STUDIES ON MODIFIED BITUMEN'S USING FOURIER TRANSFORMER INFRARED SPECTROSCOPY

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ABSTRACT

Bitumen is a multiphase colloidal system with asphaltene molecules dispersing in maltenes. To improve its properties, bitumen is often modified with an additive that may or may not be reactive. Crumb Rubber and Polymer modifiers are reactive additives used to increase the viscosity of bitumen. One problem of Modified Bitumen concerns poor compatibility between modifier and bitumen.

Given the complexity of bitumen, the nature of its reaction with these modifiers is in many respects unclear. To better understand the reactions between bitumen and modifier, we have used Fourier Transform Infrared Spectroscopy (FTIR). FTIR analysis shows few new peaks (wavenumber) for modified bitumen's indicating that physical alteration is the main changes in the modified bitumen's. In this investigation, attempts were made to successfully apply FTIR in both quantitative and qualitative analysis of modified bitumen's. It was concluded that FTIR is an excellent tool for quality control of modified bitumen's.

Keyword: HMA, CRMB, FTIR ,BITUMEN

1.0 Introduction

Bitumen is defined as a "virtually involatile, adhesive and waterproofing material derived from crude petroleum or present in natural bitumen, which is completely or nearly completely soluble in toluene, and very viscous or nearly solid at ambient temperatures". [1] Solubility in toluene superior to 99% is asked for in the paving specifications. [2] It is one of the widely used materials for the construction of pavement.

In the last decade, the high volume of road transportation combined with high stresses caused by heavy vehicles and an insufficient degree of maintenance started to lead to the rapid deterioration of the pavement. This concludes that bitumen in its pure form is not suitable for modern pavements and undergoes too many types of failure during its service time. This is the reason for interests in bitumen modification field. After being clarified by many laboratories and field tests many types of materials were used to modify bitumen properties and performance.

In this paper, it is shown that Fourier transform infrared spectroscopy (FTIR) can provide a qualitative assessment of bitumen modifiers. The polymer distribution in the blend and their molecular size, in related to bitumen is investigated and explained by their contribution to entropy. These results are related to the kinematic viscosity of the blends and the (in) compatibility is explained by these statistics.

1.2. Objectives of the Present Study

- To address the practical applicability of Fourier Transformer Infra-Red spectroscopy (FTIR) technique in commonly used paving material.
- To study the particulate matter distribution of the selected polymers of Elastomeric type such as Styrene Butadiene Styrene (SBS) (Finaprene and Finawax) and Waste tyre rubber (Crumb) in the modified bitumen blend using Fourier Transformer Infra Red spectroscopy (FTIR).
- To determine polymer impact on the low and high temperature performance of binders.
- To Investigate the compatibility and stability of the modifier in the bitumen-polymer blend.

2.0. Literature Review

2.1. Composition of Bitumen

The characteristics and composition of bitumen depend in large part on the source of the mother crude oil. The chemical complexity of bitumen precludes any precise molecular identification. Consequently, it is often conveniently characterized by its chromatographic fractions, the maltenes and the asphaltenes, which are, respectively, soluble and insoluble in n-heptane. The maltenes can be fractionated into oils and resins. Further oils can be fractionated into saturates, aromatics. [3, 4].

Asphaltenes are defined as the insoluble part of a bitumen (or a crude oil) in n-heptane (ASTM D3279) but soluble in toluene. These are the more studied bitumen fractions because of their viscosity building role. [5] Asphaltenes form a black powder at room temperature and are largely responsible for the black color of the bitumen. Asphaltenes are the highest molecular weight components of bitumen. Saturates usually amounts for 5–15 wt. % of the paving grade bitumen. [6] Fourier-Transformer Infra-Red spectroscopy (FTIR) reveals different branching structures and some long aliphatic chains. Very few polar atoms or aromatic rings are present. Aromatics are also called naphthene aromatics, are the most abundant constituents of bitumen together with the resins, since they amount for 30–45 wt. % of the total bitumen. Resins, also called polar aromatics, can be numerous (30–45 wt. %). [11] Depending on the solvent used, they can outnumber aromatics. They play a crucial role in the stability of bitumen, since they act as a stabilizer for the asphaltenes.

