

Determination of Polymer Content in SBS Modified Asphalt Binder using FTIR Analysis

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Abstract

Polymer is sometime used in asphalt binders to enhance asphalt pavements performances. However, the quantity or percent polymer used in binders is often unknown because this a proprietary info to the binder producer or supplier, but not to the user, paving contractors or agencies. This has created a complexity in determining how %polymer affects the performance of pavements built using polymer modified asphalt (PMA) binders. To this end, this study has employed the fourier transform infrared (FTIR) spectroscopy method to determine polymer content in an unknown PMA binder. In essence, a neat binder (non-polymer modified base binder) was mixed with four different percentages (known) of Styrene-Butadiene-Styrene (SBS) polymer to produce modified binders. Next, FTIR analysis was performed on the neat/base binder, as well as the modified binders. The FTIR results show that polymer modified binders have two significantly large peaks due to presence of SBS polymer. One peak is for the styrene functional group at wavenumber 699 cm^{-1} and other peak is for butadiene functional group at wavenumber 966 cm^{-1} . The FTIR analysis also shows that the peak value increases with increment of polymer content. Using these peak values and the light intensity absorbed by different %polymer binders, a relationship (called calibration curve) between peak ratios versus %polymer was developed. It is hoped that this calibration curve will be useful in determining polymer content in any polymer modified asphalt binder.

Keywords

Fourier transform Infrared spectroscopy, polymer content, polymer modified asphalt, quantitative determination

1. Introduction

Asphalt binder is the main binder material currently used for highway pavement construction. The rheological properties of a binder play a significant role on the performance of a hot mix asphalt (HMA) pavement. The main source of the asphalt binder is the refining process of crude oils. However, these conventional asphalt binders failed to provide satisfactory performance in case of high traffic routes as

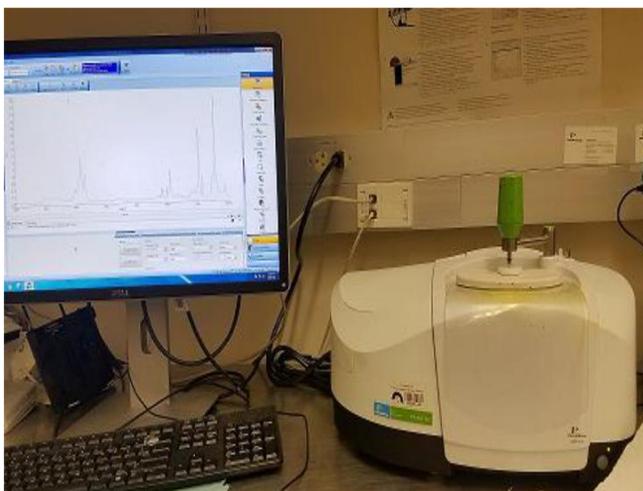
well as in diversified weather conditions. Therefore, binders are being modified with different types of polymers to enhance the performance and durability of the pavement. The styrene-butadiene-styrene (SBS) is one of the most popular elastomeric polymer used to improve the elastic properties of the binder. Past studies show that the increasing SBS content improves the stiffness of the binder (Airey, 2003; Tarefder and Yousefi, 2016). However, Champion *et al.* (2001) reported that higher polymer blends display a heterogeneous structure with a polymer-rich dispersed phase. Sengoz and Isikyakar (2008) also reported that high polymer content negatively affects performance of asphalt. Because when polymer content is high, asphalt becomes discretely dispersed in polymer matrix. In addition, high polymer content reduces the workability and increases the phase separation problem. Therefore, it is very important to know the chemical properties and the percentage of polymer content in order to characterize the PMA. However, most of the current specifications for asphalt binder currently available are performance based. These specifications lack the ability to accurately determine the polymer content in a PMA. Therefore, several studies were performed to determine the polymer content in an unknown polymer modified binder. Loucks and Seguin (1991) provided a process for determining the polymer content in a polymer modified asphalt using gel permeation chromatography (GPC). This method determines the asphalt content based on the molecular weight distribution. However, the molecular weight of asphaltenes are closed to molecular weight of the polymer (Mansoori, 2009). Later, Kosińska *et al.* (2016) developed a method using high performance GPC and size exclusion chromatography (SEC) to distinguish between modified binders and unmodified binders. On the other hand, Chen and Lin (2000) found that elastic recovery provided a good means by which separate polymer-modified and neat binders. Han *et al.* (2009) developed a method based on viscosity-temperature curve to determine polymer content in asphalt. These performance based method can identify the presence of polymer; however, these methods failed to determine the amount of polymer mixed with the neat binder. Finally, Molenaar *et al.* (2004) reported that fourier transform infrared (FTIR) spectroscopy can be used to determine the presence of polymers in polymer-modified binders. However, they also stated that FTIR analysis is unsuitable for quantitative analysis without the availability of calibration curves.

