Sādhanā (2019) 44:128
https://doi.org/10.1007/s12046-019-1107-z

Influence of refinery processing methods on ageing of bitumen

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MS received 22 May 2018; revised 27 January 2019; accepted 4 February 2019; published online 29 April 2019

Abstract. This investigation reports the influence of processing condition (air rectification and component blending) on ageing and stress relaxation behaviour in bitumen. FTIR spectra were recorded on two samples of bitumen at unaged, short-term aged and long-term aged conditions. Indices such as aliphaticity, aromaticity, carbonyl and sulphoxide calculated from the FTIR spectra were used in the analysis. It was seen that the ageing compounds in the air-rectified bitumen were higher at the end of the production process compared with the blended bitumen while the rate of oxidation compounds formed during short-term and long-term ageing was higher in the blended bitumen. In addition, a stress relaxation test was performed at 25°C in the unaged, short-term and long-term ageing conditions. Since the formation of ageing compounds leads to change in 'stiffness' and hence a change in the stress relaxation behaviour of the material, it is seen that the stress relaxation results are in line with the material behaviour as seen from the FTIR tests.

Keywords. Bitumen; Blended; air rectified; FTIR; ageing; carbonyl; sulphoxide; stress relaxation.

1. Introduction

In India, 90% of the highways and runways are constructed with bituminous mixtures. The binder used in the construction of bituminous layers plays a key role towards the performance of the pavement. The bituminous binders are manufactured from the fractional distillation of crude oil. India has 12 bitumen producing refineries [1] following two methods for bitumen production, and they are component blending and air rectification.

In the component blending process, the vacuum residue is mixed with propane in the deasphalting unit to separate deasphalted oil from asphaltene-rich pitch called propane-deasphalted pitch or PDA pitch [2]. The PDA pitch is then blended with heavy oil to meet the specification requirement for a targeted grade of bitumen. In an air rectification process, the vacuum residue is subjected to a continuous supply of air at controlled pressure and temperature to obtain the desired grade of bitumen [2]. This is a process similar to the air blowing except that the material is subjected to a mild degree of air blowing in terms of reduced oxygen rate, temperature and duration [3]. To exert complete control over the production process in terms of variables such as oxygen utilisation, temperature control and to process a wide variety of feed specific to the production of paving grade bitumen, the Biturox process is now used in India [4]. Since the basis here also is an air-rectified process, bitumen produced from the Biturox process will henceforth be considered as air-rectified bitumen in this study.

It is possible to obtain the same grade of bitumen from each of the two processes: component blending and air rectification. However, the nature of the two resulting binders is different. In one case (blended bitumen), a high-viscosity material is reduced to the targeted viscosity while in the other case (air-rectified bitumen), a low-viscosity material is converted to the same targeted viscosity. Hence, the air-rectified and blended bitumens undergo completely different thermal histories during processing [5, 6] and are expected to have different thermo-rheological behaviours during service due to the difference in the ageing kinetics.

The ageing referred to in this investigation corresponds to the ageing that occurs due to the oxidation of certain fractions present in bitumen with atmospheric oxygen. Ageing in bitumen is expected to occur in two stages: in the first stage, there is an initial oxidation spurt wherein the formation of oxidation compounds occurs at a significantly higher rate [7, 8]. This stage is also accompanied by the aromatisation process, wherein there is a conversion of the aliphatic fractions of bitumen into aromatic fractions. In the second stage, oxidation occurs comparatively at a much slower rate [7, 8].

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In an air rectification process, the material is subjected to a continuous supply of air under controlled conditions at temperatures of about 160–240°C for time periods varying between 5 and 10 h [9]. Under such conditions, bitumen is expected to undergo a certain degree of oxidation, resulting in the formation of carbonyl compounds, especially esters, which can link two different molecules and thereby lead to the formation of higher molecular weight compounds [9]. Depending on the blending time, and temperature, the magnitude of oxidation is expected to be different [10]. Corbett [11] has shown that a typical air blowing process exerts a negligible influence on the saturation fraction of bitumen. The bitumen with the highest naphthene aromatics fraction exerted the largest increase of asphaltenes and thereby higher increase in viscosity. However, Moschopedis and Speight [5] showed that the oxygen uptake during the conventional air blowing process depends on the oxygen present in the natural bitumen. In their study, an oxygen increase of about 1.16 times present in the natural bitumen has been reported on selected bitumen samples.