2.2. Rheology Of Bitumen

Rheology can be defined as a science dealing with the flow and deformation of various materials, where the flow is taken in a general sense. [7] The use of bitumen in paving applications has generated a lot of interests in its rheological properties, because of their importance in the manufacture and quality of bituminous pavements long before that, ancient users of bitumen observed the strong effect of temperature on its consistency. [7, 8] But due to its highly viscous character at room temperature, giving rise to a confusing and somewhat imprecise description such as pasty or semi-solid [8], bitumen rheological behavior remained hard to quantify. The consistency tests used in past were complicated to interpret in rational terms and those were proved sufficient for specification purposes until the development of modern modified bitumen's a lot of research work was devoted in the past years to better describe and understand bitumen rheology.

The first attempt to measure the viscosity of a bituminous-like substance was probably that by Von Obermayer, who used three rheometers (sliding plate, parallel plate and torsion plate) to characterize a tar as early as 1877. Trouton started his experiments on the subject in 1904, and derived his celebrated ratio between tensile and shear viscosity using pitch. He seems to be the first author to describe the non-Newtonian behavior of pitch, based on the departure from linearity of the early deformation rate in tensile creep and on its non-proportionality to stress. [7] From then on, many experimental set-ups were proposed [7, 8] and a general agreement was found on the marked non-Newtonian behavior at room temperature of most bitumens in the1950s. [18] As a result, Pfeiffer and co-workers correctly attributed the non-Newtonian effects to viscoelasticity, and interpreted it as a consequence of the gel structure of the materials. [7,8] In modern terms, their measurements would account for the presence of delayed elasticity and some non-linearity, a behavior now known to be present in every bitumen. [8] The first modern description of bitumen viscoelastic properties was probably that by Van der Poel, who combined static creep measurements with dynamic experiments at various temperatures. It is important to understand the stress-strain behavior in order to predict the engineering performance of any material. According to Van Der Poel (1965), for a given temperature and time of loading, the mechanical properties of bitumens can be expressed in terms of a stiffness modulus (S) defined as S=STRESS/STRAIN.

From then on, many results were accumulated using a procedure very similar to that by Van der Poel, based on the use of dynamic experiments quantifying the rigidity of bitumen by means of its complex modulus. [8]

At low temperatures (typically below −20 °C), the shear modulus reaches a constant value of order 1 GPa independent of temperature and frequency corresponding to the glassy state. This value is typical of amorphous organic materials such as polymers. In parallel, the phase angle diminishes down to 0°. At high temperatures (typically above its softening temperature, that is above 60 °C), bitumen is a viscous Newtonian liquid characterized by a temperature-dependent. In-between these two asymptotic behaviors, the mechanical response of a bitumen is intermediate between that of an elastic solid and a viscous liquid and is thus said to be viscoelastic. [24]

2.3 Polymer Modified Bitumen

Polymer additives to reinforce bitumen are now widely used in the industry as commercial products. The idea to mix bitumen and rubber dates back to 1823, a patent for natural rubber added into tar was granted to English manufacturer Hancock. [9] In 1873, another patent for bitumen paving binder with one weight percent of latex (wt. %) was granted to Samuel Whiting. In 1902, a French company first used the rubber modified bitumens on the pavement roads. [26] Since the World War II, more and more polymers have been used in bitumen pavement to improve the road performance, increase the service life of the pavement, meet the heavy traffic demands, and save costs of maintenance. According to a survey conducted in 1994, over 18 **million** kilograms of styrene/butadiene type polymers were used for paving bitumen modification. [13] Ponniah and Kennepohl reported that, the incremental life-cycle cost analysis showed that the PMA is cost-effective, providing that the cost of PMA does not exceed the cost of conventional bitumen by more than 100%. PMA are therefore chosen to reduce life cycle costs in many cases. In the present, some new techniques, including micro surfacing or using emulsion chip seals on heavy traffic roads have been applied to modified binders. It is realized that binders often require modification to meet the needs for low temperature resistance to thermal cracking, and high temperature resistance to rutting. It is predicted that more and more polymer modified bitumens will be used for specific applications in the near future because of their outstanding performance. [10]

3.0 Material and Methods

3.1 Selection of Materials

3.1.1 Selection of Base Bitumen

Bitumen VG-30 grade was chosen as base bitumen for preparation of polymer/bitumen blends in this study.

