

Oxidative Aging Characterization of Pyro-Oil Modified Binders Using Fourier Transform Infrared Spectroscopy

Nikita Taran Bhagat^{1*}, Hemantkumar Prakash Hadole¹, Mahadeo Sambhaji Ranadive¹

¹ Civil Engineering Department, College of Engineering, Pune, Maharashtra, 411005, India

* Corresponding author's e-mail: bhagat.nikita14@gmail.com

ABSTRACT

In order to obtain asphalt binder with enhanced quality to resist distresses like rutting, fatigue, and low-temperature cracking, there is a need to focus on asphalt binder modification. The accumulation of plastic waste is a direct result of the daily rise in plastic demand. One of the effective and trending ways of reducing the impact of plastic waste on the environment is to pyrolyze it and use the oil obtained from it as fuel for power generation, heating, extraction of chemicals, or as an asphalt binder modifier. This paper deals with the modification of VG30 binder with pyro-oil obtained from High Density Polyethylene (HDPE) plastic waste, and analysing the effect of modification on the short term aging of the binders. Pyro-oil is yielded from the pyrolysis process of HDPE at about 750 °C. The modified binders were prepared by adding 1%, 2%, and 3% pyro-oil by total weight of VG30. The binders were short-term aged and the changes in their chemical functionalities before and after aging were evaluated using fourier transform infrared (FTIR) spectroscopy. Results of the FTIR test were used to calculate functional group indices for evaluating the aging characteristics of the modified binders. It was observed that the pyro-oil interacts chemically with VG30 and binder chemistry is influenced by aging. It was also observed that, modification with pyro-oil increases the resistance to aging of the binders.

Keywords: pyro-oil, aging, asphalt binder, FTIR, carbonyl, sulfoxide.

INTRODUCTION

Asphalt binder is the most commonly used material in pavements. It is a hydrocarbon product yielded by removing light fractions (such as liquid petroleum gas, gasoline, petrol, and diesel) from crude oil during the process of refining [1, 2]. However, the crude oil reserves are depleting rapidly, which has become a matter of concern for flexible pavement industry. Also, rapid development of highway transportation network, increased traffic load, higher traffic volume, and insufficient maintenance have led to many severe distresses in flexible pavements such as rutting, fatigue, and low temperature cracking [3]. The asphalt binder is largely prone to oxidative ageing which makes the material stiffer. Aging of asphalt binder is one of the major reasons for development of pavement distresses [2]. The diminishing crude oil reserves, growth of flexible pavement networks all over the

world, and increased traffic volume have created a need of asphalt binder modification with different modifiers [3, 4]. For this purpose, the partial or complete replacement of asphalt binders with a alternate binding materials is an emerging area of research [5]. Various modifiers for the partial replacement or modification of asphalt binder such as lime, waste plastic, rubbers, polymers, nano materials, bio-oil from woodstock, organic waste, swine manure etc., are used [4, 6–8].

Plastics are utilized in many facets of daily life, however, due to their widespread use, they have significantly harmed the environment and depleted resources when they are disposed of in the surroundings [9]. About 8.8 million tonnes of plastic are dumped in the ocean annually, disrupting the marine ecology, and by 2025, it is estimated that trash will dominate fish in the water. Since the majority of plastic garbage is nonbiodegradable and can take up to 500 years to degrade, around

22% to 43% of it ends up in landfills and prevents soil fertility. Every day, 15,000 tonnes of plastic waste are created in India, but only 6000 tonnes are collected [10]. The creation of fuel or the recycling of valuable compounds from pyrolysis have both received a lot of attention as potential solutions to these issues. Bio-oils produced from biomass or plastic waste materials are considered as potential alternatives to partially or completely replace crude oil-based asphalt binders used in flexible pavements [11, 12]. Hadole et al. (2021) [13], had used the pyro-oil obtained from HDPE for the modification of asphalt binders and studied the moisture susceptibility of the resulting binders. Kulkarni & Ranadive (2020) [14], studied the effect of LDPE pyrolysis oil modification on the cutback bitumen and its behavioural properties. In this study, the oil obtained from the pyrolysis of HDPE plastic waste, referred as Pyro-oil hereafter, is used for modification of the asphalt binder.

Fourier Transform Infrared (FTIR) spectroscopy test is the most widely used method for measuring the oxidation products in a material. It is also used for determining the oxidation products, and tracking changes in asphalt binder's chemical composition during its production and aging [15, 16]. Krasodonski et al. [17], used FTIR to study the oxidation stability of oils and lubricating greases. The functional group changes that occur during the modification of asphalt binder as well as after the aging of the binder are commonly analysed from the variations in FTIR spectra of original and modified binders pre and post aging.

