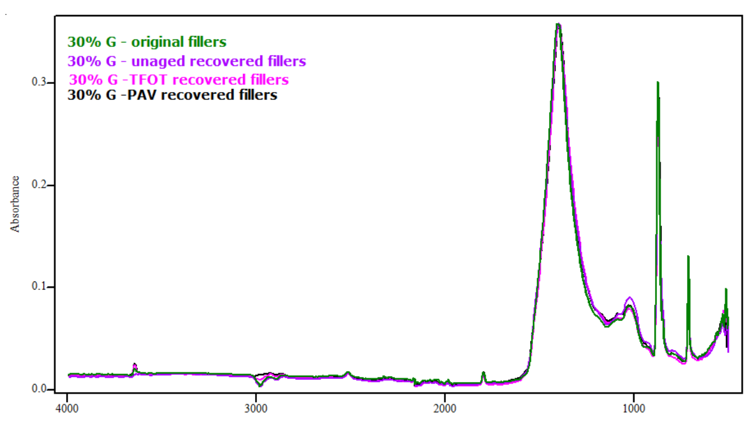
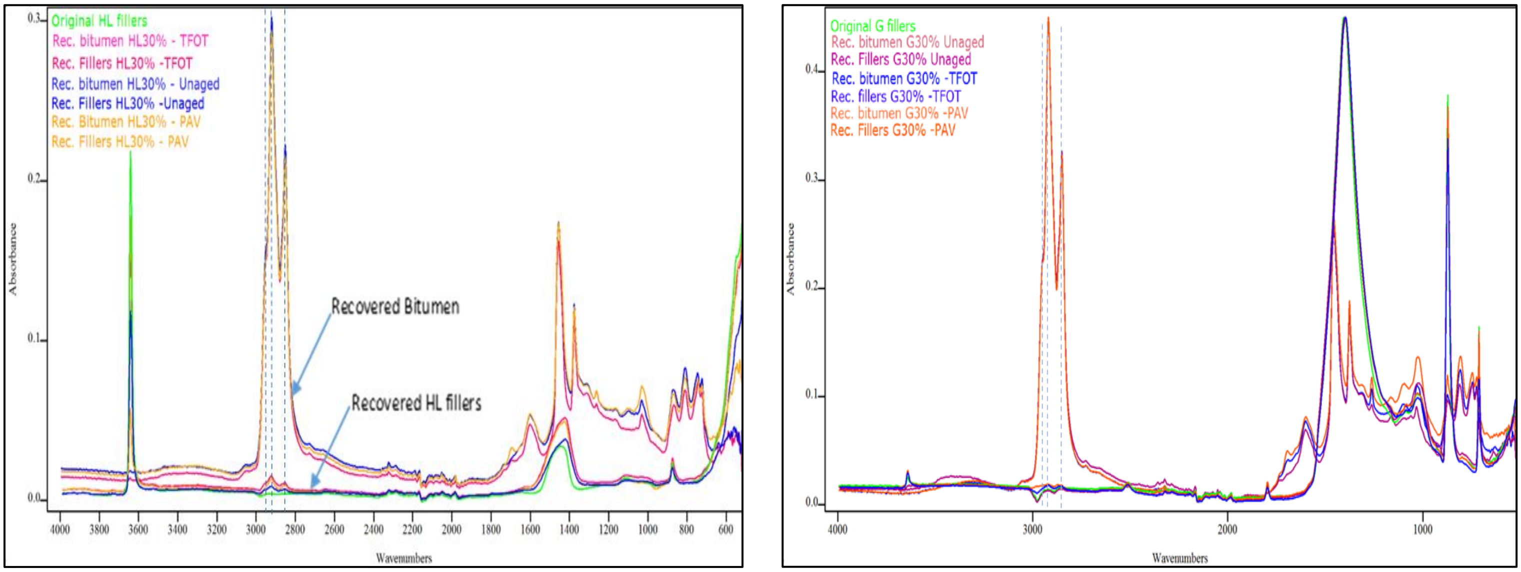


(c)

Figure 10. FTIR spectrum of the original and the recovered mastics after different ageing stages (a) 15%-HL (b) 30%-HL (c) 30%-G

Thus, in order to further investigate this phenomenon, a quantitative analysis of the changes in the filler absorption at the corresponding wavenumbers was performed. Furthermore, the changes in the mastics and the recovered bitumen at these same wavenumbers were also investigated. The FTIR spectra for both recovered fillers and bitumen from the HL30% mastics and the FTIR spectra of the fillers and bitumen recovered from G30% are presented in Figure 11.