In a component blending process, the pitch is blended with one or more lighter fractions at different proportions at temperatures between 100 and 150°C. Here, it is to be noted that there is no influence of pressure or supply of air as compared with the air rectification process. Ishai and Yuval [6] showed that blended bitumen samples exhibit lower viscosities, higher ductility and higher temperature susceptibility compared with the straight-run bitumen. The same authors have also showed that bitumen produced from component blending process has a higher susceptibility to ageing compared with a straight-run bitumen [6]. Here also, the increase in asphaltenes and the decrease in polar aromatics have been observed as major steps in the ageing mechanism. The ageing kinetics of bitumen upon subsequent ageing, such as short-term ageing, can be different in the two bitumens considering the history of the material during its production process [12].

Also, in the paper by Ishai and Yuval [6], no reasons were mentioned for the higher temperature susceptibility observed for the blended bitumen. One can propose a hypothesis for the same by understanding the kinetics of oxidation. In an air blowing/air rectification process, conversion of naphthene aromatics and polar aromatics into asphaltenes takes place [13]. It is said that increased presence of asphaltenes can reduce the temperature susceptibility as asphaltenes exhibit the lowest temperature susceptibility among the four bitumen fractions [14]. It is thus expected that the asphaltene content is higher in air-blown bitumen and hence the air-blown/air-rectified bitumen is expected to possess a lower temperature susceptibility compared with the blended bitumen.

FTIR spectroscopy is the most preferred technique to study the ageing compounds formed in bitumen as it can distinguish specific compounds in bitumen based on their molecular vibrations [15–18]. These oxidation compounds have been identified to be primarily carboxylic acids, ketones, esters, anhydrides and sulphoxides [8]. Aromatisation process has also been observed during ageing. While there are different techniques available to quantify such compounds in bitumen, an FTIR spectrum exhibits distinct peaks in the carbonyl, sulphoxide, aliphatic and aromatic regions. Hence one can quantify the magnitude of oxidation compounds formed and the extent of aromatisation at different stages of ageing. It should be noted here that the terms *magnitude* and *extent* are used to denote different aspects of the oxidation process. The term *magnitude* is used in the case of oxidation compounds to denote the ‘quantity’ of carbonyl compounds. In the second case, the aromatisation ‘process’ is referred to and hence the term *extent* is used. This technique has been applied for bitumen and found to be successful in the identification of certain compounds responsible for ageing in bitumen [19, 20].

Studies have attempted to evaluate the influence of oxidation compounds on the rheological properties of bitumen. Most of the works have measured the viscosity or the dynamic modulus from oscillatory shear test to correlate the same to the carbonyl area [8, 9, 21, 22]. In all these studies, it was seen that the increase in ‘stiffness’ exhibited a linear relation to the increase in carbonyl area. The slope of the linear fit or in other words the rate of increase in ‘stiffness’ with carbonyl area depends on the type of binder [22]. This linear relationship was observed to be valid irrespective of the oxidation temperature [21]. However, such direct relationship could not be observed in the case of sulphoxide indices. The contribution of sulphoxide indices to the increase in viscosity depends on the oxidation temperature as the decomposition of sulphoxides is initiated after a certain degree of oxidation [21].

In all the tests discussed earlier, viscosity or the dynamic modulus is used as an indicator of ‘stiffness’. These parameters are commonly used considering the ease in which they can be measured. However, the validity of such parameters in representing the rheological response of the material is questionable [23]. Studies have shown that stress relaxation tests on binders were able to precisely capture the rutting response of the bituminous mixtures [24]. Since the test can be performed in the non-linear regime also, it can be considered as a potential test to capture the rheological response of the binders [24].

In this study, two types of binders, one from a refinery using a component blending process and another from a refinery using air rectification process, are analysed. To compare the ageing components in both the binders, the binders are tested in unaged (UA), short-term aged (SA) and long-term aged (LA) conditions. FTIR spectroscopy is performed on these binders and to quantify the ageing compounds, indices such as carbonyl index, sulphoxide index and aromaticity index are calculated. A stress relaxation test is performed for all the binders at the various ageing conditions at 25°C, in a sense corresponding to the room temperature at which FTIR is performed.