The FTIR test is used for qualitative and quantitative characterization of the chemical nature of binders [15]. Generally, area of band or peak height in a spectrum are used to calculate the concentration of a functional group bond. Band area instead of peak height is used especially to quantitatively analyse the oxidative aging of bituminous binders. This is done for two reasons; (1) there is less variation in the results of band area [18], and (2) single peak height may be insufficient to contain several vibrations that may occur in a band [19] a road ageing, along with two ageing conventional tests: the Rolling Thin Film Oven Test (RT-FOT). Carbonyl (C=O) and sulfoxide (S=O) indices are mostly used to quantify the oxidative aging of binder [15]. Hadole & Ranadive (2023, 2022) [20, 21], analysed the effect of oxidative aging on the pyro-oil modified binders using C=O and S=O indices. Yang et al. (2015) [18], had considered some more bonds to analyse the effect of aging on

the variation in these bonds. This study also considers the indices for more bonds to analyse the effect of oxidative aging on these bonds.

The objective of this paper is to determine the effect of pyro-oil modification on the oxidative aging resistance of the binders using FTIR spectroscopy. The analysis of the results is divided into three parts; (1) the aging of binders happening during the modification, (2) the oxidative short-term aging of binders, and (3) the effect of aging on different functional groups of binder.

EXPERIMENTAL PROGRAM

Materials

The following materials were considered under this study.

Base binder

Viscosity graded binder (VG30) was selected as base binder. The base binder was collected from Indian Oil Corporation Limited, Mumbai, Maharashtra (India).

HDPE pyro-oil

Municipal Solid Waste samples were collected from Karad and Pune cities in Maharashtra, India. The HDPE plastic waste was segregated from the MSW samples. Catalytic pyrolysis of HDPE waste was done at about 750 °C using the pilot pyrolysis plant set up in Transportation Engineering Laboratory of College of Engineering, Pune, Maharashtra. The process of pyrolysis and the yield is explained in details by Kulkarni & Ranadive, (2021) [22].

Laboratory work

The methodology followed and laboratory experimental work undertaken in this research is explained as follows.

Modification of VG30

The important parameters to be considered for modification of asphalt binders are shearing time, rate of shearing, and blending temperature [23]. Blending of base asphalt VG30 with HDPE pyro-oil was done for modification at temperature of about 140-150 °C, at about 4000 rpm for 20 minutes using high shear mixer. 1%, 2%, and 3% pyro-oil

Table 1. Physical characteristics of base and modified binders

Test	Reference	VG30	POMB1	POMB2	POMB3
Penetration at 25 °C (1/10 mm)	IS 1203/ ASTM D5	55	61	81	87
Softening Point (°C)	IS 1205/ ASTM D36	46	44	41	39
Ductility (cm)	IS 1208/ ASTM D113	78	87	88	90
Viscosity at 60 °C (poise)	IS 1206(2)	2856	2920	2914	2874
Kinematic viscosity at 135 °C (cSt)	IS 1206(3)	345	410	355	348
Viscosity at 150 °C (poise)	IS 1206(1)	-	2	1.6	1.2
After Rolling Thin Film Oven Test					
Loss in mass (%)	IS 9382	<1	0.69	0.64	0.82
Softening Point (°C)	IS 1205/ ASTM D36	79	63	58	58

by weight of VG30 was used to modify the same and named as POMB1, POMB2, and POMB3 respectively. The physical properties of the base and modified binders are presented in Table 1.

Short term aging of binders

The aging of binder that happens during the mixing, laying and compaction of a flexible pavement is known as short term aging, which is associated with stiffness and viscosity increment of bituminous binder. The base and modified binders were aged by Rolling Thin Film Oven Test (ASTM D2872) [24] at 163 °C for 85min to get short term aged binders.