It can be observed from both Figure 11 that the wavenumbers for the increased bands in the spectrum for the recovered fillers correspond to bitumen peaks. The peaks at these wavenumbers in the recovered bitumen are well defined. The four prominent peaks observed in the 3000–2800 cm^{-1} region correspond to the stretching vibration absorption bands of the alkyl (C-H) in CH_2 and CH_3 of asphalt binder [9, 27]. This means in other words that these wide absorption peaks at 3000–2800 cm^{-1} correspond to the carboxylic acid of bitumen. Strong absorption peaks at 2920 and 2850 cm^{-1} corresponds to the stretching vibration of paraffin C–H and cycloparaffin C–H. The absorption peak at 2950 cm^{-1} corresponds to stretching vibration of $–CH_3$,while the absorption peak at 2920 and 2850 cm^{-1} correspond to $–CH_2$ [28].



(a) **(b)**

Figure 11. FTIR spectrum of the recovered bitumen and fillers from the mastics after different ageing stages (a) 30%-HL (b) 30%-G

Therefore, in order to compare the adsorption of the two fillers, the increases in the area of the recovered fillers corresponding to the carboxylic acid were calculated. The results are presented as increasing percentages of the area calculated from the recovered fillers around the wavenumbers 2853, 2920 and 2950cm^{-1} compared to the original fillers. The results are presented in Table 9.

Table 9. The increases in the absorbed area around 2853, 2920 and 2950cm^{-1} for the recovered fillers from 30% vol. mastics.

	Recovered Hydrated lime Fillers	**Recovered Granite Fillers**
Un-aged	2.03	1.00
TFOT	4.30	1.31
PAV	4.33	1.08

The results in Table 9 show that the adsorption on the hydrated lime fillers for the unaged mastics is higher than the carboxylic acid adsorbed on granite fillers. Furthermore, the results show that the adsorption on the hydrated lime fillers increases as the ageing proceeds from TFOT to PAV. However, in contrast, the adsorption of the granite fillers for the calculated areas is almost the same with ageing and in all cases, it is lower than that of the hydrated lime. These results confirm that the fillers can adsorb bitumen components on their surfaces and this interaction is irreversible, as it is not restored after the recovery of the fillers and the bitumen.

Moreover, the results above also confirm the results in Table 7, which show that the carbonyl index of the bitumen recovered from hydrated lime mastics is lower than that recovered from the granite mastics. These results explain the mechanisms of how hydrated lime mitigates the ageing of asphalt mixtures and mastics. Therefore, this analysis of the results shows the beneficial effect of hydrated lime addition to the bitumen mastics and consequently to asphalt mixtures. Thus, the ability of hydrated lime to reduce the oxidative hardening could be explained by the following mechanism: Hydrated lime irreversibly adsorbs the reactive polar components on its surface and removes them from the bitumen. These adsorbed components are strongly interacting chemical functional groups, which are reactive to oxidation; thus, the removal of these components reduces the rate of formation of oxidation products such as asphaltenes and carbonyls.

Hydrated lime, as a chemically strong base, has the ability to react readily with acidic components of the bitumen such as carboxylic acids to form calcium salts such as calcium carbonate, which is insoluble. As a result, carboxylic acids and other related chemical functional groups in bitumen irreversibly react with hydrated lime;

consequently removing these acidic components from the bitumen mastic reduces the ageing and hardening. The increase in the C-H of the carboxylic acid on the recovered hydrated lime fillers is evidence of the adsorption ability of the hydrated lime particles compared to the granite filler particles as seen in Table 9.