2. Experimental investigations

2.1 *Materials*

In this study, two bitumen samples were used: one sample from a refinery using the blending process (referred to as 'blended' henceforth) and another from the refinery using air rectification process (referred to as 'air rectified' henceforth). Both the binders were tested in the UA condition. Also, the SA and LA conditions were simulated in the laboratory using the Rolling Thin Film Oven (RTFO) and the Pressure Ageing Vessel (PAV) as per ASDM D2872-2012 [25] and ASTM D6521-2013 [26], respectively.

2.2 *FTIR spectroscopy*

The FTIR spectra were recorded using a JASCO FTIR spectrometer. A solution of the sample was prepared by dissolving bitumen in THF at a concentration of 5% w/v; 20 μl of the sample was spotted on a KBr disc, and the solvent was allowed to evaporate completely before recording the spectra. All the spectra were recorded at room temperature. The spectra were recorded at a resolution of 4 cm^{-1}, averaging 32 scans. Three trials were recorded for each spectrum, and the repeatability was ensured using a *t*-test.

Sample FTIR spectra of blended and air-rectified bitumen in the LA condition are shown in figure 1. Analysis of individual peaks is tedious in FTIR spectra considering the wide variety of peaks exhibited by bitumen. Also, there is variability in the spectra induced due to the sample thickness, and hence it is required to normalise the spectra before analysis. There are two methods by which one can normalise the spectra. One method is to normalise the spectra concerning the C–H peaks and then calculate the indices. In the other method, one can calculate different indices and in the process normalise the index under consideration concerning all the other indices. The second approach is used in this paper. For details related to the normalisation procedure, one can see the article by Hofko *et al* [27].

Different indices can be calculated from the FTIR spectra for analysis [28]. To quantify the effect of ageing captured from FTIR spectra, indices such as carbonyl index, sulphoxide index, aliphaticity index and aromaticity index were calculated as shown in table 1.

Table 1. Indices calculated for bitumen from FTIR spectra.

Index	Region for integration
Aliphaticity	$A_{2700-3110}/(A_{2700-3110} + A_{1548-1633})$
Aromaticity	$A_{1548-1633}/(A_{2700-3110} + A_{1548-1633})$
Carbonyl	$A_{1675-1755}/\sum A$
Sulphoxide	$A_{1010-1043}/\sum A$

$\sum A = A_{2700-3110} + A_{1548-1633} + A_{1675-1755} + A_{1010-1043}$.

2.3 *Stress relaxation*

In a stress relaxation test, a constant strain of 5% was applied and the shear stress of the material was monitored at a constant temperature of 25°C. This test was performed in two steps. In the first step, the strain of 5% was achieved in a controlled manner in a specified time of 0.1 s. This strain is maintained constant in the second step. A schematic of the stress relaxation test is shown in figure 2. The time required to reach the specified strain value was arrived depending on trials carried out on the sample. On provision of longer times in Region I, the stress began to relax even during the application of load. The fastest rate at which the specified strain can be achieved without allowing the stresses to relax was chosen based on trial and error basis [29].

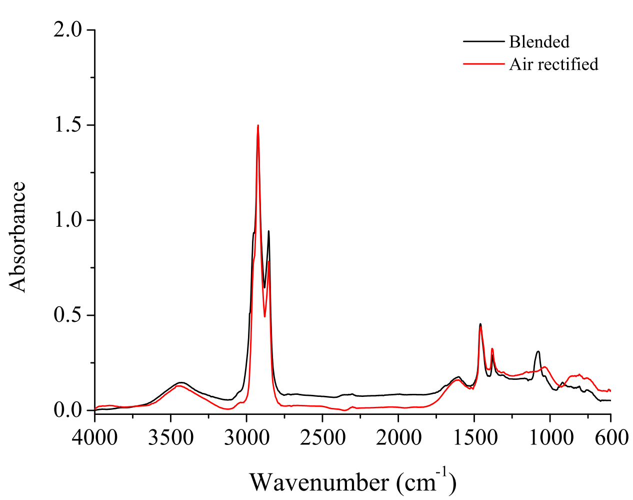

Figure 1. Sample FTIR spectra in the long-term aged condition.