Fourier transform infrared spectroscopy

FTIR test was performed on the base and modified binders for both unaged and aged conditions, at the Central Instrumentation Facility, Department of Chemistry, Savitribai Phule Pune University, Maharashtra, India. The effect of oxidative short-term aging on the base and modified binders was analysed by using various bond indices. The bond indices were calculated using the following equations;

Carbonyl index:

$$I_{C=O} = \frac{A_{1640-1740}}{\sum A} \quad (1)$$

Sulfoxide index:

$$I_{S=O} = \frac{A_{1030}}{\sum A} \quad (2)$$

Aromaticity:

$$I_{Ar} = \frac{A_{1600}}{\sum A} \quad (3)$$

C-O Bond index:

$$I_{C-O} = \frac{A_{1120+1205}}{\sum A} \quad (4)$$

Aliphatics of CH₂:

$$I_{Al_{CH_2}} = \frac{A_{1456+2920+2850}}{\sum A} \quad (5)$$

Aliphatics of CH₃:

$$I_{Al_{CH_3}} = \frac{A_{1375+2960}}{\sum A} \quad (6)$$

Aromatics of C-H:

$$I_{Ar_{C-H}} = \frac{A_{700-900}}{\sum A} \quad (7)$$

where: A₁₆₄₀₋₁₇₄₀ – area of band from 1640 to 1740 cm⁻¹;

A₁₀₃₀ – area of band around 1030 cm⁻¹;

A₁₆₀₀ – area of band around 1600 cm⁻¹;

A₁₁₂₀₊₁₂₀₅ – area of bands around 1120 and 1205 cm⁻¹;

A₁₄₅₆₊₂₉₂₀₊₂₈₅₀ – area of bands around 1456, 2920 and 2850 cm⁻¹;

A₁₃₇₅₊₂₉₆₀ – area of bands around 1375 and 2960 cm⁻¹;

A₇₀₀₋₉₀₀ – area of bands between 700 to 900 cm⁻¹;

∑A – total area of bands.

RESULTS AND DISCUSSION

Changes in the spectra of modified binders

The peaks corresponding to functional groups in the FTIR spectra of Pyro-oil and base binder

respectively are shown in Fig. 1a and Fig. 1b. It is observed that pyro-oil and binder show difference in spectra, which may be primarily because of the difference in chemical compounds of the materials. The peaks were normalized to make the process of comparison easier. From the figures it is seen that the major peaks for the base binder VG30 were located at 2952 cm^{-1} (CH_3 stretch), 2920 and 2850 cm^{-1} (CH_2 stretch), 1373 cm^{-1} (CH_3 bend), 1456 cm^{-1} (CH_2 bend), 1020 cm^{-1} ($\text{S}=\text{O}$), 1585 cm^{-1} ($\text{C}=\text{C}$ stretch), 700 to 900 cm^{-1} ($\text{C}-\text{H}$ bend), 1640 to 1750 cm^{-1} ($\text{C}=\text{O}$ stretch). The pyro-oil spectra show additional peaks at $3472, 3070\text{ cm}^{-1}$ ($\text{O}-\text{H}$ stretch), 1265 and 1153 cm^{-1} ($\text{C}-\text{O}$ stretch). The peaks at 3472 and 3070 cm^{-1} represent the

alcohol functionalities and the peaks at 1153 and 1265 cm^{-1} are indicative of ethers, esters and acids present in the pyro-oil.

The spectra of VG30 and pyro-oil modified binder (POMB) is superimposed and represented in Fig. 2 for comparison. Since pyro-oil modified binders showed similar variation in spectra, only 1% pyro-oil modified binder (POMB1) is considered for comparison in the figure. From the figure, it can be seen that, no new peaks were observed after the addition of pyro-oil in the base binder, indicating that there is no formation of any new functionalities in the modified binder.

However, there are several shifts in the peaks are observed in the spectra of POMB1 as