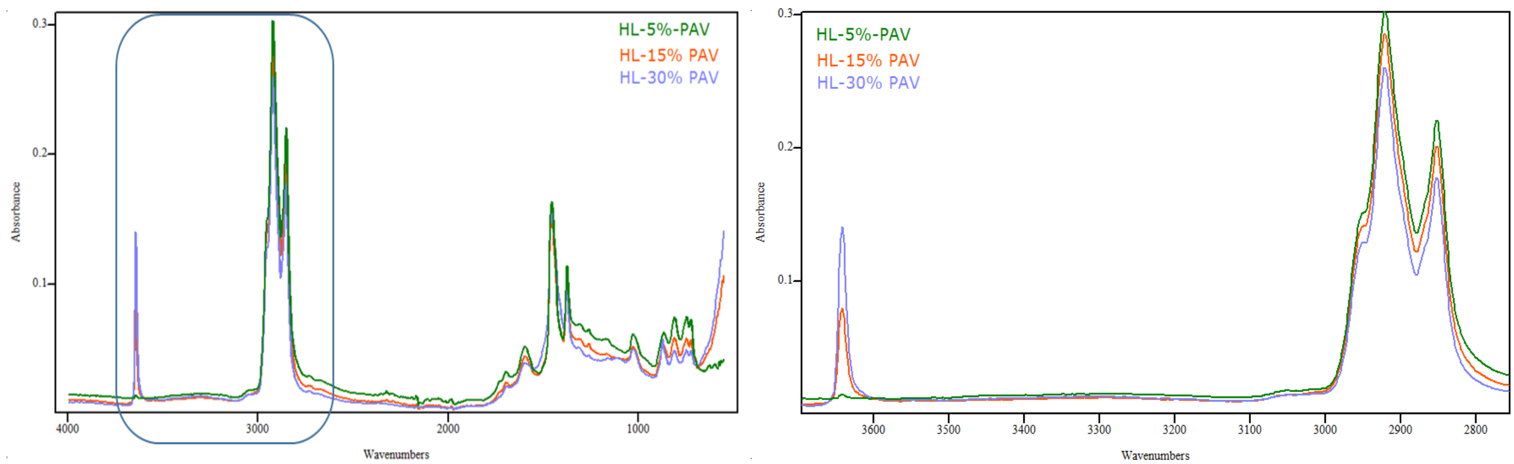
In addition, the results in Figure 10(a), Figure 10(b) and Figure 11(a) show the increase of the lime, especially from the TFOT aged mastics. This Calcium Carbonate peak ($CaCo_3$) for the recovered hydrated could prove the interaction of the acidic components of the bitumen with the hydrated lime forming calcium carbonate.

The results of this study confirm the previous observations by researchers about the ability of hydrated lime to irreversibly adsorb some components of the bitumen, which consequently reduces the rate of ageing [16, 19, 29, 30].

Furthermore, to investigate the changes of the bitumen mastics with different filler percentages after ageing, the changes in the FTIR absorbed area of Carboxylic Acid O-H and C-H stretch, which can be characterised by the absorption observed in the area between 3000 - 2500 (broad, v), was investigated.

The sums of the areas characterised by the peaks at 2853, 2920 and 2950cm^{-1} for different mastics with different filler concentrations after PAV ageing were calculated and compared. The FTIR spectra for the wavenumbers of interest for different mastics with different fillers concentrations are presented in Figure 12(a) and Figure 12(b) for hydrated lime mastics and granite mastics respectively. The results of the calculated areas are shown in Table 10.

From Figure 12(a), it can be observed that with the increasing of the hydrated lime fillers in the mastics, the intensity of the Calcium Hydroxide peak increases as observed at the wavenumber 3640 cm^{-1}. In addition it can be noticed that there is a decrease in the area between 3000-2800cm-1, which corresponds to the stretches of the carboxylic acids. This change was quantified and the areas of these peaks were calculated and compared. From Figure 12(b), it can be seen that at the same wavenumbers corresponding to the carboxylic acids of the bitumen there is only a decrease of the peaks at the higher granite filler contents in the mastic 30%G.