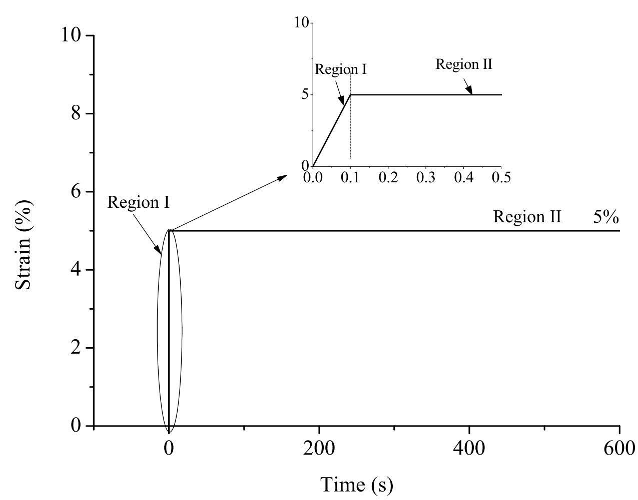

Figure 2. Schematic of stress relaxation test.

The time of measurement of shear stress was fixed based on the rate of the relaxation of shear stress. The material was considered to achieve a steady state when the rate of reduction in shear stress reduced below 0.1 Pa per second. The time at which the steady state was achieved was taken as the time for monitoring the relaxation of stresses. Considering the three ageing conditions, a time of 600 s was uniformly chosen for monitoring the stress relaxation.

3. Analysis and discussion

3.1 *Evolution of carbonyl regime during ageing*

The increase in carbonyl peak at 1700 cm^{-1} upon ageing can be seen in figure 3 for the blended bitumen. In the carbonyl region from 1700 to 1800 cm^{-1}, one can observe peaks at different positions depending on the predominant carbonyl compounds present in the material, and that formed during subsequent ageing. For the spectra shown in figure 3, one can see that peaks are observed at 1700, 1715, 1733 and 1749 cm^{-1}, which are seen clearly in the spectra measured in the LA condition (figure 4). The peak at 1700 cm^{-1} corresponds to the carboxylic acid, the peak at 1715 cm^{-1} to the ketone, the peak at 1733 cm^{-1} and the peak at 1749 cm^{-1} to dicarboxylic anhydrides [8]. However, for the air-rectified bitumen, it can be seen that there is only one broad peak seen at 1700 cm^{-1}. This peak has to be deconvoluted to understand the nature of carbonyl compounds present in the material.

Deconvolution of peaks was performed using the peak analyser software available in Origin Pro 8.5 [30] (figure 5). The peaks were identified, and the peak positions were assigned based on the second derivative of the spectra. It can be seen that only the carboxylic compound is predominant in the spectra of air-rectified bitumen. Generally,

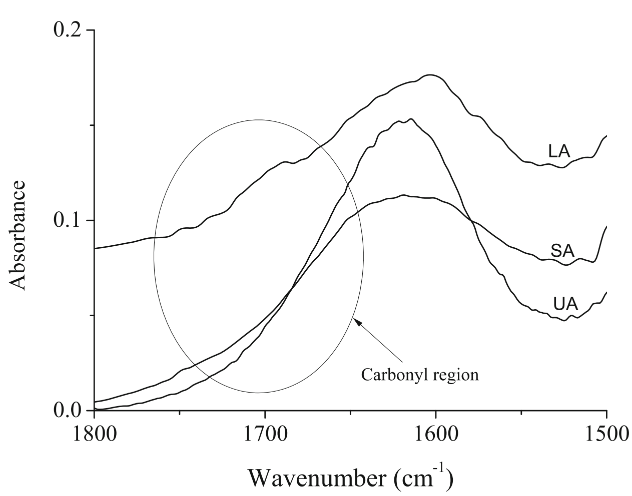

Figure 3. Carbonyl regime for the binder from Mumbai refinery in different ageing conditions.