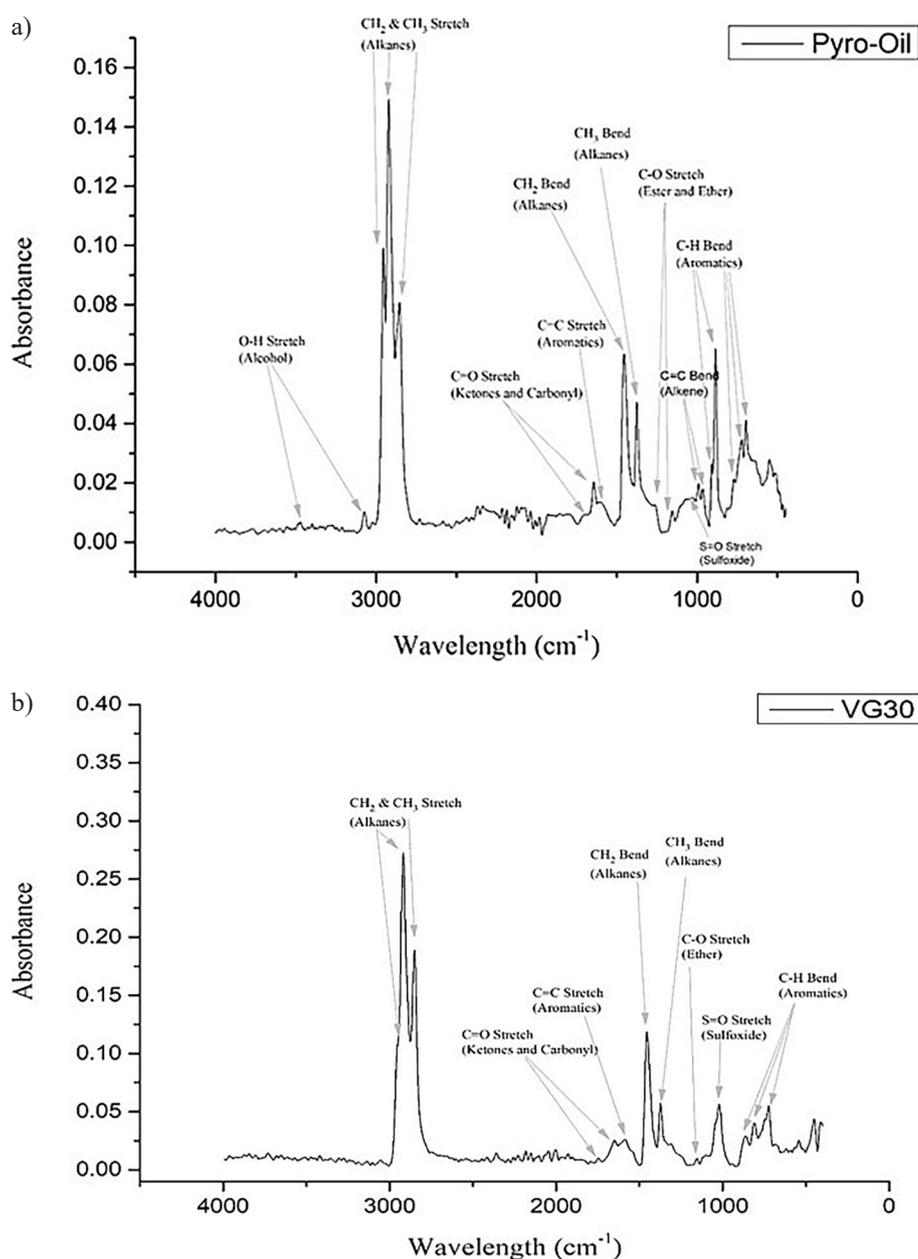


Fig. 1. The spectra and functional groups in (a) Pyro-oil and (b) Base binder VG30