3.1.2 Selection of Modifiers

In this thesis, three polymers were chosen to blend with the base bitumen. The selected polymers are as listed below

1. Styrene-Butadiene-Styrene (SBS)
    a.Finaprene

3.2 Finaprene Modifier

Finaprene is polystyrene-polybutadiene thermoplastic tribloc radial copolymer. Because of its high molecular weight vulcanization or additive is not required for cross-linking.

Finaprene provides excellent cohesive and elastic properties to the modified road binder. Finaprene elastomers are widely used in polymer alloys, as modifiers and they enhance the compatibilisers of thermoplastic resins. Their compatibilising properties are essential, for example, in the recycling of plastics, allowing compounding of normally incompatible polymers like styrene's and polyolefin's bituminous binder.

Finaprene is used in a wide variety of climates and finds applications in the very hot as well as the coldest temperatures. Finaprene modified bitumens are used in a wide range of applications including surface dressing, asphalts, slurry seal, mastic asphalts, microsurfacing and sealants. The physical appearance of Finaprene is a relatively rigid white crumb or powder. Its crumb shape, along with the medium molecular weight confers excellent properties along with an easy dispersion and optimum storage stability to the modified road binder. Both mechanical and thermal properties (low and high temperature) are enhanced by using Finaprene.

Figure 3.1: Finaprene

3.3 Preperation of PMB

Polymer modified bitumen (PMB) binders were prepared by blending bitumen of Viscosity grade 30 (VG-30) with the selected polymers at a varying concentration of 1%, 2%, 3%, 4% for SBS polymers .

The detailed procedure of PMA mixing is as follows.

1. Weigh the bitumen sample, and calculate the amount of the selected polymer.
2. The bitumen is continuously stirred and heated.
3. The selected polymers of known concentration were added while the temperature of bitumen is up to 160^0 C for SMS modifier .
4. When the temperature reaches 180^0 C, maintain it for one hour and the bitumen is continuously stirred to have proper blending of polymer and bitumen.
5. The addition of the polymer is carefully controlled. Since a higher addition rate results in polymer conglomeration and lumps, which could be problematic.

3.4 Morphology of Polymer-Bitumen (PB) Blend

The blending can yield the three different types of morphology in polymer/asphalt after the hot mixing.

First Type: The mix is completely homogenous, this case rarely occurs. In this case, the oil in the bitumen is responsible for complete salvation of the polymer. Although the modified binder is absolutely stable, the binder mechanical properties including elasticity and tensile strength change little only viscosity increases. [33]

Second Type: The mix is heterogeneous, this is the case of the so called incompatibility since the bitumen and the polymers are separated.

Third Type: the mix is micro-heterogeneous [44], and is made up of two distinct finely interlocked phases. This case is most important; it represents the so called compatibility. Compatible polymer "swells" by absorbing some of the oily fractions of the bitumen to form a polymer phase distinct from the bitumen phase including the rest of the oils, plus the resins and asphaltenes.

3.5 Methodology Adopted in Testing Pb Blend

3.5.1 Modified Bitumen Tests

The behavior of bitumen should be explained by its chemical composition and structure. However, the chemical complexity of bitumen makes it very difficult to use chemical analyses to characterize its performance. For this reason, physical property measurements become the primary means in the performance evaluation and selection of bitumen.

The tests conducted for modified binder were carried out as per the specifications provided in IRC-SP-53-1999 and IS-15462-2004. They are described in the following sections.

3.5.2 Microscopy of Bitumen Modifiers

The chemical nature of the polymer plays a key role in checking its compatibility with the bitumen. The microscopy measurements were carried out on Fourier Transformer Infrared Spectroscopy (FTIR). Standard squashed slides of polymer/bitumen blend are prepared and viewed under spectrum. The molecular size of the modifiers is correlated with viscosity results to know the influence of polymer in bitumen-polymer blend and its performance at varying temperature.

4.0 Laboratory Investigations and Analysis

4.1 Conventional Tests

Bitumen is available in a variety of types and grades. To judge the suitability of these binders' various physical tests like penetration, ductility, softening point, flash and fire point and elastic recovery test have been specified by various agencies.