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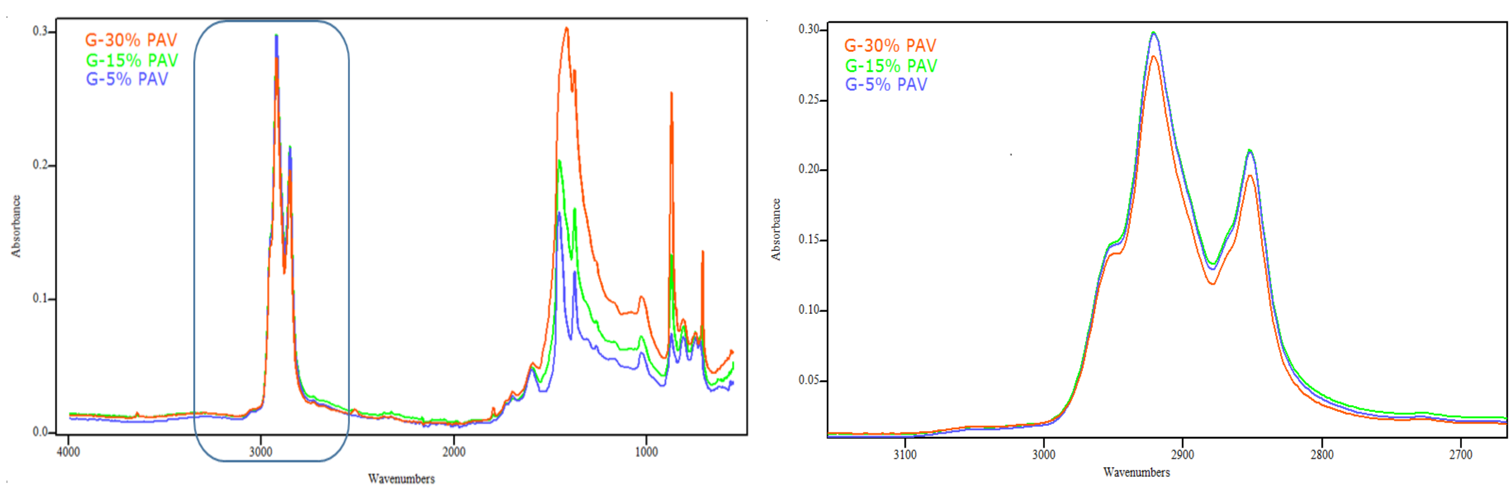


(b)

Figure 12. FTIR spectra of the mastics with different filler concentrations after PAV ageing (a) hydrated lime (b) Granite

Furthermore, the results from Table 10 show that the decrease of the calculated area for hydrated lime mastics is more than that of the granite mastics. These results confirm the discussion above that hydrated lime has a higher ability to adsorb these bitumen components. Moreover, as can be seen by increasing the hydrated lime concentration in the mastics the adsorption increases (the calculated area decreases for the mastics).

Table 10. Comparing the sum of the area 3000-2800cm^{-1} of the granite and hydrated lime mastics FTIR spectra.

	HL-Mastics	**G-Mastics**
5%	12.16	12.10
15%	11.45	12.04
30%	10.61	11.32
40/60 bitumen	12.05	12.05

In concluding the testing performed in this stage and the results observed in this part of the study, the following remarks can be made:

- The ageing indices after TFOT and PAV ageing are significantly affected by the concentration of the filler, especially at higher concentrations.

- The effect of filler type and its properties significantly affect the ageing indices. Hydrated lime decreases the ageing indices more than the other fillers do after TFOT and PAV ageing.
- Increasing the concentration of hydrated lime in the mastics tends to decrease the ageing indices for the concentrations used in this study. However, increasing the granite filler concentration in the mastics resulted in increasing the ageing rather than reducing it.
- For the bitumen recovered from the mastics, the recovered binder from the hydrated lime mastics is always softer than that recovered from the granite mastics for the same ageing conditions. In addition, the bitumen recovered from the hydrated lime mastics shows significantly higher phase angles than bitumen recovered from the granite mastics.
- The chemical analysis of the changes on mastics, recovered fillers and bitumen, revealed that some interactions happened between the hydrated lime and some fractions of the bitumen. This effect is less pronounced in the case of granite fillers.
- The results from the FTIR test on the recovered bitumen from the mastics show that less carbonyls were produced after TFOT and PAV ageing for the hydrated lime mastics compared to the granite mastics, which shows the beneficial effect of hydrated lime on ageing.
- The results for the asphaltenes content test on the recovered bitumen show the same conclusion as the FTIR carbonyl index, which shows less ageing products present in the recovered bitumen from the hydrated lime mastics than in bitumen recovered from the granite mastics.

