# Microstructural and Functional group analysis of Polyphosphoric Acid-Modified Natural Bitumen.

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## Abstract

Bitumen is made up of a variety of hydrocarbons of various sizes and polarities, as well as heteroatoms and metal traces. It has complex surface microstructures that influence its rheological properties and, as a result, its efficiency as a pavement binder. Bitumen is often modified to improve its consistency. However, bitumen modification poses a range of challenges, one of which is the modifier's compatibility with bitumen, which if not met could result in phase separation during long-term storage. Another issue is a change in chemical composition, which may have an effect on efficiency when in operation. The use of polyphosphoric acid (PPA) for the modification (at 160$^{o}$C and 240$^{o}$C) of Agbabu Natural bitumen in South West Nigeria is reported in this paper. Scanning Electron Microscopy (SEM)/Energy Dispersive Spectroscopy (EDX) and Fourier Transform Infrared Spectroscopy were used to classify the unmodified natural bitumen and the PPA-modified bitumen. The results revealed that as concentration and temperature rise, so does the homogeneity of the PPA in the bitumen matrix. The functional group analysis revealed the development of new peaks and the disappearance of others that were present in the unmodified natural bitumen, thereby showing chemical interaction between PPA and the natural bitumen.

**Keywords;** *bitumen; pavement;FT-IR; SEM.*

## INTRODUCTION

Bitumen serves as a binder in asphalt concrete, a composite material used in the construction of road layers which contain mineral aggregate, filler and additives. Despite its low content (ca.5%), the effect of bitumen on properties of concrete and therefore, on the pavement performance is critical. In order to achieve a long-lasting road surface and stability of rheological condition in severe service temperatures, bitumen for paving construction is required to have a wide range of viscoelasticity (Loeber *et al.*, 1998). Bitumen, on the other hand, is a complex chemical mixture of hydrocarbon molecules with small amounts of structurally analogus heterocyclic species and functional groups comprising sulphur, nitrogen, and oxygen atoms, as well as trace amounts of metals (Ogunsuyi, 2009; Ogunsuyi *et al*., 2011). Therefore, in order to improve the viscoelasticity of bitumen, modifiers applied to neat bitumen are carefully chosen to ensure compatibility. Examples of such modifiers are plastomers, crumb rubber, sulfur, synthetic resins, paraffins and acids (Golzin and Hamid, 2011). However, the major acid currently in use for refinery-sourced bitumen modification is Polyphosphoric Acid (PPA) (Shahriar, 2017). Several authors (Baldino, 2013; Lesueur, 2009; Masson, 2008; Masson and Collins, 2009; Rossi *et al*., 2012) investigated PPA's interaction with bitumen model compounds. PPA alteration

follows various pathways depending on the chemical composition of bitumen, which is closely related to the crude oil geographical source, according to these studies. Since polarity enhances PPA dissociation (into PPA and $H^+$), disrupting the hydrogen bond network formed within the agglomerates of asphaltene micelles, PPA reactivity increases with bitumen enclave polarity (Catarina *et al*., 2016). As a result, the asphaltene fraction's molecular weight is reduced, and the distribution of asphaltenes in the remaining fractions (i.e. saturates, aromatics, and resins) is altered, shifting the bitumen towards a more elastic gel-type structure (Golzin and Hamid, 2011). Microstructures of bitumen develop to different forms depending on crude oil source, thermal history, and sample preparation method. While some bitumens display surface microstructures with fine domains, flake-like domains, and dendrite structuring, 'bee-structures' with wavy patterns, several micrometers in diameter and tens of nanometers in height are commonly seen in other bitumens (Xiaokong *et al*., 2015). Although the greater proportion of bitumen used for highway and airport pavement construction worldwide is from crude oil distillation in the refinery, increasing attention is being paid to natural asphalt deposits because they tend to adhere better to the surface of mineral aggregates in asphaltic concrete due to their composition and in particular higher content of oxygen and asphaltogenic acids (Adedimula, 2000). However, not all naturally occurring bitumen meet the requirements for use in road construction leading to the need for modification (Petersen, 1987). This research was therefore aimed at modification of the Nigerian natural bitumen using PPA in order to enhance its engineering properties for paving applications.