The binders were subjected to conventional tests as per Indian Standards are as follows:

- Penetration Test (IS: 1203-1978)
- Softening Point Test (IS: 1205-1978)
- Ductility Test (IS: 1208-1978)
- Elastic Recovery Test (IS: 15462- 2004, ANNEX-A)
- Flash & Fire Point Test (IS: 1209-1978)
- Specific gravity Test (IS: 1202-1978)

Table 4.1 Conventional Test Results of Various Binders

Test Description and Criteria	Finaprene modified bitumen	Finaprene modified bitumen	Finawax modified bitumen	Finawax modified bitumen
Modifier added (%)	**1**	**2**	**3**	**4**
Penetration (mm) at 25 ^{0}C (IS:1203-1978)	38	35	32	32
Softening Point in deg. C (IS:1205-1978)	61	63.5	65	66
Ductility (cm) (IS: 1208-1978)	50	54	58.20	57.85
Elastic Recovery in % (Min 50%) at 15 ^{0}C (Appendix 1 IRC:SP:53-2002)	66	70	72	73.5
Flash Point in deg. C (Min 230 ^{0}C) (IS: 1209-1978)	258	267	268	270
Fire Point in deg. C (IS: 1209-1978)	269	285	294	298
Specific gravity (IS: 1202-1978)	1.000	1.120	1.180	1.220
Separation, Difference in Softening Point ^{0}C,(IS 15462-2004)	1	2	1	2

4.2 Fourier Transformer Infrared Spectroscopy (FTIR)

4.2.1 Working of FTIR Spectroscopy

Fourier Transform Infrared Radiation (FTIR) is a type of spectroscopy IR analysis that uses infrared radiation to record molecule movements via computer-based programs. It uses a formula called Fournier Transform and a scheme of conversion called Michelson Interferometer. FTIR spectroscopy is a multiplexing technique, where all optical frequencies from the source are observed simultaneously over a period of time known as ***scan time***. [11].

Fourier Transform is a mathematical equation that converts the spectral signal performed by a computer from a time domain towards a frequency domain. Its mechanism of action is based on the Michelson Interferometer modulation.

Spectrum is the graph that shows movement of compounds when they undergo a reaction involving infrared radiation. The movement of compound is actually a vibration, which results to the emission of energy measured in wavelength or wave numbers. Thus, the absorption spectrum is a plot of wavelength vs. a beam of radiation. [12]

Figure 4.1: Fourier Transformer Infrared Spectroscopy

Molecules are flexible, moving collections of atoms. The atoms in a molecule are constantly oscillating around average positions. Bond lengths and bond angles are continuously changing due to this vibration. A molecule absorbs infrared radiation when the vibration of the atoms in the molecule produces an oscillating electric field with the same frequency as the frequency of incident IR "light". All of the motions can be described in terms of two types of molecular vibrations. One type of vibration, a stretch, produces a change of bond length. A stretch is a rhythmic movement along the line between the atoms so that the interatomic distance is either increasing or decreasing. The second type of vibration, a bend, results in a change in bond angle. These are also sometimes called scissoring, rocking, or "wig wag" motions.

A molecule absorbs a unique set of IR light frequencies. Its IR spectrum is often likened to a person's fingerprints. These frequencies match the natural vibrational modes of the molecule. A molecule absorbs only those frequencies of IR light that match vibrations that cause a change in the dipole moment of the molecule. [11]

The infrared spectrum for a molecule is a graphical display. It shows the frequencies of IR radiation absorbed and the % of the incident light that passes through the molecule without being absorbed. The spectrum has two regions. The *fingerprint* region is unique for a molecule and the *functional group* region is similar for molecules with the same functional groups. [58]

The nonlinear horizontal axis has units of wavenumbers. Each wavenumber value matches a particular frequency of infrared light. The vertical axis shows % transmitted light. At each frequency the % transmitted light is 100% for light that passes through the molecule with no interactions; it has a low value when the IR radiation interacts and excites the vibrations in the molecule.

A portion of the spectrum where % transmittance drops to a low value then rises back to near 100% is called a "band". A band is associated with a particular vibration within the molecule. The width of a band is described as broad or narrow based on how large a range of frequencies it covers. The efficiencies for the different vibrations determine how "intense" or strong the absorption bands are. A band is described as strong, medium, or weak depending on its depth. [13].