- The results from the FTIR tests on the recovered fillers prove the ability of hydrated lime to irreversibly adsorb some of the bitumen components (carboxylic acid products). This reduces the formation of the ageing products and consequently reduces age hardening. Unlike hydrated lime, the granite fillers do not exhibit this ability to react with bitumen.

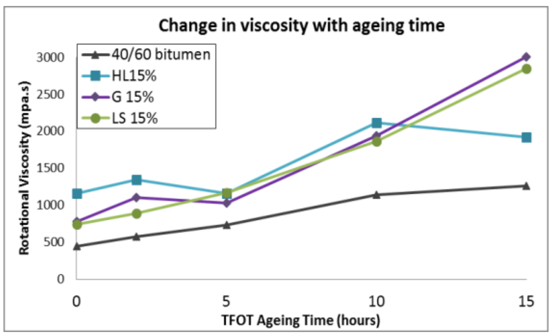
Further investigation into the effect of fillers on the ageing rate of the mastics rather than using the standard ageing methods of TFOT and PAV, which can provide results only at two ageing stages, would be useful. Therefore, an ageing time study was proposed to investigate the ageing rate changes with different filler contents. The ageing time study will be discussed in the following section.

3.4. Stage 2: Aging time study

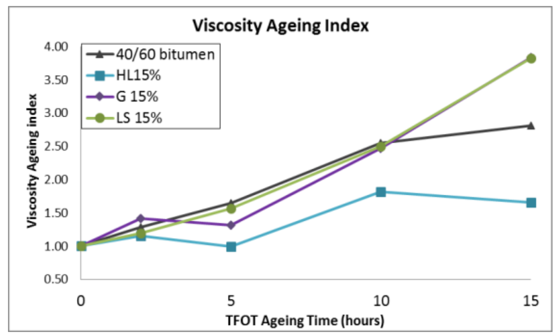
As discussed above, the mineral fillers can adsorb or catalyse the bitumen during ageing. The intensity of the influence of the mineral fillers on ageing keeps changing as the ageing continues, due to the changes in their adsorbing and catalysing abilities. Thus, it was felt that the ageing study with the standard TFOT and PAV ageing time is not enough to describe the whole situation about how the mineral fillers can affect the bitumen ageing. Therefore, mastics with different fillers at various percentages of filler volume concentration were further studied in order to show the effect of hydrated lime on the rate of stiffening and ageing of the mastics.

The mastics were aged in the TFOT oven at 163˚C at a thickness of 2.2mm for different ageing times (2, 5, 10 and 15 hours). The empirical tests including the viscosity at 135˚C and the softening point were carried out at each ageing level. The ageing indices were calculated from these tests. In addition, the rheological changes were determined by the changes in the complex modulus with ageing.

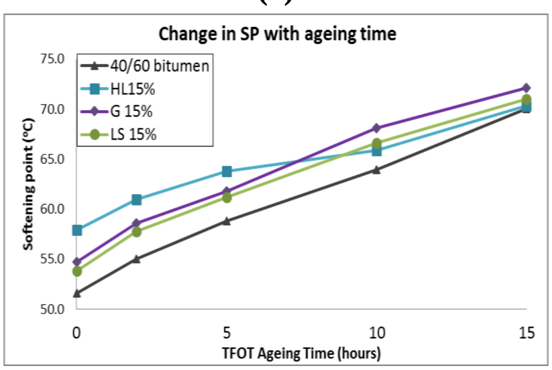
The effect of the TFOT ageing time on the properties such as viscosity, softening point and the complex modulus of the 15% vol. filler concentration mastics and the calculated ageing indices are presented in Figure 13. The results of the mastic ageing show that the mastic and bitumen stiffening increases with the ageing time. The rate of mastic stiffening keeps changing as the time of the TFOT ageing proceeds.