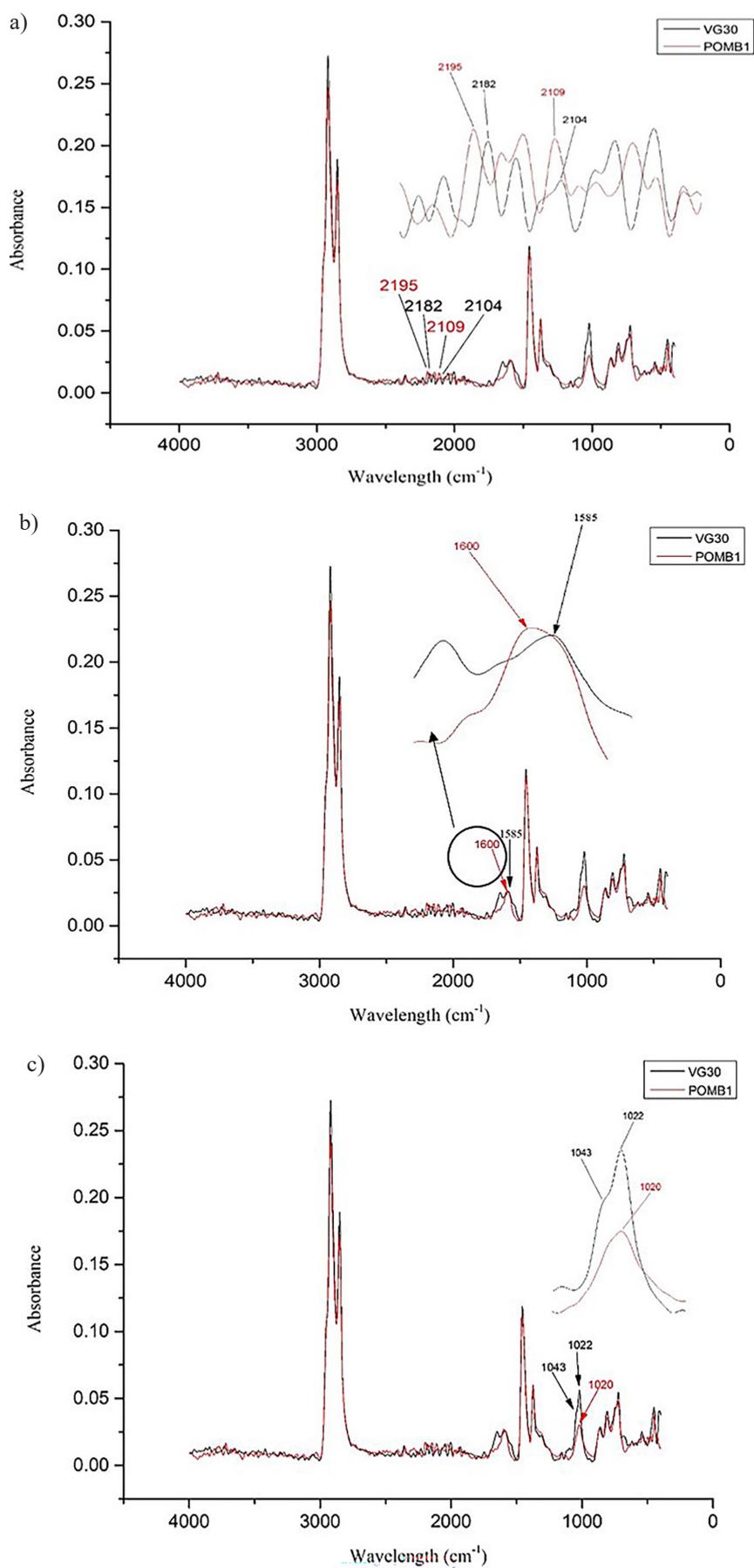


Fig. 2. Spectra of base binder VG30 and pyro-oil modified binder (a) shift in peaks (b) shift in aromatic peak (c) shift in sulfoxide peak

compared to VG30. For example, the peaks at 2182 and 2104 cm^{-1} are found to be shifted left to 2195 and 2109 cm^{-1} respectively after modification with pyro-oil, as can be seen in Fig. 2a. This is an indicative of chemical reaction between the molecules of HDPE pyro-oil and molecules of base binder VG30.

Figure 2b shows the variation of peak from 1585 cm^{-1} to 1600 cm^{-1} in the POMB spectra which corresponds to the aromatic functional groups having C=C bonds stretching. Along with the shift in peak, an increase in absorbance value is observed indicating the increase in aromatic compounds in the modified asphalt. A corresponding decrease in the absorbance of aliphatic compounds is observed at wave numbers 2952 cm^{-1} (CH_3 stretch), 2920 and 2850 cm^{-1} (CH_2 stretch) and 1456 cm^{-1} (CH_2 bend). This shows that the aliphatic compounds are converted into aromatics after the modification with pyro-oil. Similarly, the peaks corresponding to the sulfoxide (S=O) functional group, is found to be shifted from 1022 cm^{-1} to 1020 cm^{-1}

after modification as shown in the Fig. 2c, while the peak at 1043 cm^{-1} found to be vanished in the POMB1 spectra. This means that a chemical interaction has happened between the molecules of base binder and pyro-oil. Also, the absorbance value of sulfoxide functional group is reduced from 0.56 to 0.30 in the POMB1 spectra, which is an indicative of the reduction of sulfoxide group to sulphide group in the modified binder by reducible functional group esters present in the pyro-oil.