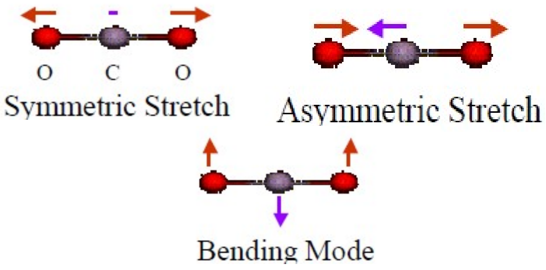

Figure 4.2: Diagrammatic representation of Movements of Molecules

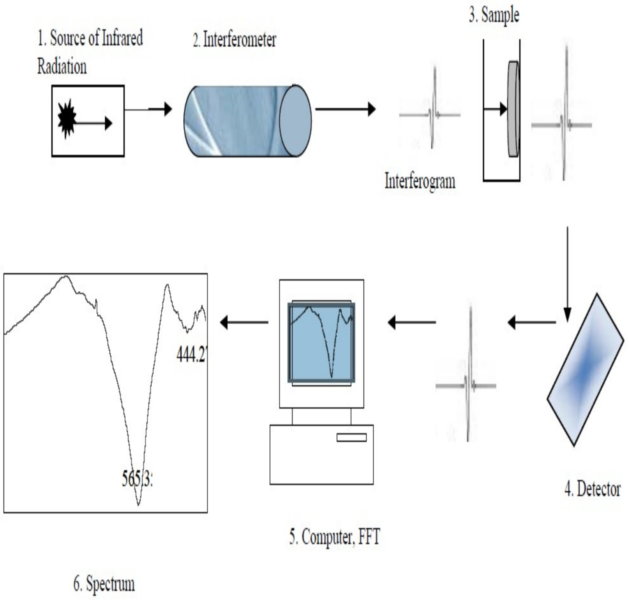

Figure 4.3: Experimental Set-up for Fourier Tran Infrared Spectroscopy

4.2 Fourier Transformer Infrared Spectroscopy (FTIR)

4.2.1 Working of FTIR Spectroscopy

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Fourier Transform is a mathematical equation that converts the spectral signal performed by a computer from a time domain towards a frequency domain. Its mechanism of action is based on the Michelson Interferometer modulation.

Spectrum is the graph that shows movement of compounds when they undergo a reaction involving infrared radiation. The movement of compound is actually a vibration, which results to the emission of energy measured in wavelength or wave numbers. Thus, the absorption spectrum is a plot of wavelength vs. a beam of radiation. [12]

4.2.2 Preparation of Sample for FTIR Scan

- Heat 100g of modified bitumen sample to not more than 100°C for 20 minutes.
- Apply approximately 1g of liquid modified bitumen to wax paper.
- Measure 100 mg of KBr powder.
- Place KBr powder into 13 mm die press for 2 minutes at 10,000 psi.
- Place KBr pellet on top of 1g of modified bitumen sample.
- Apply another wax paper on top of KBr pellet and gently press until a thin transparent coat of modified bitumen is applied to KBr pellet.
- Place the KBr pellet in the cell holder and position the most uniform region of the pellet in the path of the beam.
- Scan the sample from 4000 cm^{-1} to 400 cm^{-1}, and record data.