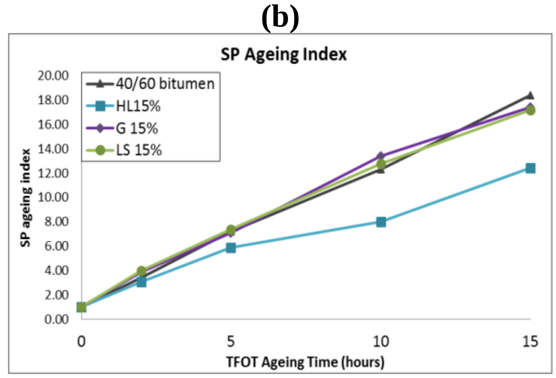
(a)



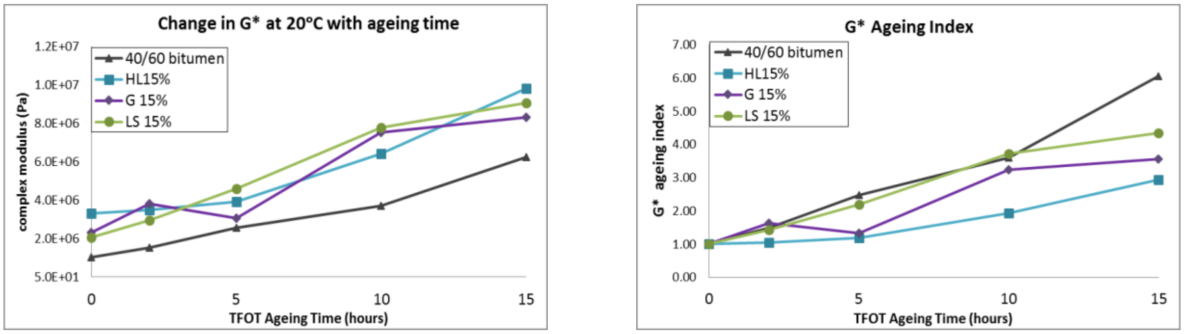
(b)



(c)



(d)



(e) (f)

Figure 13. The effect of TFOT ageing time on the properties of the mastics of 15% vol. concentration and the ageing indices. (a) Change in viscosity with ageing time (b) Viscosity ageing index (c) Change in softening point with ageing time (d) Softening point ageing index (e) Change in G* with ageing time (f) G* ageing index

It can be noticed from the results, that the rate of change in viscosity, softening point and the complex modulus for the pure bitumen is almost consistently increasing. However, the effect of the filler on ageing rate keep changing (increasing or decreasing the ageing rate) as the time in the TFOT proceeds. It can be noticed from Figure 13 that hydrated lime at 15% vol. concentration has the lowest ageing index compared to the other fillers. Moreover, the effect of hydrated lime to reduce the aging becomes clearer and more pronounced for the longer aging times.

The comparison between the 30% vol. mastics aged in the TFOT oven at a thickness of 2.2mm after different ageing times is presented in Figure 14. Comparing the ageing of the mastics of 15% vol. fillers to the 30% vol. filler mastics, it can be noticed that the concentration of fillers has an effect on the aging rate. It is observed in Figure 14 that the rate of ageing experiences more changes at higher filler concentrations than observed for the 15% filler content. It can be noticed as well that the mastics exhibit different behaviours and rates of change with the ageing time for the different filler concentrations. This change is more pronounced for the granite mastics than the hydrated lime mastics. However, it can also be noticed that the ageing indices for the hydrated lime mastics are the lowest for all cases.