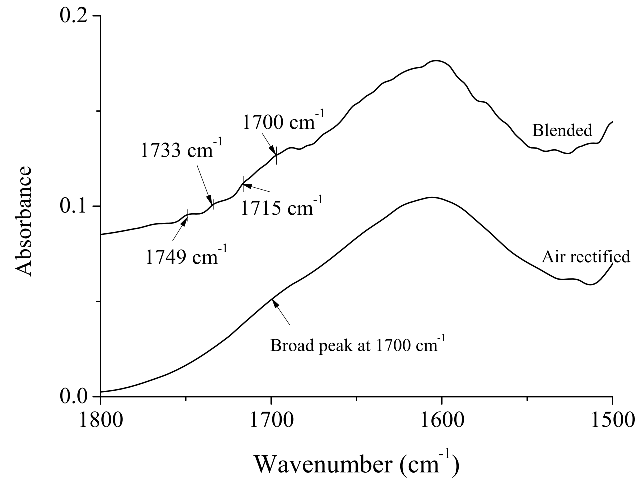

Figure 4. Carbonyl regime in LA condition for samples from different refineries.

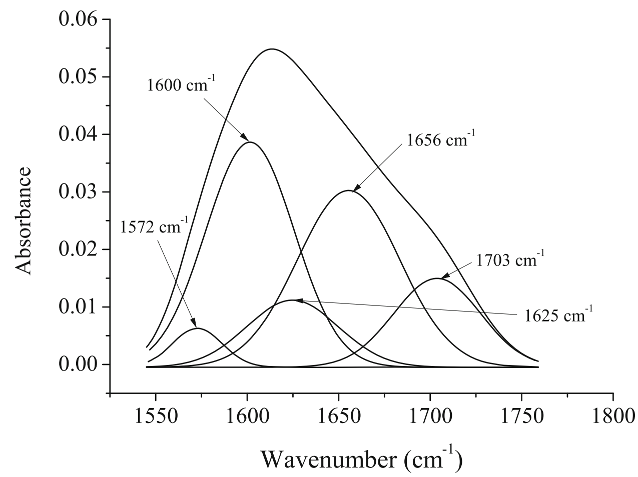

Figure 5. Deconvoluted carbonyl regime in the LA condition for air-rectified bitumen.

during the air rectification process, esters are formed as oxidation products. However, such a peak could not be observed in air-rectified bitumen. This can be due to two reasons: either the peak is of a lesser magnitude such that the carboxylic acid peak overlaps it or the formation of ester in air rectification process depends on the carbonyl compounds present in the crude source itself. At this point, without the data corresponding to the spectra of the crude source, one cannot comment about the nature of carbonyl compound.

Figure 6 shows the carbonyl index at different ageing conditions for both the binders. In the UA condition, the blended bitumen has the least carbonyl index of 0.0016 followed by the air-rectified bitumen with a carbonyl index of 0.0025. As discussed earlier, there is a certain amount of oxidation during the air rectification process, and at the end of the production process, a higher magnitude of oxidation products is expected in air-rectified bitumen. This is true in

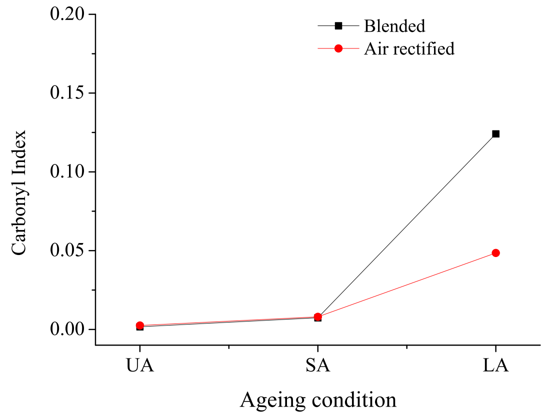

Figure 6. Carbonyl indices in different ageing conditions.

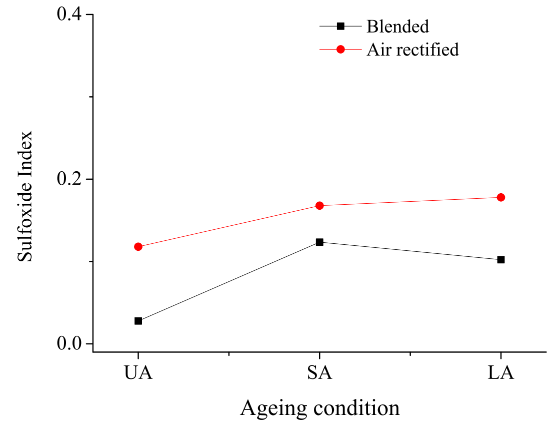

Figure 8. Sulphoxide indices in different ageing conditions.

the case of blended and air-rectified bitumen with the air-rectified bitumen exhibiting 1.5 times higher carbonyl area compared with the blended bitumen. The magnitude of carbonyl area in the air-rectified bitumen thus depends on the carbonyl compounds present in the crude source and its influence on the subsequent ageing during the production process.