## Material and Methods

The natural bitumen was collected from one of the observatory wells at Agbabu. Agbabu is located on the bitumen belt of south-western Nigeria. The belt lies within latitude 0060381N-0060401N and longitude 0040341E-0040371E, falls within the eastern Dahomey Basin and spans across Edo, Ondo and Ogun States (Bakare *et al*., 2015).



### Modifier

Polyphosphoric acid (PPA) with concentration of 105% phosphoric acid (84% $P_2O_5$) was used in this study. It has a specific gravity of 2.06g/ml.

### Purification of the natural bitumen

The bitumen sample was spread to a thickness of 1 cm in a tray. Then, at room temperature, 1.0 g of calcium chloride was spread over the sample and manually stirred for 5 minutes with a stirring rod. To remove any remaining moisture, the mixture was placed in a 65ºC oven. The bitumen was dehydrated and dissolved in 1000 mL of chloroform before being filtered. Vacuum evaporation of the solvent was used to recover the bitumen portion of the filtrate.

### Preparation of Modified Binders

A shear mixer was used to prepare the PPA modified samples. In an iron container, (100g) of natural bitumen was heated to a fluid state. PPA was gradually added to the UNB once the temperature reached 160ºC. To achieve a homogeneous mixture, the temperature of the mixture was kept at 160°C for 1 hour while the mixer speed was kept at 1200rpm. FT-IR, SEM, and EDX techniques are used to characterize these blends as well as base bitumen.

**Experimental Studies**:

Three modified binder formulations were prepared at 160ºC with 2%, 4%, 6% of PPA. These formulations are termed PPAMB2160, PPAMB4160, PPAMB6160**.**Another set of three modified formulations were prepared at 240ºC with 2%, 4%, 6% of PPA. These formulations are termed PPAMB2240, PPAMB4240, PPAMB6240**.** The unmodified natural bitumen is termed UNB**.**

**FTIR (Fourier Transform Infrared Spectroscopy) of Modified Binder**:

A SCHIMADZU FT-IR 8400S analyzer was used for the FT-IR analysis. The instrument's wavenumber range is 400 to 5000 $cm^{-1}$, with a resolution of 0.5 $cm^{-1}$. Figure 2-3 depicts the spectra.

**SEM (Scanning Electron Microscopy).**

The microscopic structure of natural and modified bitumen was studied using a high-performance, variable pressure scanning electron microscope (PHENOM pro-X) with a resolution of 4.0nm. Its computer-controlled 5 axis stage is housed in a specimen chamber that can hold specimens weighing up to 0.5kg. Focus, stigmator, gun saturation, gun alignment, contrast, and brightness are all standard automated features of the instrument.
Figure 4 shows micrographs of the unmodified and modified bitumen.



## RESULTS AND DISCUSSION.

### Functional group analysis

The FTIR spectra of the unmodified and modified bitumen are stacked in Figures 2 and 3. Four prominent peaks in the bitumen spectra observed at 2924$cm^{-1}$ correspond to the asymmetric and symmetric stretches of C-H in $CH_2$ and $CH_3$ for unmodified natural bitumen, UNB. At 1456 $cm^{-1}$ and 1375 $cm^{-1}$, the same functional group's bending vibration is observed, indicating the asymmetric and symmetric bend of $CH_3$ (Silverstein et al. 1981, Smith 1998). There is also a significant aromatic peak at 1605 $cm^{-1}$, indicating that C=C stretch (in-ring) aromatics are present. Aside from these well-defined peaks, there are a few other interesting peaks, such as peaks appearing at 3420 $cm^{-1,}$ which indicate hydrogen bonded N-H/O-H groups (Olabemiwo *et al*., 2016). Another peak of interest is the S=O vibration peak, which occurs at 1033 $cm^{-1}$, and the carbonyl peak, which occurs at 1705 $cm^{-1}$ and is attributed to carbonyl stretch C=O (str) in ketones, aldehydes, and carboxylic (Hou *et al*., 2018). Both of these peaks are commonly used to describe bitumen ageing (Petersen,1986). The peak at 721 $cm^{-1}$, which indicates the presence of molecules with more than four carbon atoms in a row, is also of interest. Furthermore, shoulders around 868$cm^{-1}$, 815$cm^{-1}$, and 744$cm^{-1}$ could be due to aromatic bending C-H modes, which correspond to C-H bend in aromatics. In comparison to natural bitumen, there are new absorption peaks at 966 $cm^{-1}$ (P-O-P stretching) and 494 $cm^{-1}$ (P-O-P bending) after modification with PPA at both temperatures of modification. These changes suggest that the PPA may have disrupted