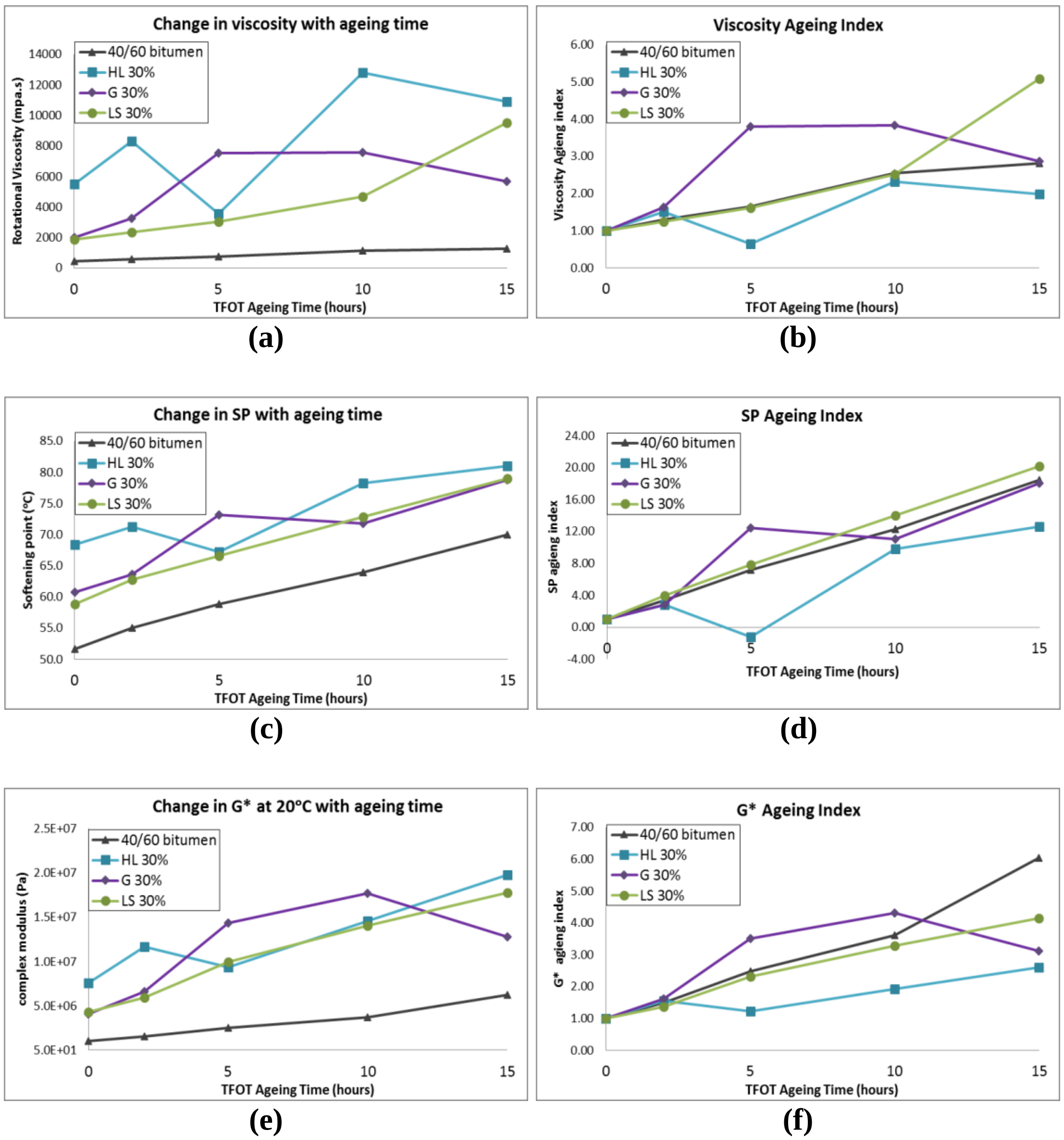


Figure 14. The effect of TFOT ageing time on the properties of the mastics of 30% vol. concentration and the ageing indices (a) Change in viscosity with ageing time (b) Viscosity ageing index (c) Change in softening point with ageing time (d) Softening point ageing index (e) Change in G* with ageing time (f) G* ageing index

It is known that the effects of fillers on the asphalt mastics are directly related to their characteristics and the degree of concentration in the bitumen-filler system. There are diverse studies, which have assessed the effect of using mineral fillers on the ageing of the bitumen mastics and mixtures. The addition of filler can delay the ageing of bitumen as the filler particles are an obstacle to the diffusion of oxygen into the body of the bitumen thus, reducing the ageing oxidative products. As a consequence of this, the ageing of the mastics that contain fillers is expected to be less regardless of the filler nature or the physical and chemical properties.

However, the results show that the ageing indices for the granite mastics at 30% vol. concentration at some ageing stages is higher than that of the pure bitumen. This effect is not the same for the hydrated lime.

Significant differences were observed between the ageing rates of the mastics with different mineral fillers. The results show that the nature of the fillers (acidic or basic nature) can significantly affect the ageing rates. Granite fillers (acidic minerals) have the ability to catalyse bitumen oxidation, thus accelerating the bitumen ageing. In contrast, basic minerals, such as hydrated lime, show a greater ability to adsorb some components of the bitumen which can decelerate bitumen ageing. This is the reason the filler mastics exhibit these different effects.