From the above discussion it reveals that the polymer content affects the rheological properties of modified binders. Past studies show that FTIR analysis is most suitable technique to determine the polymer content in modified binders. However, a calibration curve needs to be developed at first to determine the polymer content properly. Therefore, this study develops a calibration curve in order to quantify the polymer content in an unknown SBS modified binder using FTIR analysis.

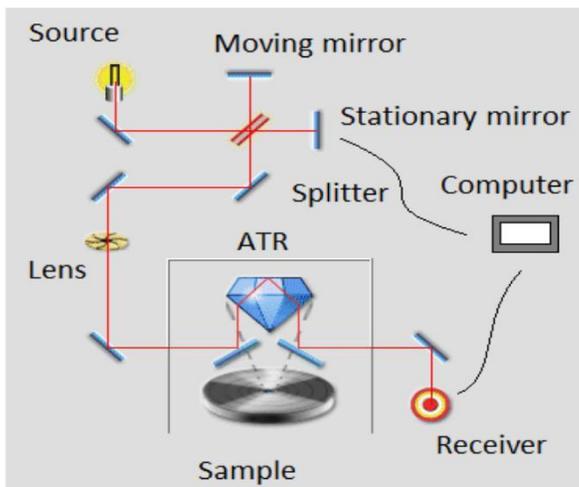
2. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy is a technique which is widely used in organic chemistry to identify the presence of different functional groups in solid, liquid or gas sample based on the energy (light) absorption of infrared by the sample. Figure 1(a) shows the FTIR device used for this analysis. Figure 1(b) shows the working mechanism of FTIR device. FTIR device passes light from a source through a beam splitter. The splitter splits the light into two beams. One beam goes to a stationary mirror and another beam goes to a moving mirror. Then both beams back to splitter to combine again. The moving length moves in order to creates constructive and destructive interferences (an interferogram). Then, the recombined light passes through an attenuated total reflection (ATR) prism and hence, passes through the sample. The sample absorbs the lights of different wavelengths depending on the vibrations of existing different functional groups, and remaining light is received by a detector. The detector then reports intensity of light versus time for all wavelengths simultaneously. Finally, a mathematical function called a Fourier transform is used to convert an intensity versus time spectrum into an intensity versus frequency spectrum with help of a computer. FTIR spectroscopy exploits the fact that molecules absorb specific frequencies those depends on their characteristic chemical structure. These absorbed frequencies are known as resonant frequencies which match the transition energy of the bond or group that vibrates. Depending on the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling, the

bond energy is different for different functional groups. Therefore, each functional group has distinct FTIR spectrum.



a) PerkinElmer FTIR device

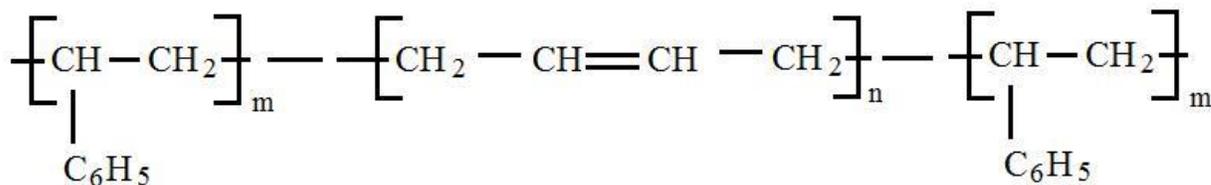


b) FTIR mechanism

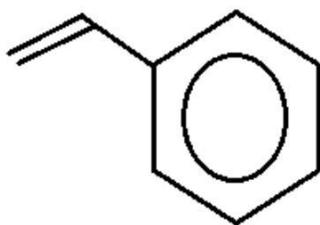
Figure 1: FTIR device used in this study