3.2 *Evolution of sulphoxide regime during ageing*

Figure 7 shows the sulphoxide peak at 1032 cm^{-1} for the blended bitumen. Figure 8 shows the sulphoxide index at different ageing conditions for all the binders. The sulphoxide index is 0.118 and 0.028, respectively, for the air-rectified and blended bitumen in the UA condition. A higher magnitude of sulphoxide compounds is thus seen for the air-rectified bitumen with the same exhibiting four times higher sulphoxide index compared with the blended bitumen. One can also see a reduction in the rate of formation of sulphoxide compounds in the LA condition. This is attributed to the decomposition of sulphoxides in prolonged ageing conditions [7, 20]. In such ageing conditions, the formation and decomposition of sulphoxides occur simultaneously and depending on the predominant mechanism, one can see an increase or decrease in the sulphoxide index [7].

3.3 *Evolution of aliphaticity and aromaticity during ageing*

The aromatisation process, another component of the ageing mechanism, exhibits different behaviours in the bitumen samples. The aromaticity index is shown in figure 9. The aromaticity index is (1–aliphaticity index), and hence the discussion pertains to the aromaticity index. The absolute magnitude of aromaticity index is observed to be higher for air-rectified bitumen. The air-rectified bitumen samples are expected to exhibit a higher aromaticity index due to the increased polarity as a result of the ageing

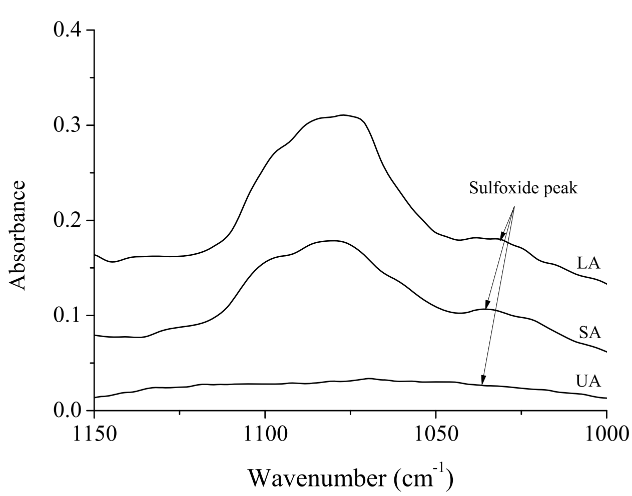

Figure 7. Sulphoxide regime for different binders in unaged condition.

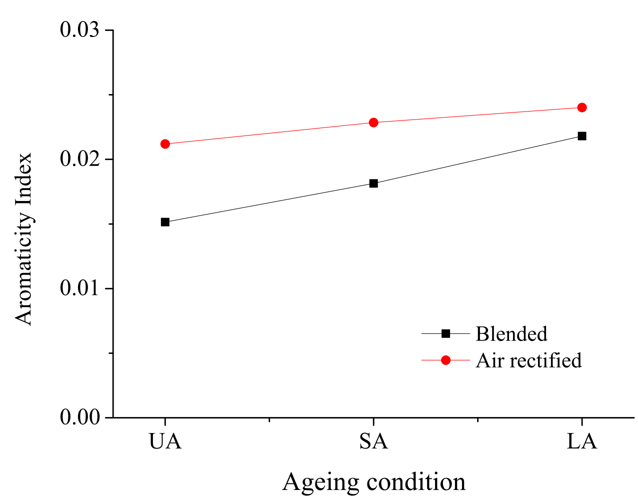

Figure 9. Aromaticity indices in different ageing conditions.

process. The formation of polar molecules and the aromatisation process lead to an increase in the asphaltenes as a result of the oxidation process [5, 6].