Anderson et al.,1994 [20] stated that aggregates with the least adsorption of highly polar fractions, such as granite, exhibit the highest catalytic effect in bitumen oxidation. In contrast, fillers showing the highest adsorption effect, such as the hydrated lime, exhibited the smallest catalytic effect. The higher oxidative ageing of the granite mastics is related to the stronger catalytic ability of the granite fillers. However, the lower ageing indices for the hydrated lime mastics are related to the greater adsorption ability of hydrated lime.

In general, it can be concluded that the ageing rate of the bitumen filler mastics depends on both the catalytic and adsorption effects. These two factors are changing with ageing time in the TFOT. This is clear for the granite mastics at 30% vol. concentration, where it can be observed that the ageing indices for the granite mastics keep increasing for the first few hours; however after some time they reduce and keep decreasing. In addition, it can also be seen from the results above that the increase of the ageing index of hydrated lime mastics is not as severe as in the granite mastics. This indicates that the function of delaying age hardening by adsorption of polar components from bitumen to hydrated lime is relatively stable and continuous during the whole ageing programme.

4. Conclusions

From the discussion and the results from the stiffening and ageing tests performed, the following conclusions can be summarised:

- From the results of the stiffening effects of the fillers on bitumen mastics, it was observed that the granite fillers have almost the same stiffening effect with the different bitumen binders used in preparing the mastics. However, this is not the case for the hydrated lime. Furthermore, it was observed that the same hydrated lime concentrations in mastics can result in significantly different stiffening ratios with different binders.

- Comparing between mastics containing hydrated lime and granite fillers on the stiffening of the mastics and the recovered binders showed that the complex moduli of the hydrated lime mastics were much higher than those of granite mastics. This effect was more pronounced at higher filler concentration. In contrast, the recovered bitumen from hydrated lime mastics is softer than the bitumen recovered from granite mastics.
- In general, from both the short-term and long-term ageing, it was observed that the ageing indices are affected by the concentration of the filler, especially at higher concentrations. In addition to that, the effect of filler type was very significant on the ageing indices as it was noticed that hydrated lime decreases the ageing indices more than the other fillers. Furthermore, the ageing evaluation indicators used can in some cases rank the mastics differently; this effect was more pronounced after PAV ageing compared to TFOT ageing.
- From the TFOT and PAV ageing simulations, it was observed that increasing granite filler concentration in the mastics resulted in increasing mastic ageing rather than reducing it. In contrast, generally, increasing the concentration of hydrated lime in the mastics decreases the ageing. These findings indicate that for each filler there will be a different optimum filler concentration that will result in the best stiffening effect on the mastics, as well as better ageing mitigation.
- The results from the FTIR test reveal that the carbonyl (C=O) was significantly affected by the fillers mixed with the bitumen. Furthermore, for the recovered bitumen, a lower carbonyl index and less asphaltenes content for the bitumen recovered from the hydrated lime mastics was observed. This could prove the

ability of hydrated lime particles to adsorb polar components of bitumen. Furthermore, the asphaltenes content of the recovered bitumen is well correlated with the results of the carbonyl indices.

- The results from the FTIR tests on the recovered fillers prove the ability of hydrated lime to irreversibly adsorb some of the bitumen components (carboxylic acid products) and thus reduce the formation of ageing products and consequently reduce age hardening. Unlike hydrated lime, the granite fillers do not exhibit this ability to react and adsorb bitumen components.
- From the ageing time study, the results of the mastic ageing show that the mastic stiffening increases with the ageing time. The rate of mastic stiffening as evaluated by different ageing indices keeps changing as the time of the TFOT ageing proceeds. The fillers can increase or decrease the ageing of the mastics as the time in the TFOT proceeds.
- From the ageing time study, the higher oxidative ageing of the granite mastics is related to the stronger catalytic ability of the granite fillers. However, the lower ageing indices for the hydrated lime mastics is related to the greater adsorption ability of hydrated lime.
- It is recommended for the future studies to use other available fillers in order to have extended and detailed knowledge of ageing mechanism and effect of fillers on the ageing rate. In addition, the analysis based on advanced techniques such as atomic force microscopy, high-pressure gel permeation chromatography can also be applied to investigate the change in chemical composition of mastics after ageing. Also, the change in rheology after ageing can be studied through

bending beam rheometer. The data obtained from advanced techniques in combination with this study may assist in providing additional insight for future work.

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