3. Chemical Structure of SBS Polymer

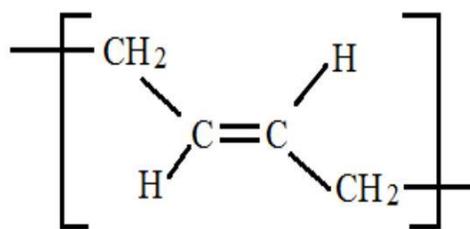
To utilize the FTIR analysis for polymer modified binder, it is very important to know the chemical structure of the polymer. The styrene-butadiene-styrene (SBS) is triblock copolymer of polystyrene and polybutadiene (Figure 2(a)).



a) Styrene-butadiene-styrene (SBS)



b) Styrene



c) Butadiene

Figure 2: Chemical structure of SBS polymer

The polystyrene (also known as ethenylbenzene) is an aromatic compound with the chemical formula of $C_6H_5CH=CH_2$. It is a mono-substitute benzene where one hydrogen is replaced by an ethenyl functional group (Figure 2(b)). As a mono-substitute benzene, the polybutadiene generates two characteristic absorption peaks at wavenumber 699 cm^{-1} and at wavenumber 757 cm^{-1} respectively. On the other hand, the chemical formula of butadiene is $H_2C=CH-CH=CH_2$. The polybutadiene has a trans-alkene structure (Figure 2(c)) and generates characteristic peak at wavenumber 966 cm^{-1} . However, for terminal mono-substitute alkenes, it also generates two peaks at wavenumber 911 cm^{-1} and at wavenumber 993 cm^{-1} respectively. In addition, there is another peak at wavenumber 1450 cm^{-1} due to presence of methylene groups (CH_2). Figure 3 shows the absorption spectrum of SBS polymer.