the hydrogen bond network in the bitumen, which includes pyrrole and indole functional groups. Similarly, after PPA modification, the 1033 $cm^{-1}$ peak attributed to sulphoxides was no longer present. Peaks in the 3420-3500 $cm^{-1}$ region, on the other hand, are less intense at 240°C than at 160°C. This revealed that the polymeric species O-H group reacts with natural bitumen at a higher temperature, indicating that the O-H group is no longer in a free state. Peak shifting and a reduction in peak intensities in the PPA modified bitumen's infrared spectra are major indicators of structural changes in the bitumen after PPA addition. The absence of sulphoxides indicates that PPA reacted with sulphoxides, which are oxygenated functional groups that cause pavement aging. This result is consistent with previous research by Masson and Collins (2009) and Bakare *et al*., (2015)

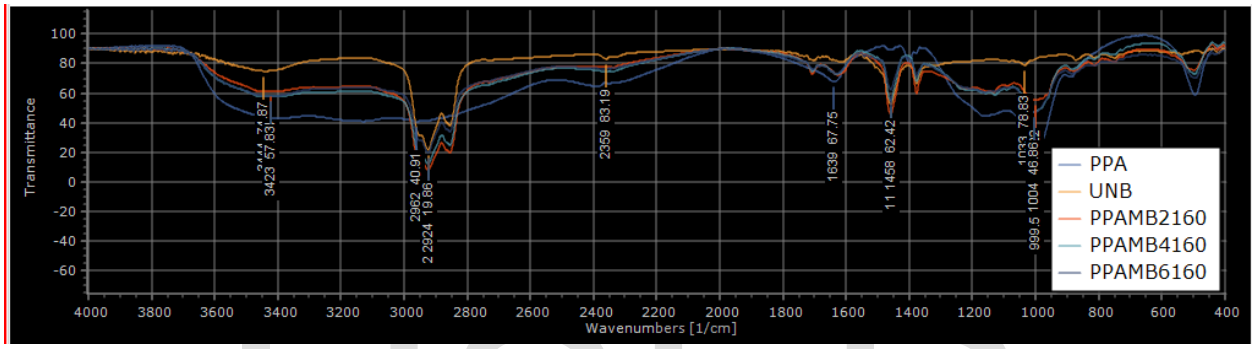



Figure 2: FTIR spectra of **PPA**, **UNB** and modified binders at 160°C.

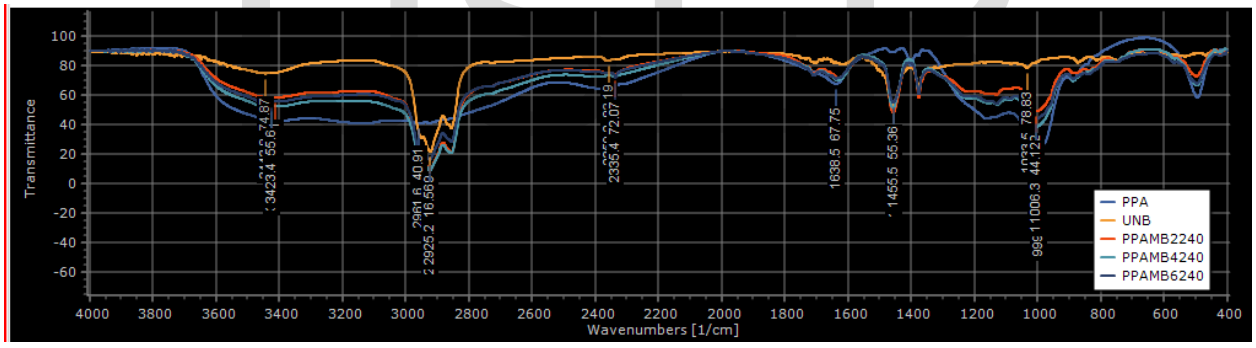
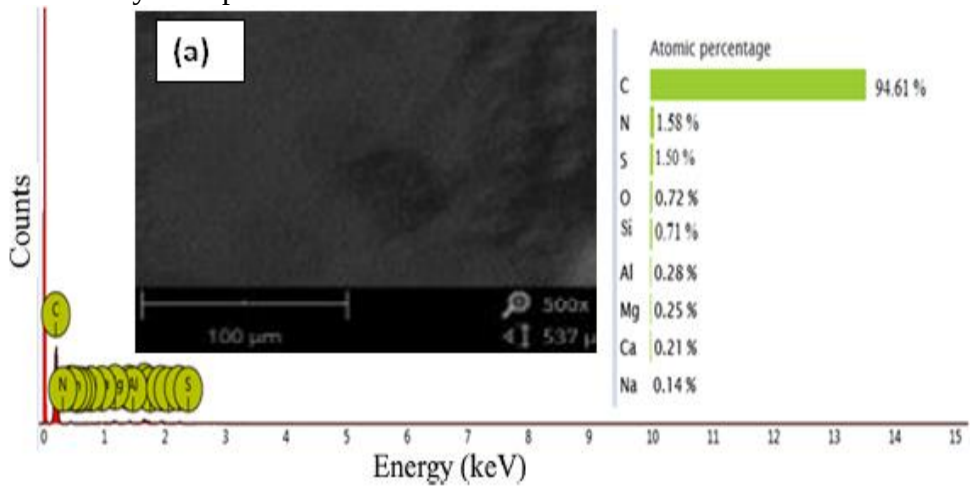