3.4 *Calculation of ageing indices*

To understand the influence of production process on the subsequent ageing in bitumen, the indices in SA condition were normalised with the indices observed in UA condition, and the indices in the LA condition were normalised with that in the SA condition as shown in table 2. For the blended bitumen, 443% increase in carbonyl area was observed upon SA and 1675% upon LA. On similar lines, one can see that the magnitude of increase in sulphoxide index upon SA is 444%, and 83% upon LA for the blended bitumen (see table 2). For the air-rectified bitumen, the increase in carbonyl area ranges between 317% and 607% and that for the sulphoxide index varies between 142% and 106%. The reduced sulphoxide index upon LA in the blended bitumen can be attributed to the decomposition of sulphoxides, and this is observed to be higher in the case of blended bitumen.

3.5 *Stress relaxation*

Figure 10 shows the relaxation of torque for both the binders in LA condition. The behaviour of the material represented by stress relaxation and torque relaxation can be considered to be analogous as shear stress and torque can be scaled by the rheometer constant. A close observation of this plot reveals three distinct zones. Zone 1 shows a decrease in shear stress at a decreasing rate, zone 2 indicates the relaxation of stresses at a constant rate and zone 3 shows the decrease in shear stress at an increasing rate. Such zones were used by Dick and Pawlowski [31] to analyse the behaviour of different rubber samples. In addition, parameters such as peak torque, slope (slope of the zone 2), regression line intercept (y-intercept of the log–log regression line corresponding to predicted shear stress at 1 s), integrated area (area under the stress–relaxation curve between predefined boundaries), time for a given % drop in shear stress and % drop of shear stress in a given

Table 2. Normalised ageing indices.

Index	Blended		Air rectified	
	SA/UA	LA/SA	SA/UA	LA/SA
Aliphaticity	99.45	99.33	99.63	99.53
Aromaticity	119.47	119.86	107.64	104.73
Carbonyl	443.1	1675.05	317.35	606.94
Sulphoxide	443.9	82.77	142.17	105.97

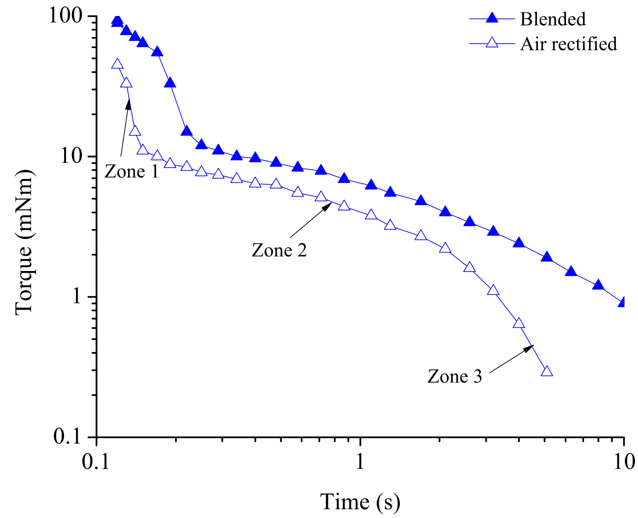

Figure 10. Torque relaxation in LA condition.

time were defined and used to compare the processing quality of different rubber samples.

From figure 10, one can observe all the three zones for the air-rectified binder as indicated. For the blended binder, one can see only zone 1, zone 2 and the initiation of zone 3. The presence of zone 3 indicates that the shear stress decreases at an increasing rate and is expected to reach zero shear stress much earlier compared with a material that is in zone 2 at the same instance of time. In this regard, the torque is expected to relax much faster for the air-rectified material compared with the blended material in the LA condition. The torque at any instance of time is also higher for the blended binder compared with the air-rectified binder. However, one cannot say the same thing about the binders in the UA condition. Figure 11 shows the relaxation of torque for the two binders in UA condition. From this figure, it is seen that the torque for the air-rectified material is *marginally* higher compared with the blended material for the first 5 s of testing. After 5 s of relaxation, the torque of the two materials are comparable, with a maximum variation of 10%. From figure 11, it is also seen that one cannot clearly distinguish the three zones as in the case of LA condition.