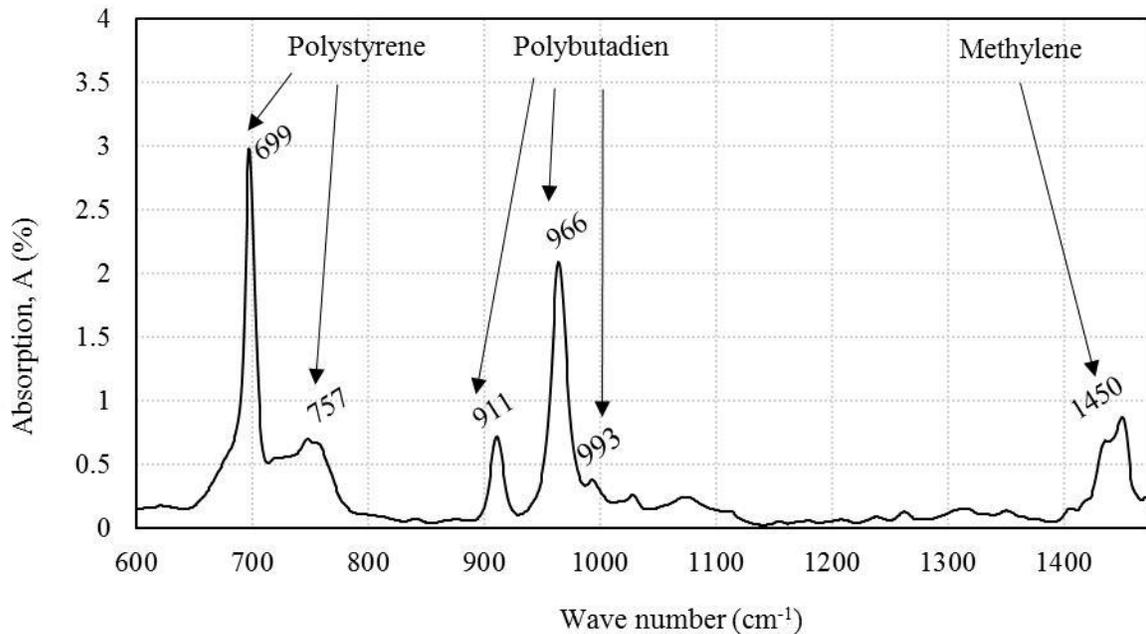


Figure 3: FTIR spectrum for SBS polymer

4. Development of Calibration Curve

4.1 Methodology

To construct FTIR calibration curve, a neat binder (non-polymer modified) was selected. Then, the neat binder was mixed with 4 different percentages of SBS polymer (1%, 3%, 5%, and 7%) by weight. The polymer mixing process was accomplished by using a high shear mixer at 1200 rpm and 180°C for 2 hours (until the polymer mixed with the binder properly). Then, the FTIR analysis of each laboratory generated polymer modified binders were performed to generate the FTIR curve. For simplicity, peak values at wavenumber 699 cm^{-1} (for styrene) and peak at wavenumber 966 cm^{-1} (for butadiene) were considered for this analysis. Later, using the peak values and percentage of modifier contents of the binders were used to generate the calibration curve. Finally, polymer content of unknown binders (field collected PG 70-28+) was determined using the calibration curve.

4.2 Detection of Polymer

Figure 4 shows the generated FTIR spectra for SBS polymer, neat binder and modified binder with 5% SBS. It shows that the neat binder has no peaks at wavenumber 699 cm^{-1} (for styrene) and peak at wavenumber 966 cm^{-1} (for butadiene), which indicates that the neat binder has no SBS polymer in it.

However, the neat binder has two peaks at wavenumber 1375 cm^{-1} and at wavenumber 1450 cm^{-1} which are for the methyl groups (CH_3) and methylene (CH_2) groups respectively. On the other hand, modified binder with 5% SBS has two small peaks at wave number 699 cm^{-1} and 966 cm^{-1} which indicates the presence of styrene and butadiene polymers (thus SBS polymer) in the mixture.

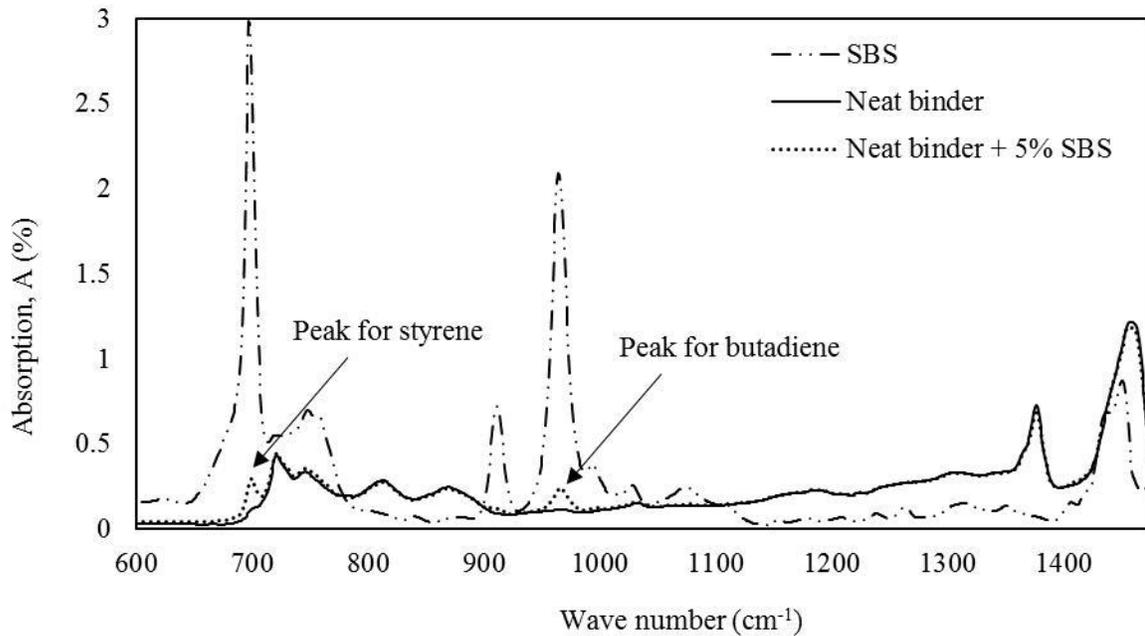


Figure 4: Use of FTIR to detect presence of polymer

4.3 Calibration Curve

Figure 5 shows the FTIR spectra of base binder and other 4 laboratory generated modified binders. It shows that all modified binders have noticeable peak values at wave number 699 cm^{-1} and 966 cm^{-1} . The peak values increase with increment of polymer content. For example, the modified binder with 7% SBS has highest peak values than the other binders. On the other hand, modified binder with 1% SBS has the smallest peak values among the modified binders. Neat binder has no peaks at those two locations.