Figure 4.4: Preparation of Sample for FTIR Scan

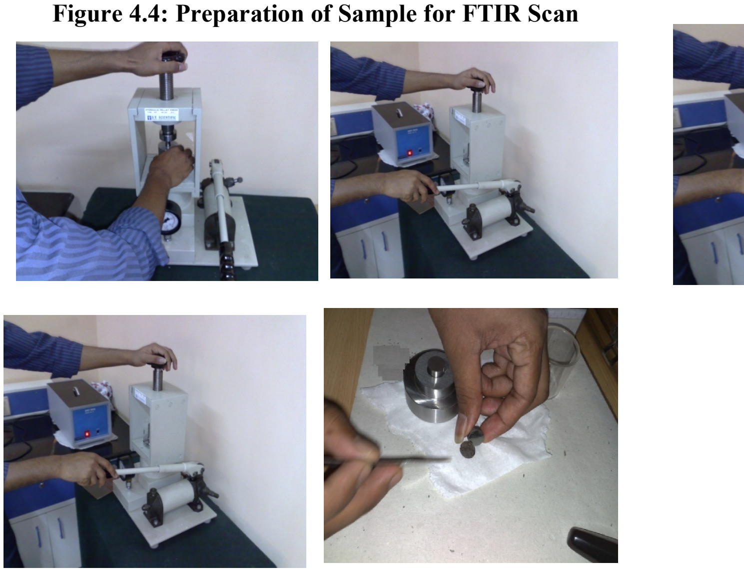

Figure 4.5 Pelleting the Sample

Figure 4.6: Working of FTIR Spectrometer

5.0 Analysis and Discussions

5.1 FTIR Scan Result of Base Bitumen

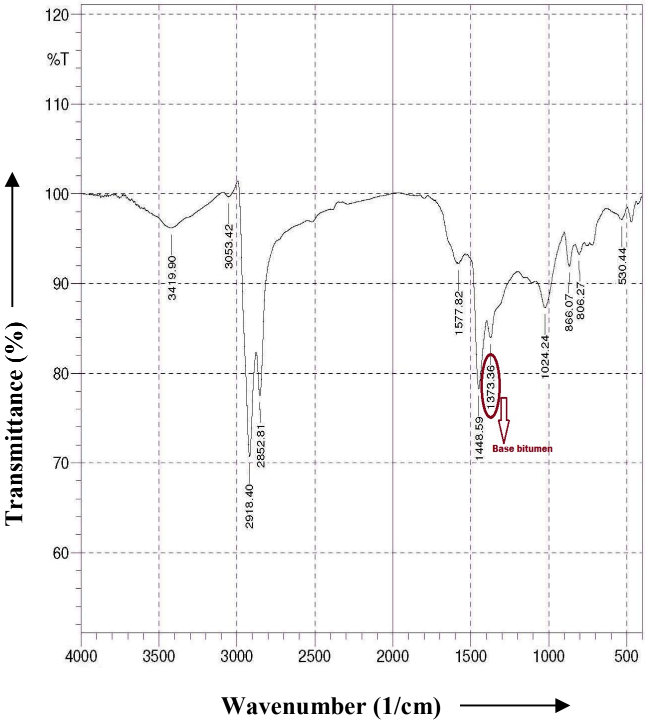

Figure 5.1: FTIR scan results of Base Bitumen

Table 5.1: FTIR scan details of Base Bitumen

No.	Peak	Area	No.	Peak	Area	No.	Peak	Area
1	530.44	0.422	4	1373.36	1.837	7	1577.82	0.670
2	806.27	1.642	5	1466.66	10.531	8	2918.4	9.866
3	1024.24	2.004	6	1448.59	8.168	9	3419.9	1.430

5.2 FTIR Scan Result of Finaprene Modified Bitumen (FMB)

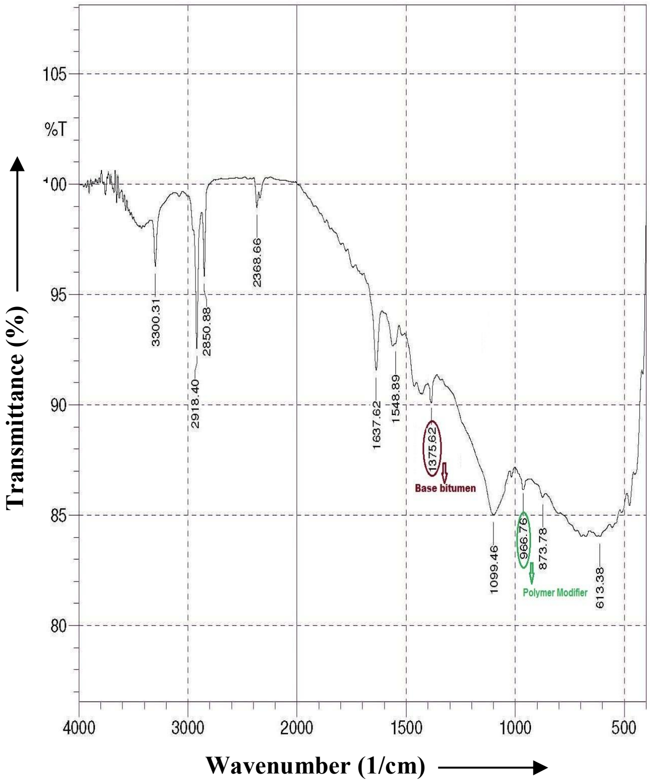

Figure 5.2: FTIR scan results of FMB at 1% concentration of Finaprene

Table 5.2: FTIR scan details of FMB at 1% concentration of Finaprene

No.	Peak	Area	No.	Peak	Area	No.	Peak	Area
1	613.38	4.012	5	1375.62	1.683	9	2368.66	0.081
2	873.78	4.578	6	1427.37	1.694	10	2850.88	0.417
3	966.76	4.128	7	1548.89	0.592	11	2918.4	1.197
4	1099.46	19.003	8	1637.62	1.852	12	3300.31	1.125