Figure 3 shows the bond indices of various bonds found in the base and modified binders, which helps in understanding the oxidation during modification, during aging and other chemical changes in the binders. It is found that the C=C bond index has a very slight decrease after modification of VG30 with pyro-oil. This may be because of the higher percentage of aliphatic molecules present in the base binder than that in the pyro-oil, which helps in the reduction of the reactive (polar) double bonded aromatic molecules present in pyro-oil, resulting in the decrease

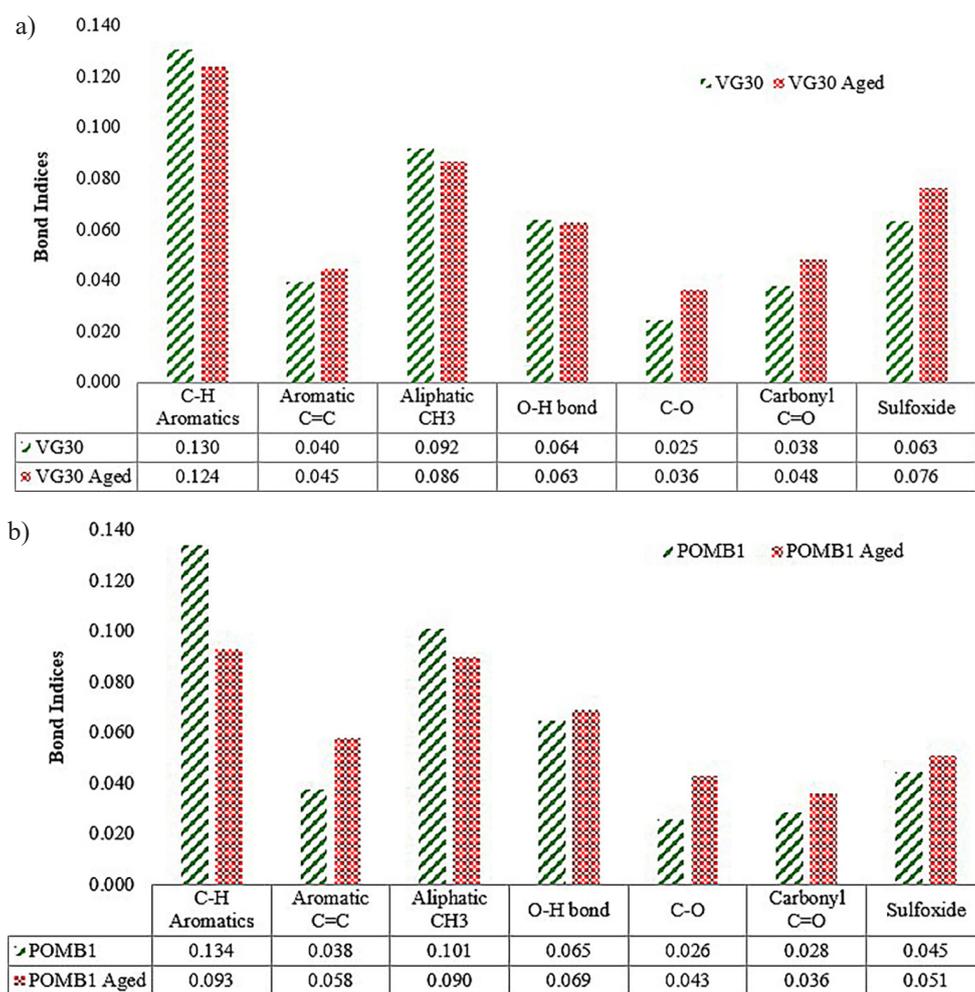


Fig. 3. Bond indices of (a) VG30, (b) POMB1

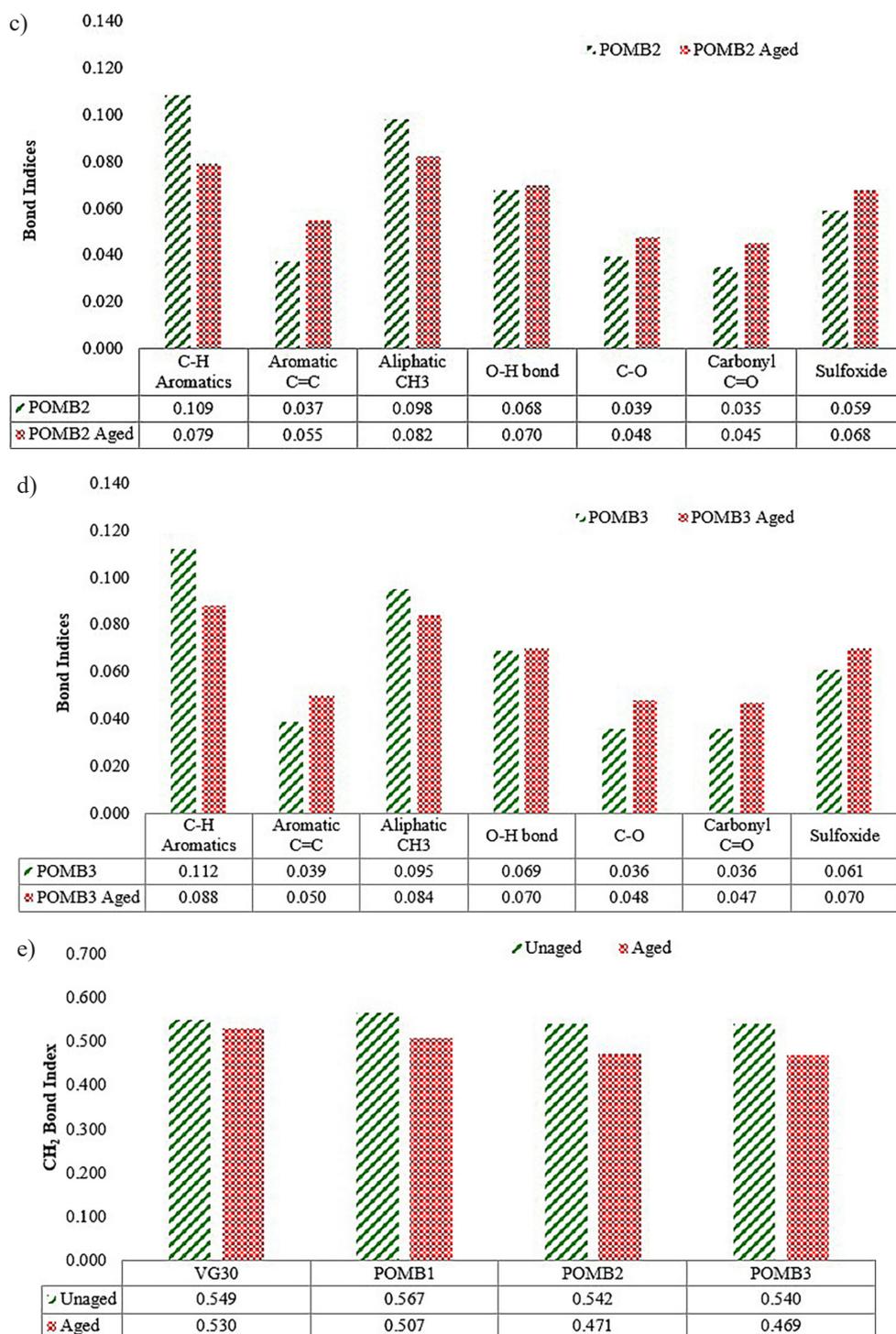


Fig. 3. Cont. Bond indices of (c) POMB2, (d) POMB3, and (e) CH₂ bond for all binders

of C=C bond in aromatics and increase in C-H bonds in aromatics of POMB1 and POMB2. The corresponding increase in the aliphatic indices of CH₃ and CH₂ bands is also observed from the Fig. 3b, Fig. 3c, Fig. 3d and Fig. 3e respectively in POMB1, POMB2 and POMB3.

The oxidation effect during the modification process is observed in the form of increase in the numbers of alcohols, ethers and esters in the

pyro-oil modified binders. This can be seen from the increased O-H, C-O bond indices in POMB1, POMB2 and POMB3 as compared to that found in base binder VG30.

Aging at modification stage

The carbonyl and sulfoxide (C=O and S=O) indices are considered as the major factors

governing the aging of bituminous binders as carbon and sulphur are more prone to oxidation. From the Figure 3 it can be observed that the pyro-oil modified binders did not age during modification process as there is no increase in carbonyl and in fact a significant decrease in carbonyl content is observed from 0.038 to 0.028, 0.035 and 0.036 for VG30, POMB1, POMB2 and POMB3 respectively. Similarly, the sulfoxide index is also found to be decreased from 0.063 to 0.045, 0.059 and 0.061 for VG30, POMB1, POMB2 and POMB3 respectively. The possible reason for this reduced carbonyl and sulfoxide indices is the smaller number of ketones, carboxylic acid and sulphur atoms or sulphides present in the pyro-oil.