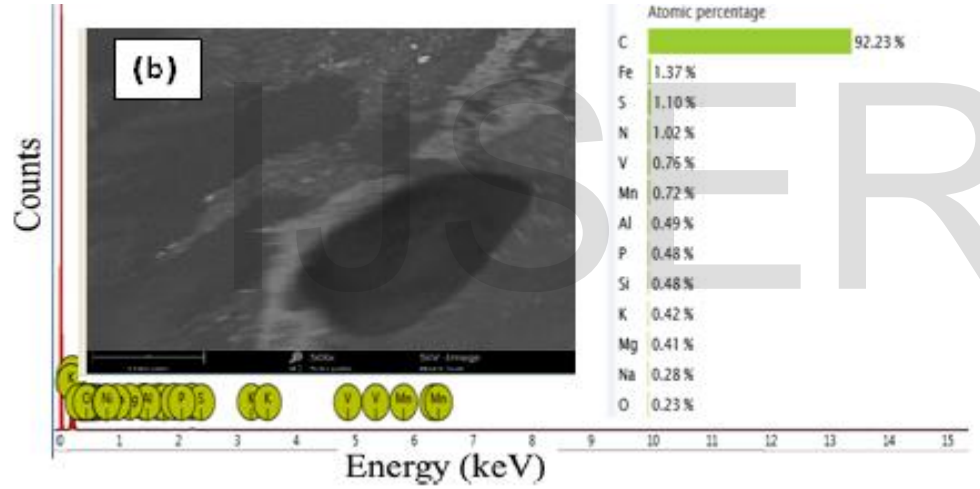

Figure 3: FTIR spectra of **PPA**, **UNB** and modified binders at 240°C.

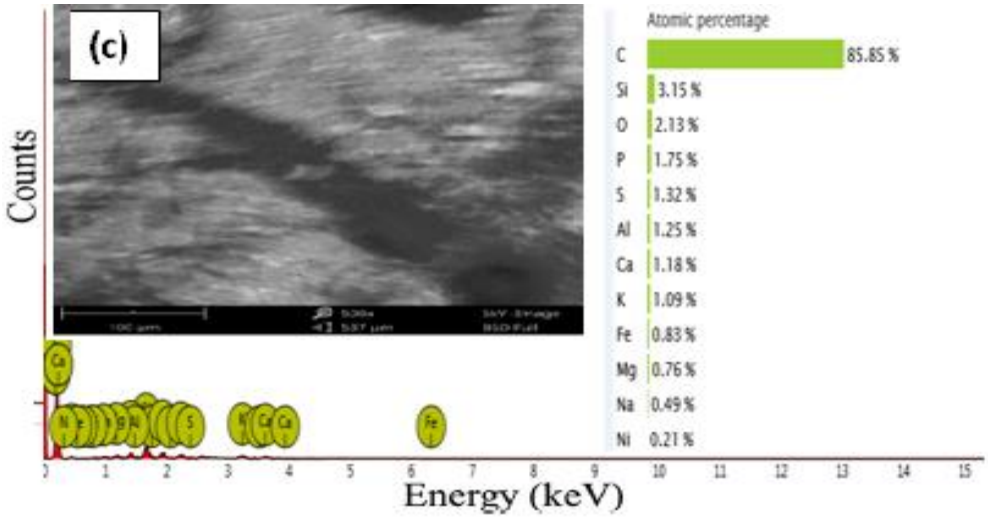
## Microstructural Analysis:

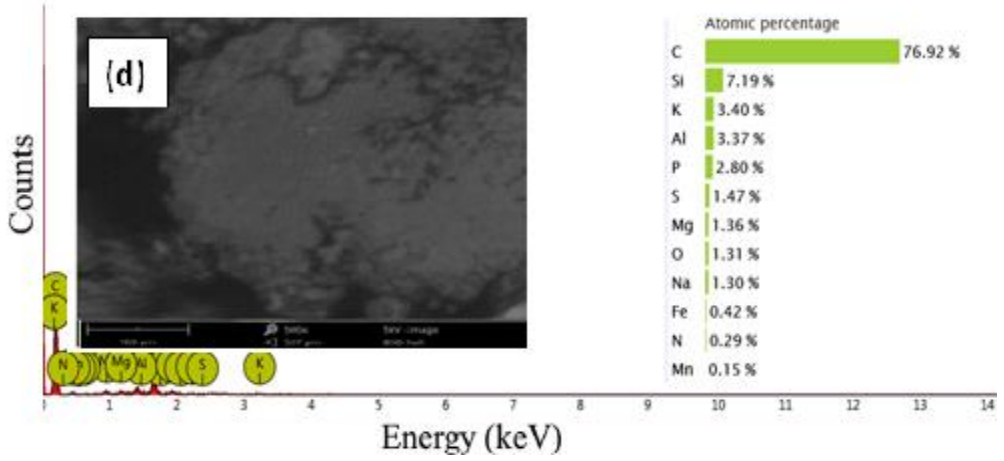
The microstructure of PPA-modified bitumen was investigated using SEM, as was the distribution state of PPA in natural bitumen and the structure of the continuous and discontinuous phases. The continuous bitumen phase (dark portion) of PPA modified bitumen has the morphology of bitumen, while the discontinuous phase is the dispersed PPA. Figure 4 shows SEM images of natural bitumen that has not been modified and modified bitumen (a-g). The SEM image of natural bitumen at a magnification of 500, as shown in Figure 4a, corresponds to the literature (Gupta *et al*., 2012), and its structure is a homogeneous single phase. The homogeneous structure is not preserved at all three ratios at each temperature of modification because PPA has chemically reacted with bitumen. The degree of PPA dispersion into the bituminous phase is shown in these micrographs. This PPA dispersion is more pronounced in PPAMB6240, which contains 6% PPA and was modified at 240°C. The degree of dispersion indicates how well the modified bitumen can prevent phase separation in service or

during long-term storage. As a result, in service, PPAMB6240 will most likely have the least phase separation**.** The EDX results back up this claim; Figures 4 (b,c,d,e,f,g) show that the modified bitumen samples contained phosphorus as a result of the modification. And as the dosage of PPA was increased, this element became more prominent. This confirms that PPA was successfully incorporated into the bitumen matrix.




(d)
Counts
Energy (keV)
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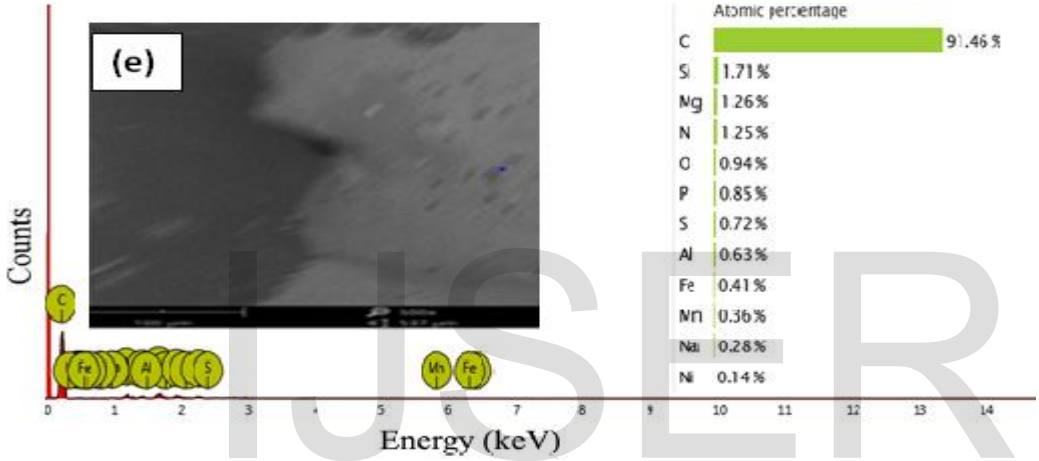
Si 7.19 %
K 3.40 %
Al 3.37 %
P 2.80 %
S 1.47 %
Mg 1.36 %
O 1.31 %
Na 1.30 %
Fe 0.42 %
N 0.29 %
Mn 0.15 %