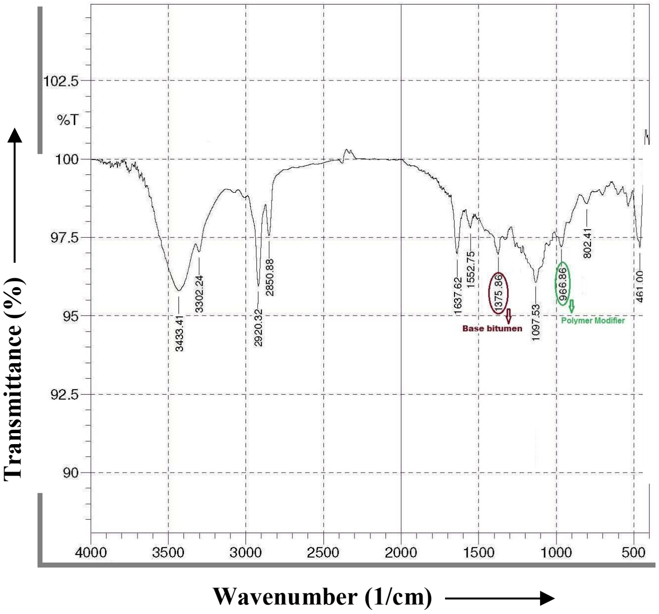

Figure 5.3: FTIR scan results of FMB at 2% concentration of Finaprene

Table 5.3: FTIR scan details of FMB at 2% concentration of Finaprene

No.	Peak	Area	No.	Peak	Area	No.	Peak	Area
1	461 .00	0.589	5	1375.86	0.175	9	2850.88	0.547
2	802.41	0.421	6	1446.66	0.153	10	2920.32	1.158
3	966.86	0.438	7	1552.75	0.399	11	3302.24	1.547
4	1097.53	6.807	8	1637.62	0.305	12	3433.41	3.933

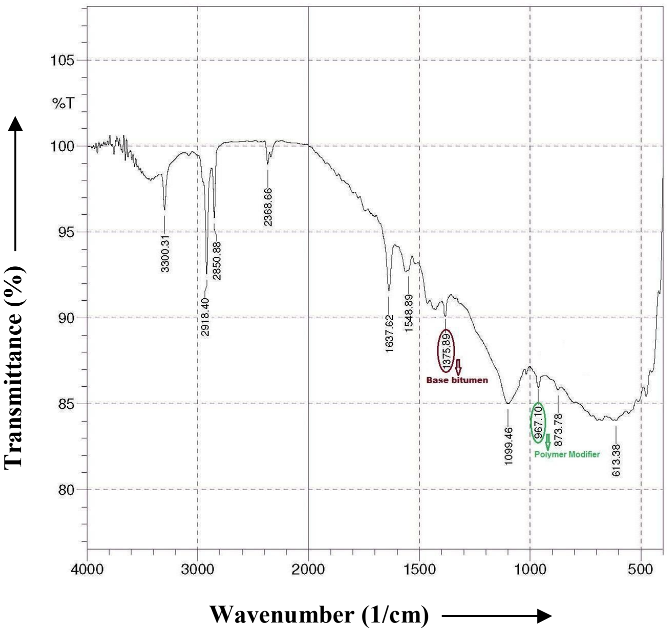

Figure 5.4: FTIR scan results of FMB at 3% concentration of Finaprene

Table 5.4: FTIR scan details of FMB at 3% concentration of Finaprene

No.	Peak	Area	No.	Peak	Area	No.	Peak	Area
1	613.38	3.939	5	1375.89	1.672	9	2368.66	0.103
2	873.78	4.405	6	1427.37	1.719	10	2850.88	0.451
3	967.10	4.295	7	1548.89	0.613	11	2918.4	1.218
4	1099.46	17.938	8	1637.62	1.903	12	3300.31	1.141