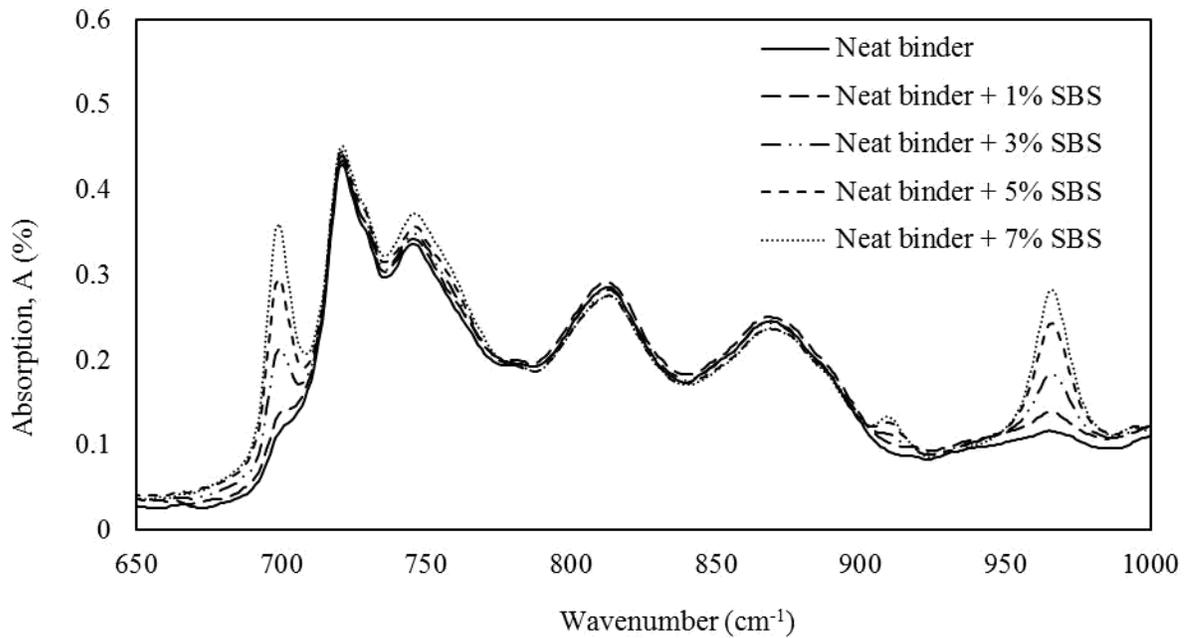


Figure 5: FTIR spectra for neat and modified binders

As absorption peak values at wavenumber 699 cm^{-1} and 966 cm^{-1} increases with increment of polymer content, a calibration curve was developed based on this relationship. For each binder, peak values at wavenumber 699 cm^{-1} and 966 cm^{-1} added together and then, combined value was divided by peak value at wavenumber 1375 cm^{-1} in order to get the absorption peak ratio. Finally, absorption peak ratio versus polymer content was used to develop the calibration curve. Figure 6 shows the absorption peak ratios for different binders. Then, a linear regression line was fitted with the data. The relationship is shown in Equation 1. The R-squared value was found 0.9936 which indicates a good correlation.

$$\text{Absorption peak ratio} = 0.0437 \times \text{polymer content} + 0.1559 \quad (1)$$