(e)
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Mg 1.26 %
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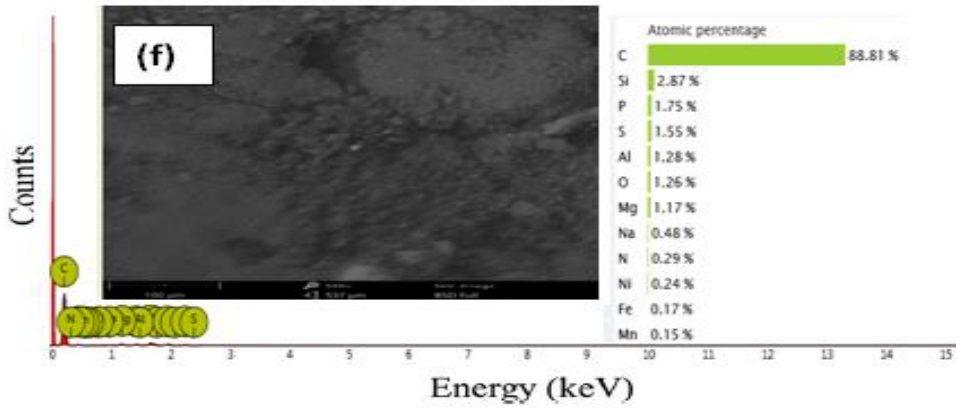
Al 0.63 %
Fe 0.41 %
Mn 0.36 %
Na 0.28 %
Ni 0.14 %


(f)
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Ni 0.24 %
Fe 0.17 %
Mn 0.15 %

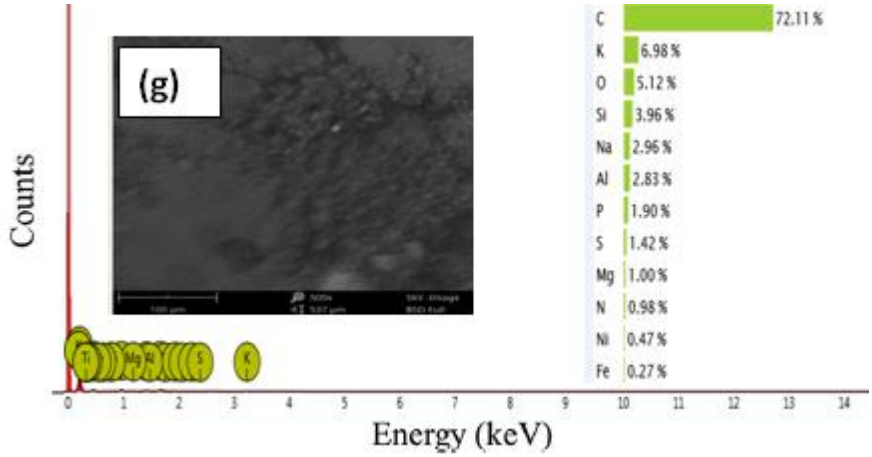


**Figure 4 (a-g):** SEM/EDX spectra of UNB, PPAMB2160, PPAMB4160, PPAM62160, PPAMB2240, PPAMB4240, PPAMB6240.

## CONCLUSION

PPA can be successfully incorporated into the bitumen matrix; FT-IR spectra of modified blends show the disappearance of some peaks (which were very prominent in pure bitumen) and the appearance of some new peaks, indicating that structural changes occur when PPA is added to natural bitumen. Pavement ageing is reduced as a result of such structural changes. PPA disperses well in the natural bitumen phase, according to SEM analysis, depending on the temperature of modification. This would reduce phase separation during storage, improving the physical and engineering properties of the material.



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