The 'stiffness' or in a sense the torque required for a given strain level, is seen to depend on the ageing condition. In the UA condition, the air-rectified material exhibits a higher stiffness while the blended material exhibits a higher stiffness in the LA condition. The response of the two binders indicated in figure 6 can be compared here, wherein the blended material exhibits lower oxidation compounds in the UA condition. If one can relate an increased carbonyl area with increased stiffness, it is seen that the stress relaxation test results are in line with the observations from the FTIR results. However the rate of ageing is seen to be higher in the blended material, resulting in higher ageing compounds in the LA condition. The effect

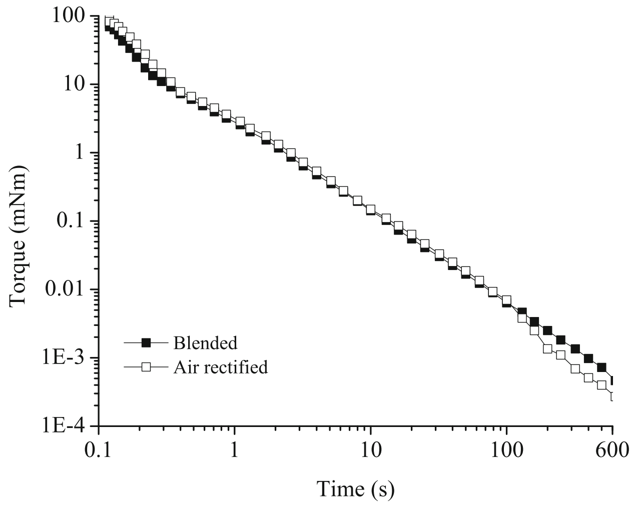

Figure 11. Torque relaxation in UA condition.

Table 3. Parameters from stress relaxation test.

Binder	UA	SA	LA
Peak torque (mNm)			
Blended	76	120	94
Air rectified	89	85	47
T_{10s}			
Blended	0.16	0.35	0.96
Air rectified	0.16	0.35	0.43

of higher oxidation compounds is reflected in terms of the increased stiffness for the blended material in the LA condition.

To further validate the difference in behaviour of the materials at different temperatures, the peak torque and the % of peak torque at 10 s (T_{10s}) are calculated as shown in table 3. It is seen that the peak torque is higher for air-rectified material when compared with the blended material in the UA condition. This can be attributed to the 'stiffer' behaviour of the air-rectified material due to the increased carbonyl compounds observed as a result of the production process. However, in SA and LA conditions, it is seen that the blended material exhibits higher torque compared with the air-rectified material. This is again in line with the results from FTIR spectroscopy and the stress relaxation results, which show that the rate of ageing is higher for a blended material.

The T_{10s} calculated for different ageing conditions is shown in table 3. It is seen that T_{10s} increases with ageing condition. Also, it is to be noted that T_{10s} is identical for both the materials in the UA and SA conditions. In the LA condition, it is seen that T_{10s} is higher for the blended material compared with the air-rectified material. It can thus be said that the 'stiffness' of the binders depends on the production process and this is subject to variation depending on the ageing condition. However, the production process influences the relaxation of torque only in the LA condition.

4. Summary

The following are the salient observations from the analysis performed in this study.

- At the end of the production process, the magnitudes of carbonyl and sulphoxide compounds are observed to be higher in case of air-rectified bitumen compared with the blended bitumen due to the oxidation compounds formed upon air rectification.
- Upon subsequent ageing in the laboratory, it is seen that the normalised carbonyl and sulphoxide indices are higher for the blended bitumen compared with the air-rectified bitumen. A reduction in normalised sulphoxide index is observed in the blended bitumen upon LA due to the decomposition of sulphoxides.
- The aromaticity index is seen to be higher for the air-rectified bitumen compared with blended bitumen. The difference in aromaticity index between the two samples is not as pronounced as the carbonyl or sulphoxide indices.
- In the UA condition, the air-rectified material exhibits higher peak torque while in the SA and LA conditions, the peak torque is higher in blended material. Hence if one considers the increased carbonyl area to contribute to increase in stiffness of the material, the results from the stress relaxation test can be considered to support the results obtained from FTIR spectroscopy.

Acknowledgement

The authors would like to thank the management of Mar Baselios College of Engineering and Technology, Thiruvananthapuram, India, for providing the financial support of this project.

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