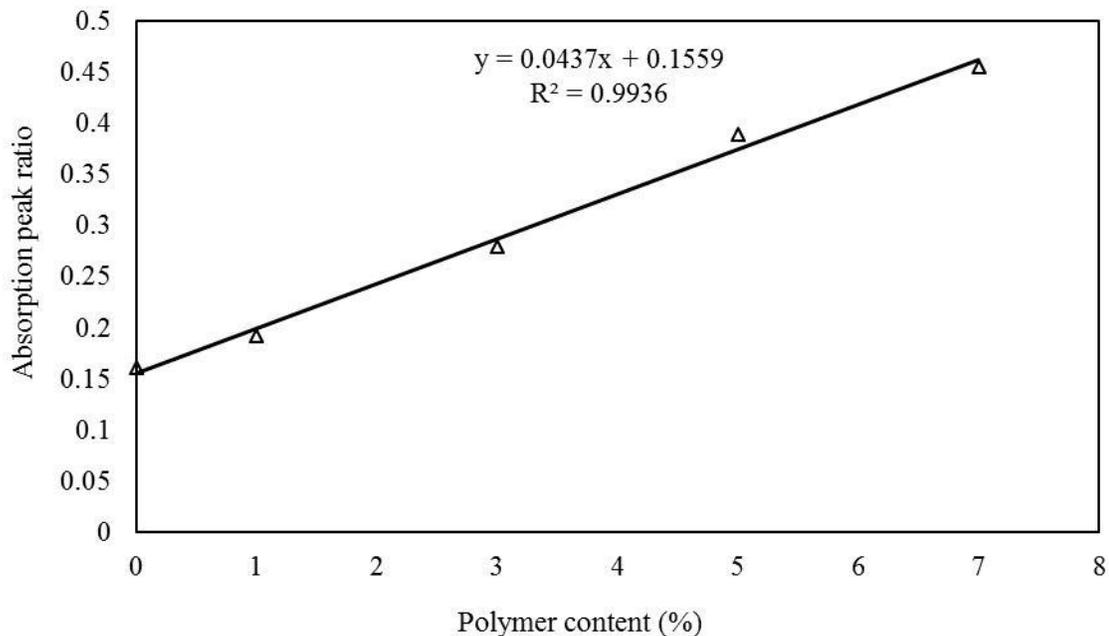


Figure 6: Developed calibration curve for determination polymer content

4.4 Application of Calibration Curve

The developed calibration curve was used to determine the polymer content of two unknown binders (PG 70-28+ and PG 70-28). Figure 7 shows the FTIR spectra for PG 70-28+ binder and PG 70-28. FTIR analysis shows that PG 70-28 has no peak at wavenumber 699 cm^{-1} (for styrene) and peak at wavenumber 966 cm^{-1} (for butadiene) which indicates the absence of polymer in the binder. On the other hand, PG 70-28+ has two small peaks at wave number 699 cm^{-1} and 966 cm^{-1} which indicates that both styrene and butadiene (thus SBS polymer) are present in the binder. The absorption peak ratio was found as 0.365 and using the Equation 1 polymer content was calculated as 4.78% (Figure 8). Actual polymer content of PG 70-28+ reported the by the asphalt supplier is 4.5%. The determined values using calibration curve provides only 4% error for this case.