Short term aging

The effect of short term aging on the base and modified binders is evaluated from the various FTIR indices shown in the Figure 3. The general trend of increase in O-H, C-O, C=O and S=O is observed for the base and pyro-oil modified binders. The figures show that carbonyl and sulfoxide indices increase with short term aged VG30, POMB1, POMB2 and POMB3 binders than that of the unaged binders. However, the increase in carbonyl and sulfoxide indices after aging in POMB1, POMB2 and POMB3 is less than that of VG30. The increased C=O and S=O indices respectively after aging are 12.5% and 15.79% less in POMB1, 6.25% and 10.52% less in POMB2, while 2.08% and 7.9% less in POMB3 than those of VG30. This indicates that pyro-oil modified binders resist aging better up to 2% pyro-oil content by weight of binder. However, the carbonyl and sulfoxide index values increase with the increasing percentage of pyro-oil with aging, indicating decreasing resistance to aging with increasing pyro-oil content. This is because of the increase in carbon and sulphur content, with the increase in percentage of pyro-oil, that are prone to oxidation.

From the traditional method of analysing aging in the form of quantification of carbonyl and sulfoxide, the binders can be arranged in decreasing order of aging resistance as POMB1 > POMB2 > POMB3 ≥ VG30.

Effect of aging on other functionalities

In this study, the effect of aging is analysed in terms of changes in different bond indices also such as C=C, C-O, O-H, C-H and aliphatic

functional groups like CH₃ and CH₂. The C=C index, can also be called aromaticity, represents the aromatic compounds present in the binders. From Figure 3 it can be observed that there is a significant increase in the aromaticity for the base and pyro-oil modified binders after short term aging. The increase in aromaticity is due to the conversion of aliphatic hydrocarbons into aromatic hydrocarbons due to the dehydrogenation during aging. Therefore, an increase in aromaticity is interrelated with the corresponding decrease in the aliphatics containing CH₃ and CH₂ groups. This can be observed from the figures as well. The increased number of aromatic compounds form clusters by joining together to form dense intertwined network of compounds resulting in an increased viscosity [15] three modified binders (elastomer, plastomer, and crumb rubber. This fact can also be observed from Table 1, where the viscosities of pyro-oil modified binders are found to be increased as compared to that of VG30. The increase in C=C bond index is found to be 12.5%, 52.63%, 48.65% and 28.21% in VG30, POMB1, POMB2 and POMB3 respectively after aging. The corresponding decrease in aliphaticity (CH₃ and CH₂ indices) is found to be 9.98%, 21.47%, 29.42% and 24.73% respectively.

The C-H bond in aromatics is found to be decreased in all the binders, which is an indicator of the replacement of hydrogen atoms in the aromatics with other heteroatoms (like N, S, O, Cl, Fe, etc.) or functional groups. This results in an increase in the molecular weight of the aromatic compounds and in the C:H ratio of the binders. This increase in molecular weight compounds form a resistance to flow of the binder resulting in increased viscosity. The decrease in C-H bond index is substantially more in pyro-oil modified binders than that in the base and Sasobit modified binders. POMB1, POMB2, and POMB3 showed a 30.60%, 27.52% and 21.43% decrease in C-H bond index after aging, whereas VG30 and SMB showed merely 4.62% and 8.94% decrease respectively. This indicates that addition of pyro-oil to the base binder increases the amount of larger molecular weight compounds in the binders.

The C-O, and O-H bond indices are found to be increased for all the binders except the base binder. The C-O, and O-H can be an indication of oxidation as oxygen molecules invades in the binder system during aging. Yang et al. [18], said that increased concentration of C-O and O-H bonds are representative of oxidation, and that the oxidation

happens until the ratio of C:O decreases. Since the C-O and O-H bond represents the ethers, esters, alcohols and acids, increase in their concentration indicates that concentration of these functional groups is increased in the binders during aging.

CONCLUSIONS

The study intended to evaluate the effect of pyro-oil modification on the aging behaviour of asphalt binders. FTIR spectroscopy was found to be the best tool for measuring and analysing the oxidation products in the binders by determining different functional group bond indices. The following conclusions are drawn from the study. The spectra of pyro-oil and base binder VG30 are different and show some different functionalities because of the difference in chemical composition of the materials. Although there are no new peaks observed after modification with pyro-oil in the POMB spectra, there are several shifts in peaks indicating the chemical reaction between the pyro-oil and VG30. The carbonyl and sulf-oxide indices of POMB1 decrease indicating no aging of POMB1 during modification in terms of carbonyl and sulfoxide indices. The aging of pyro-oil modified binders after the short-term aging can be seen from the increase in C=O, S=O and C=C indices. However, the extent of aging is less for POMBs as compared to that for VG30. Aging increases the aromaticity and decreases the aliphaticity of pyro-oil modified binders as compared to VG30. This increased aromaticity is responsible for the increase in viscosity of binders.

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