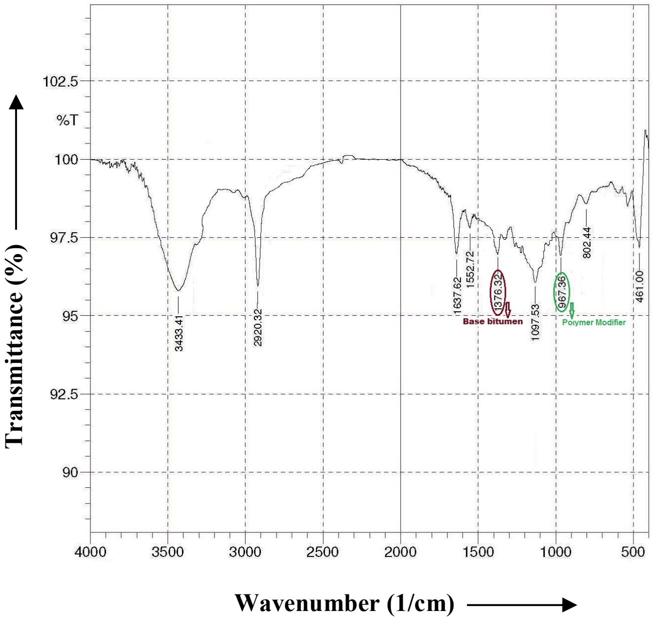

Figure 5.5: FTIR scan results of FMB at 4% concentration of Finaprene

Table 5.5: FTIR scan details of FMB at 4% concentration of Finaprene

No.	Peak	Area	No.	Peak	Area	No.	Peak	Area
1	461 .00	0.605	5	1376.32	0.194	9	2850.88	0.649
2	802.41	0.472	6	1446.66	0.164	10	2920.32	1.174
3	967.36	0.519	7	1552.75	0.417	11	3302.24	1.619
4	1097.53	7.070	8	1637.62	0.319	12	3433.41	3.981

5.2 Discussions

The purpose of this study was to conduct a comprehensive laboratory evaluation of the effects of several promising polymer modifiers on the physical properties of paving bitumen. A common characteristic of these paving materials is a certain degree of variability in the quality and uniformity of starting materials used in processing and production of these products. The main purpose of this investigation was to study applicability of Fourier Transform Infrared spectroscopy (FTIR) in characterization of these materials. The experimental results presented, indicate that rheological measurements can be used as a powerful tool in the design and characterization of viscoelastic blends.

- On addition of 1%, 2%, 3% & 4% modifier to base bitumen, Finaprene Modified Bitumen exhibits higher viscosity of 15.2 Pa-s, 15.23 Pa-s, 15.25 Pa-s and 15.85 Pa-s respectively at a lower temperature of 100ºC. This offers more resistance to compaction of the mix.
- The rate of segregation, if any, is governed by the molecular weight. The Compatibility and stability of modified bitumen over a period of time is assessed by Separation test. Compatibility also varies with concentration of the polymer and the higher the concentration of the polymer, the lower the degree of compatibility. The results obtained in separation tests are within the acceptable limits. This has shown that the modified bitumen is stable.

5.3. Conclusions

1.Increase in modifier concentration to base bitumen results to increase in viscosity of modified bitumen at 135^0C and at 150^0C and also this is indicated in increase in the peak area ratio. This shows that effect of polymer is significant in building viscosity relationship with the bitumen and is evident through FTIR spectroscopy.

2.Transmittance bands in the FTIR investigation indicates a linear relationship between modifier content in modified bitumen samples and the peak area ratio of modifier and base bitumen. This analysis shows that regression equation generated for various modifiers can be used to calculate modifier content of an unknown bitumen binder.

3.From the separation test and FTIR analysis it is clear that blends prepared were stable and the modifiers used are compatible with the base bitumen. As the modifier concentration increases wavenumber shifts to higher frequency and further increase in modifier concentration IR spectrum shows drastic shift in frequency of wavenumber. Thus the blend becomes unstable.

4.From this work it can be emphasized that FTIR spectroscopy is an effective tool in studying the compatibility of modifiers with the base bitumen and also FTIR is proven to be effective in polymer quantification and identification of modifier used in an unknown binder.

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