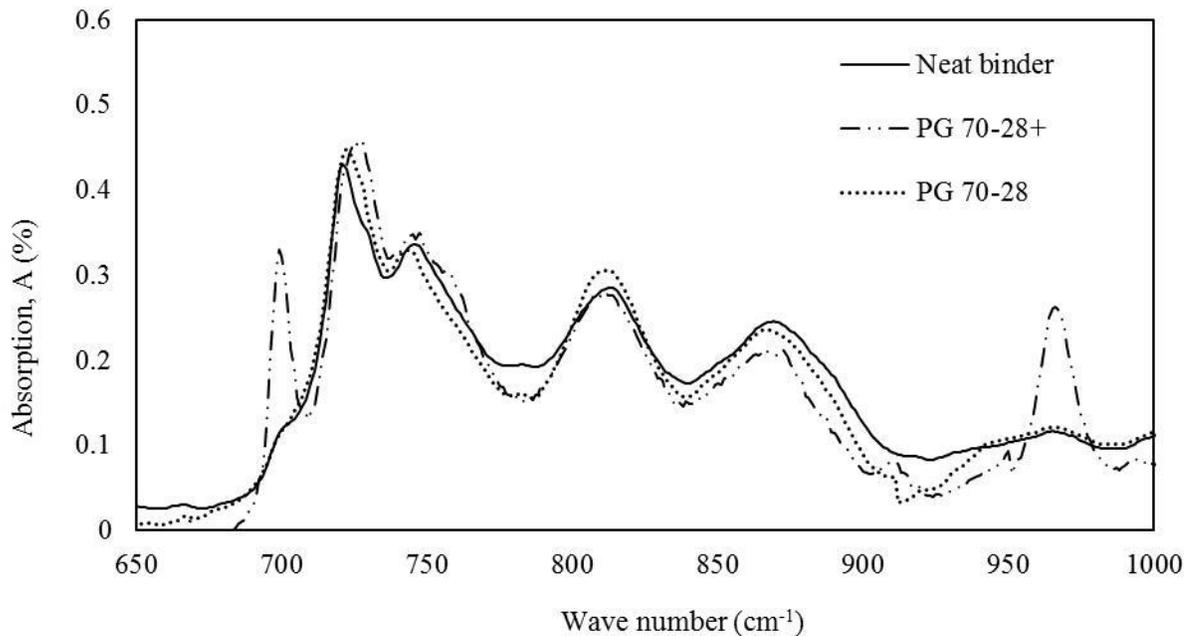


Figure 7: FTIR spectra for neat, PG 70-28+ and PG 70-28 binders

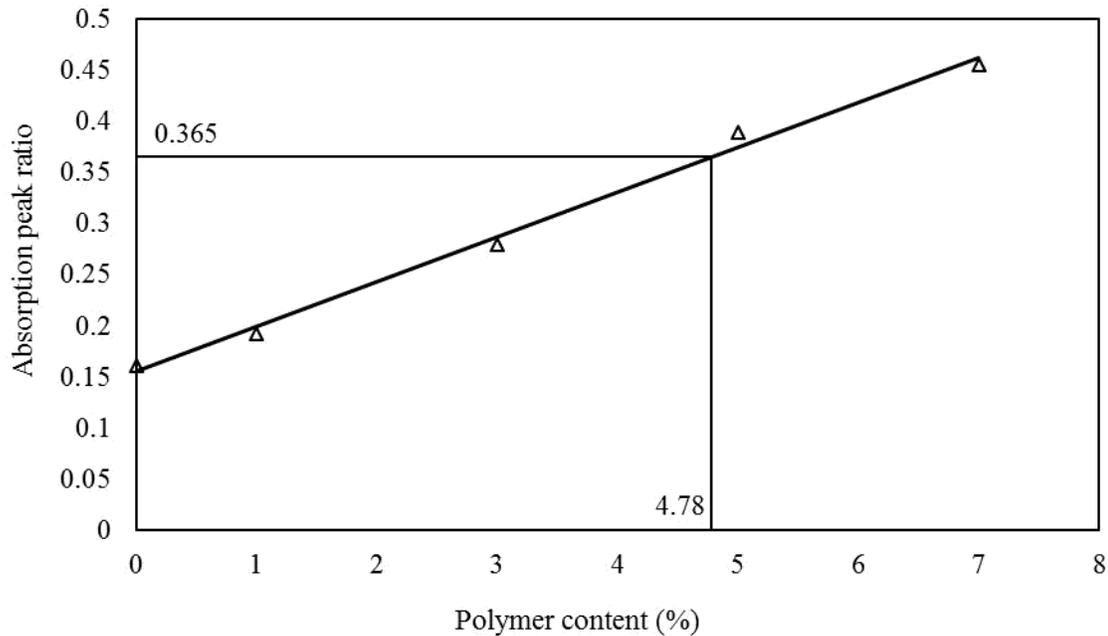


Figure 8: Application of the calibration curve to determine polymer content

5. Conclusion

Based on the results of this study, the following conclusions can be made:

FTIR is capable of differentiating between polymer and non-polymer-modified binders. SBS modified binders show noticeable peaks at wavenumber 699 cm^{-1} and peak at wavenumber 966 cm^{-1} respectively. Therefore, the FTIR spectroscopy can be a useful method to verify the presence of polymer in the binder.

The developed calibration curve shows that there is a strong linear relationship between absorption peak ratio and the polymer content with an R-squared value closed to 1.0. Therefore, the developed calibration can be useful to determine the polymer content in an unknown binder.

6. References

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